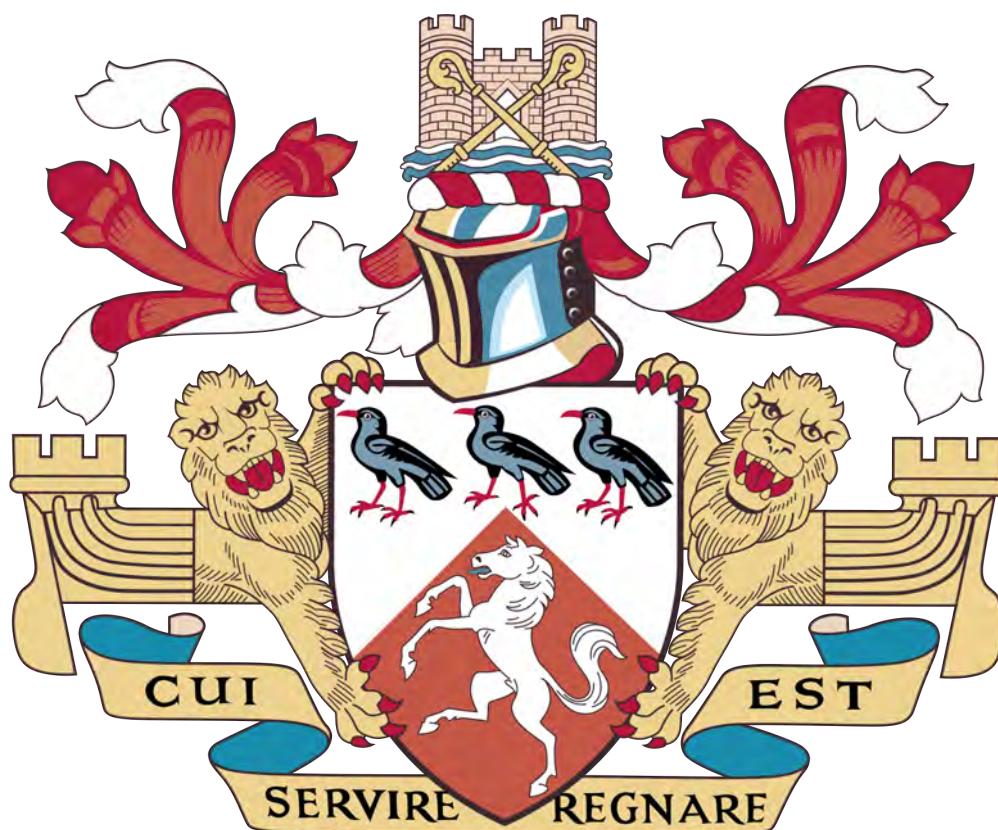


MULTISCALE SIMULATION OF PHOTOCHEMICAL AND IRRADIATION-DRIVEN PROCESSES

CAUÊ PAULA DE SOUZA





UNIVERSITY OF KENT
SCHOOL OF NATURAL SCIENCES
CHEMISTRY AND FORENSIC SCIENCE

CAUÊ PAULA DE SOUZA

MULTISCALE SIMULATION OF PHOTOCHEMICAL AND
IRRADIATION-DRIVEN PROCESSES

CANTERBURY, JULY 2026

This text was composed in L^AT_EX.
In the digital version, all intra- and extratextual references are
clickable for your convenience. The type families are
ADF Baskerville (serif), T_EX Gyre Heros (sans serif),
Latin Modern (monospaced) and Gentium (Greek).

CAUÊ PAULA DE SOUZA

MULTISCALE SIMULATION OF PHOTOCHEMICAL AND IRRADIATION-DRIVEN
PROCESSES

Doctoral thesis submitted to the School of Natural Sciences of the University of Kent as part of the requirements for the degree of Doctor of Philosophy by Research in Chemistry.

Supervisor: Dr Felipe Fantuzzi

Word count: 61 562

Canterbury, July 2026

*Was wir beobachten, ist nicht die Natur selbst, sondern Natur, die
unserer Art der Fragestellung ausgesetzt ist.*

Werner Heisenberg



Incredulità di San Tommaso

Michelangelo Merisi da Caravaggio

ὅτι ἐν αὐτῷ ἐκτίσθη τὰ πάντα ἐν τοῖς οὐρανοῖς καὶ ἐπὶ τῆς γῆς, τὰ ὀρατὰ καὶ
τὰ ἀόρατα [...]· τὰ πάντα δι' αὐτοῦ καὶ εἰς αὐτὸν ἔκτισται·

ΠΡΟΣ ΚΟΛΟΣΣΑΕΙΣ 1.16, NA28

ABSTRACT

MULTISCALE SIMULATION OF PHOTOCHEMICAL AND IRRADIATION-DRIVEN PROCESSES

CAUÊ PAULA DE SOUZA

Supervisor: Dr Felipe Fantuzzi

Photoassisted chemical vapour deposition (PACVD) is a novel near-room-temperature deposition method in which gas-phase precursors are activated by photons rather than by thermal energy. The technique can be employed in the controlled coating of thermosensitive substrates with metals, forming thin films and nanostructured patterns through area-selective deposition (ASD). This work aims towards a comprehensive multiscale simulation of a PACVD process for the deposition of ruthenium on functionalised alkanethiol self-assembled monolayers (SAMs) on gold from Ru–carbonyl precursors.

Ruthenium π -diene carbonyl complexes have emerged as promising precursors for the PACVD of Ru metal, yet their photodissociation mechanisms remain unclear. The first part of this thesis utilises quantum-chemical calculations to map the excited-state dissociation landscape of $(\eta^4\text{-diene})\text{Ru}(\text{CO})_3$ precursors [diene = butadiene (BuD), isoprene or 2-methyl-1,3-butadiene (MBuD), cyclooctatetraene (COT), 1,3-cyclohexadiene (CHD), cyclobutadiene (CBuD)]. Ground-state density functional theory (DFT) optimisations and Ru–ligand scans are combined with time-dependent DFT (TDDFT) excitations and adiabatic singlet potential energy surface profiles to identify CO- and diene-loss pathways, while energy decomposition analysis with natural orbitals for chemical valence (EDA-NOCV) and natural transition orbital (NTO) analyses rationalise the Ru–diene bonding and the character of the excited states that drive reactivity. Calculated UV–vis spectra reproduce experimental trends, including the markedly higher absorptivity and extended wavelength coverage of the COT-containing complex. CO loss is generally enabled by a range of localised metal-ligand or charge-transfer excitations and internal conversion–assisted channels. In contrast, diene loss is strongly ligand dependent: BuD, MBuD, and CHD show accessible pathways, CBuD remains resistant, and COT exhibits additional complexity due to ligand flexibility and coordination changes, all consistent with experiment. These results outline favourable stepwise routes towards unsaturated fragments and provide a basis for subsequent nonadiabatic dynamics, irradiation-driven molecular dynamics (IDMD), time-resolved spectroscopy, and multiscale simulations of the PACVD processes.

Besides their importance for various technological applications such as electroanalytical sensors, organic electronic devices, and catalysts, SAMs of alkanethiols on gold surfaces are

excellent models for organic thin films and can be functionalised to attain ASD under PACVD of metals. However, providing a consistent computational description of the unique structural features of these systems, such as adsorption patterns, chain conformations, and superlattice arrangements, is challenging, particularly within a versatile computational framework that can simulate both the structural features of these systems and their irradiation-driven chemical transformations. The second part of this thesis systematically analyses molecular mechanics (MM) force field (FF) parameters for bonded and nonbonded (van der Waals and Coulomb) interactions in alkanethiol SAMs with different terminal groups. Using structure optimisation and energy decomposition analysis, we assess the impact of FF parameters on key properties, such as the equilibrium tilt angle, ligand packing density, and nanoscale structural organisation. Based on this detailed benchmarking, we identified an optimal set of FF parameters that reproduces the experimentally determined structural and energetic properties of alkanethiol SAMs and ensures their dynamic stability at room temperature. This provides a validated general framework for simulating pristine and functionalised alkanethiol-coated substrates under thermal conditions relevant to experimental applications.

The synthesis of these two bodies of work into a multiscale simulation of the PACVD deposition of Ru on alkanethiol SAM substrates utilising the IDMD strategy implemented in the MESOBIONANO EXPLORER software package is discussed in the final part. We conclude by proposing a MM model of the Ru-containing precursors and a strategy to extract photodissociation probabilities for the IDMD simulations from the richness of data generated by the investigations mentioned above. We also discuss what is available and what is yet needed to construct the final multiscale simulation of the PACVD process, both from the theoretical and from the experimental sides. Finally, we critically assess our method and offer a direction for future improvements that will increase its predictive power and accuracy.

Keywords: TDDFT, multiscale simulation, photoassisted chemical vapour deposition, irradiation-driven molecular dynamics, self-assembled monolayers, ruthenium carbonyl complexes

ACKNOWLEDGEMENTS

Glory be to God, Creator of all things in heaven and on earth, visible and invisible, in Whom all things hold together; for Your Providence and Sustenance. May my humble exploration of Your magnificent Work be, for You, worship in spirit and in truth.

Before coming to Canterbury for this PhD, I had never left my home country, Brazil. My trajectory in science started to gain consistency when I was 14 years old and started a full-time, four-year technical course in chemistry concomitant to my ensino médio—the equivalent of years 11 to 13 in the UK. The decision to follow my current path was born there, and I never considered any other option. Much of this decision can be credited to the incentive and support of my parents, Éber and Maria Helena—thank you for always making all within your reach for me—and to the excellence, care, and inspiration of the professionals who made all efforts to guide my formation during that time. They are graciously too many to name here and my memory may fail me, but I am thankful to all of them, and I know many exceptional professionals have come to be who they are because of them. I could not, however, fail to register the names of Jairo Esteves, my general chemistry professor who fed my ever-growing love for science and showed me how to be systematic and precise from very early; Tiago Giannerini, my physical chemistry professor who made me feel very strongly in favour of a physical chemistry research career; and Cleber Haubrichs, my mathematics professor who showed me from very early the power of abstraction and the beauty of the language of the universe. It is not an exaggeration to say that my career choices were based on these three pillars.

In 2014, I started the next journey in my formation as a full-time chemistry undergraduate at the Instituto de Química of the Universidade Federal do Rio de Janeiro. This five-year course shaped and matured the core of who I am as a scientist. Once again, I became indebted to many excellent professionals, many of whom are now my colleagues in science, who have brilliantly shaped my skills and critical thinking. In particular, I would like to thank and recognise the work of my first supervisor in theoretical and computational chemistry during my undergraduate work, who then became my master's degree supervisor, Thiago Cardozo. For the many conversations, science-related and not, for the inspiration, for the patience, for the inspiring lectures and relentless efforts to manage our research group with excellence while performing the teachings and administrative work with equal dedication, thank you.

Unfortunately, most of my master's degree was done in the isolation of my home as a consequence of the COVID-19 pandemic. One of the amazing things about computational chemistry is that you can work from almost anywhere, and thus I was able to carry on with my work with minimal disruption. I look back to the group meetings and to the beautiful lectures on permutation group symmetry and spin eigenfunctions that Thiago presided with a mix of solace and sadness for such difficult times, both because of the pandemic and other personal reasons that do not belong here. Those were truly bittersweet times, and I am thankful for everyone that helped me go through it a bit more easily.

And from the isolation of my home, I went straight to leaving my country for the first time, and gained the world: since September 2022, I have come to visit ten new countries. That was one of the most important aspects of my PhD. The contact with various cultures, researchers, research contexts and institutions made me feel more connected with the scientific community and showed me very clearly what I already believed about science, but had not yet experienced: it is a *human* and *global* activity. In the current geopolitical context, with the resurgence of nationalist and fascist tendencies, this message and culture of global cooperation must be cherished, supported, and defended. I thank my official supervisor Felipe Fantuzzi and Nigel Mason, who kindly supported me, for reinforcing this conviction on me and for supporting me with all the financial needs and with overcoming the massive bureaucracy that came with all the travels and conferences that so enriched my formation. Nothing of this work would have come together without your efforts.

To Felipe Fantuzzi and Heidy Quitián-Lara I am especially indebted. The opportunity to come here to Kent for my PhD arrived right on time, when I had just received my MSc title, and yet came as a surprise. I decided to take this opportunity to the end, with all it would take. The uncertainties, complications, anxiousness, and stress of all the process were much greater than anything I had experienced so far in my career. But growing up always comes with pains. I was glad to know that my efforts resulted in my getting the only position for chemistry at the university that year. After all the pains, including the absurdly high financial cost, and a twelve-hour flight over the Atlantic, I found myself in Whitstable, hosted by Felipe and Heidy, until I found a place to call home during my stay here. In all this process, you have given me a huge support. Thank you, Felipe, for your friendship and supervision, in that order; and thank you, Heidy, for your kind friendship and patience.

I came from the socially busy times of my formation as a technician and then as an undergrad, to the isolation of my home during a global pandemic, and now to the disconnectedness of leaving one's birthplace and family behind for the first time. I was soon like an atom in the void, with all the universe to explore, yet bonded to nothing. The contact with my family became fully virtual. The friends that once I had, followed their paths, many to other countries, or other states in Brazil—which for many contexts, like in Europe, is almost the same. The pandemic severed many of the personal contacts, and my decision to leave made it more definitive (if there is anything definitive in life). But here, this lonely atom into the void came to have some good orbiting companions during this process. Besides Felipe, Heidy,

and Nigel, I have much to thank my fellow journeyers here at the University of Kent. My special thanks to Matthew Dickers, Klaudia Cielinska, Adrija Bhowmick, Anna-Maria Wirth, and Jacob Sands for the friendship, collaboration, and great moments together, that made me feel a little bit less in the void, and thank you for your patience with my idiosyncrasies. Those many travels would not have been nearly as fun without you. I loved our collaborations, and I hope more is to come.

In many occasions, this atom in the void came to meet some heavy metals. Many experienced researchers I have met during conferences honoured me with questions about my presentations and suggestions to my work. The many people I can now happily say are part of my growing professional network are high points of my journey. In particular, I would like to thank and acknowledge the collaborators that were essential for the execution of the core of this thesis: Lisa McElwee-White (it was great meeting you in person in Heidelberg), Amy Walker, and Matija Zlatar (thank you for the hospitality and the rakija during our visit in Belgrade). I hope this was only the beginning of many collaborations to come. I am glad I have met you all.

I would also like to recognise the important role the MBN Research Center team had in this work and in my growth as a researcher. Our collaborations were enriching and taught me much more than I could expect. Thank you Irina Solovyeva for your incredibly efficient work. You are truly remarkable! Thank you Alexey Verkhovtsev and Andrey Solov'yov for all the support and insightful conversations, and for hosting me and others of us from Kent for several months in your headquarters during this period.

A big thank you to Timothy Kinnear for the amazing support with high-performance computing resources, for the interesting and provocative scientific questions, and for the many cheerful conversations.

There is a kind of support that is not material or financial, nor is it directly visible, but is essential and all-encompassing. To all in Primeira Igreja Barista de Nova Iguaçu, my church in Brazil, who have backed me up with their prayer throughout these years, many of whom I am not even aware of, my most warm thank you. In special, I acknowledge the constant care from Pr Edgard Antunes (*in memoriam*), Márcia Antunes, Pr Cleibel Peixoto, Débora Peixoto, Rosemere Medeiros, e Ester Nunes.

I would like to acknowledge all the financial and technical support of the funding agencies and programmes that made all my professional development possible during the past few years, and that allowed for all the great global collaborations I care so much about. The Engineering and Physical Science Research Council (EPSRC) for my PhD scholarship (Grant No. EP/W52461X/1). The support of the RADON project (Grant Agreement No. 872494) within the H2020-MSCA-RISE-2019 call. The European Cooperation in Science and Technology (COST) for the COST Action CA20129 “Multiscale Irradiation and Chemistry Driven Processes and Related Technologies” (MultiChem) and the Innovators Grant IG20129 “Innovative Digital Control for 3D Nanoprinting” (INDICO).

During this journey, I have experienced some important historical moments. I landed in London on the day before Queen Elizabeth II's funeral. After so many years, the UK came to have a new monarch, and I was here. I watched King Charles' coronation on the TV, happening in the Westminster Abbey, which I later came to visit to see the tombs of many great scientists. I have lived through an unprecedented number of prime minister changes—Andy Burnham took office two days ago from this writing. I also came to see the first female archbishop of Canterbury installed here in this very city. On a Pentecost Sunday at the Canterbury Cathedral, on 24 May, I received communion from her hands. Outside the UK, I have seen massive protests happen in Tbilisi and in Belgrade, shortly after I had visited these cities. I have visited Hungary and then seen a somewhat better political turn in Hungary after Orbán's stepping out. I have seen from a distance my own country defend and recover its democracy, on the edge of a collapse after the worst government since the redemocratisation (and it is not entirely safe yet). I have unfortunately seen the scientific community and institutions in the USA suffer under the current administration. I have passed by Bahrain on my way to India and a few weeks later I came to know that Iran bombed the country as a consequence of the conflicts caused by the USA and Israel. Too many wars have broken out in the last few years, and many still remain. I have been closer than ever to contexts and events far greater than myself, trying to make connections and to be integrated in the international community, while many others just want to sever bonds, erect walls, secure borders, expel the foreigner... All this is to say that we never know by how many people our pathway in life is shaped, for better or for worse. But to all who positively contributed to mine and I am not aware of, I extend my gratitude. Because

*No man is an island entire of itself; every man
is a piece of the continent, a part of the main;
if a clod be washed away by the sea, Europe
is the less, as well as if a promontory were, as
well as any manner of thy friends or of thine
own were; any man's death diminishes me,
because I am involved in mankind.
And therefore never send to know for whom
the bell tolls; it tolls for thee.*

—John Donne, *Devotions upon Emergent Occasions* (1624)

Cauê Souza
22 July 2026

CONTENTS

ABSTRACT	vii
ACKNOWLEDGEMENTS	ix
LIST OF FIGURES	xvii
LIST OF TABLES	xxi
LIST OF ABBREVIATIONS	xxiii
1 CONTEXT AND SCOPE	1
1.1 ON THE MULTISCALE APPROACH	2
1.2 PROJECT DEFINITION AND AIMS	6
1.2.1 GENERAL OBJECTIVES	9
2 FOUNDATIONS	11
2.1 QUANTUM MECHANICAL METHODS	12
2.1.1 HARTREE-FOCK AND POST-HARTREE-FOCK METHODS	18
2.1.2 DENSITY FUNCTIONAL THEORY	24
2.1.3 RELATIVISTIC CORRECTIONS	30
2.1.4 THE TIME-DEPENDENT EXTENSIONS FOR EXCITED STATES	31
2.2 CLASSICAL MOLECULAR MECHANICS AND DYNAMICS	44
2.2.1 STANDARD AND REACTIVE FORCE FIELDS	46
2.2.2 MOLECULAR DYNAMICS ALGORITHMS	70
2.3 IRRADIATION-DRIVEN MOLECULAR DYNAMICS AND THE MBN EXPLORER PACKAGE	78
3 QUANTUM CHEMICAL METHODS APPLIED TO THE PHOTOCHEMISTRY OF PACVD PRECURSORS	81
3.1 INTRODUCTION	82
3.2 METHODS	84
3.3 RESULTS AND DISCUSSIONS	86
3.3.1 EQUILIBRIUM GEOMETRIES OF PRISTINE PRECURSORS AND THEIR FRAGMENTS	87
3.3.2 THE RU-DIENE BONDING	91
	xiii

3.3.3	ABSORPTION SPECTRA OF THE PRISTINE PRECURSORS-----	94
3.3.4	LOSS OF DIENE FROM PRISTINE PRECURSORS AND FRAGMENTS -----	97
3.3.5	LOSS OF CO FROM DIENE-CONTAINING FRAGMENTS-----	103
3.3.6	TOTAL FRAGMENTATION OF Ru(CO) ₃ -----	105
3.3.7	A PROPOSAL OF EXHAUSTIVE DISSOCIATION PATHWAYS-----	105
3.4	CONCLUSIONS -----	107
4	A REFINED ATOMISTIC MODEL OF ALKANETHIOL SELF-ASSEMBLED MONOLAYERS	109
4.1	INTRODUCTION -----	110
4.2	METHODS -----	113
4.2.1	EVALUATING FF PERFORMANCE VIA LIGAND TILT ANGLE -----	115
4.2.2	THE CHOICE OF OPTIMISATION STEPS FOR THE LIGAND TILT ANGLE ANALYSIS -----	116
4.2.3	ANGLE ANALYSIS ALGORITHM -----	117
4.2.4	FULL GEOMETRICAL DESCRIPTION -----	119
4.3	RESULTS AND DISCUSSIONS -----	119
4.3.1	INITIAL FORCE FIELD ASSESSMENT WITH ISOLATED LIGANDS -----	120
4.3.2	EVALUATING THE EFFECT OF NONBONDED PARAMETERS-----	121
4.3.3	TILT ANGLE ANALYSIS ON Au(111) -----	122
4.3.4	TILT ANGLE ANALYSIS ON Au(100) -----	125
4.3.5	INFLUENCE OF SURFACE COVERAGE DENSITY -----	127
4.3.6	FINAL DEPOSITION GEOMETRY ON Au(111) -----	127
4.3.7	PRELIMINARY MOLECULAR DYNAMICS SIMULATIONS -----	128
4.4	CONCLUSIONS -----	131
5	CASE STUDIES	133
5.1	INTRODUCTION -----	134
5.2	CASE STUDY 1: INVESTIGATION OF EXCITED STATES OF BODIPYS -----	134
5.3	CASE STUDY 2: SURVEY OF THE VACUUM-ULTRAVIOLET SPECTROSCOPY AND ABSORPTION CROSS-SECTIONS OF ASTROPHYSICAL ICE ANALOGUES AND THE MOLESS PROJECT -----	137
5.4	CASE STUDY 3: COLLISION-DRIVEN ALLOTROPIC TRANSFORMATION OF GRAPHENE -----	148
5.5	CONCLUSIONS -----	159
6	TOWARDS THE SIMULATION OF THE PACVD PROCESS	161
6.1	METHOD PROPOSAL-----	162
6.1.1	A MM/MD MODEL FOR THE PRECURSORS -----	162
6.1.2	IDMD APPROACHES -----	165
6.2	IMPROVING THE MODEL AND FUTURE PERSPECTIVES-----	166

6.3	FINAL REMARKS -----	167
REFERENCES		171
A	SUPPLEMENTARY DATA FOR PHOTOCHEMISTRY OF PACVD PRECURSORS (CHAPTER 3)	211
A.1	SIMULATED SPECTRA AND PRISTINE PRECURSORS NTOs -----	212
A.2	FULL SET OF SCANS AND NEB MEP WITH SUPPORTING NTOs -----	216
A.2.1	3COT -----	216
A.2.2	3CHD -----	218
A.2.3	3BuD -----	219
A.2.4	3MBuD -----	220
A.2.5	3CBuD -----	220
A.2.6	Ru(CO) _n -----	222
A.3	CARTESIAN COORDINATES FOR EQUILIBRIUM GEOMETRIES IN Å -----	223
A.3.1	RUTHENIUM COMPLEXES -----	223
A.3.2	IRON ANALOGUE COMPLEXES -----	231
B	SUPPLEMENTARY DATA FOR A REFINED ATOMISTIC MODEL OF ALKANETHIOL SELF-ASSEMBLED MONOLAYERS (CHAPTER 4)	237
B.1	ADDITIONAL ANGLE ANALYSIS RESULTS -----	238
B.1.1	ENERGY DECOMPOSITION ANALYSIS FOR ALL LIGANDS, SURFACES, AND DENSITIES -----	238
B.1.2	TILT ANGLE ANALYSIS FOR ALL LIGANDS, SURFACES, AND DENSITIES ---	244
B.1.3	FINAL GEOMETRIES FOR SAMs ON Au(111) -----	256
B.2	GEOMETRIES, TOPOLOGIES, AND FORCE FIELD PARAMETERS -----	259
C	PUBLICATIONS AND CONFERENCE PRESENTATIONS	263
C.1	FIRST-AUTHOR PUBLICATIONS -----	264
C.2	OTHER PUBLICATIONS -----	266
C.3	ORAL PRESENTATIONS IN CONFERENCES -----	273

LIST OF FIGURES

Figure 1.1	Schematic representation of a simple PACVD apparatus -----	8
Figure 2.1	Jacob’s ladder representation of DFT functionals hierarchy -----	29
Figure 2.2	Schematic representation of the potential energy terms in a typical molecular force field -----	48
Figure 2.3	Schematic representation of the modified potential energy terms in the rCHARMM force field -----	61
Figure 2.4	Two-dimensional representation of simulation boxes and boundary conditions -----	63
Figure 2.5	Illustrations of various elements in the Ewald summation method ---	66
Figure 3.1	(η^4 -diene)Ru(CO) ₃ compounds investigated in this work -----	83
Figure 3.2	General exhaustive dissociation pathways for (η^4 -diene)Ru(CO) ₃ compounds -----	87
Figure 3.3	Optimised GS geometries of the precursors and fragments -----	88
Figure 3.4	Summary of all singlet and triplet equilibrium geometries for COT-containing Ru and Fe complexes -----	90
Figure 3.5	NEB MEPS for the conversion of singlet 2COT from the η^4 edge-coordinated structure to the GS η^6 -coordinated structure in a barrierless rearrangement and singlet 0COT from the η^6 -coordinated structure to the GS η^4 centre-coordinated structure passing through an early TS with a 2.9 kcal mol ⁻¹ barrier -----	91
Figure 3.6	EDA-NOCV deformation densities (ρ) describing the interaction between diene and Ru(CO) ₃ fragments -----	93
Figure 3.7	Calculated spectra for the pristine precursors considered in this work and NTOs for selected electronic transitions representing distinct characters -----	95
Figure 3.8	Rigid scans for Ru–CHD dissociation in 3CHD accompanied by the main NTO components for electronic transitions near PEC crossings or near-degeneracies -----	100
Figure 3.9	Rigid scans for Ru–BuD dissociation in 3BuD accompanied by the main NTO components for electronic transitions near PEC crossings or near-degeneracies -----	101

Figure 3.10	Rigid scans for Ru–BuD dissociation in 2BuD accompanied by the main NTO components for electronic transitions near PEC crossings -	102
Figure 3.11	Rigid scans of representative Ru–CO bonds in diene-containing molecules -----	104
Figure 3.12	Proposed dissociation channels for PACVD precursors -----	107
Figure 4.1	Schematic representations of the alkanethiol SAM on Au(111)-----	111
Figure 4.2	Alkanethiyl structures considered in this study -----	114
Figure 4.3	Auxiliary plots for optimisation step selection utilised for the tilt angle analysis for two exemplary cases -----	118
Figure 4.4	Energy decomposition analysis as a function of ligand tilt angle for FF parameter sets 1 and 3 for HDT ^H on Au(100) with a density of 4.17 nm ⁻² -----	122
Figure 4.5	Ligand tilt angle analysis for HDT ^H on Au(111) at a density of 4.67 nm ⁻²	123
Figure 4.6	Ligand tilt angle analysis for HDT ^H on Au(100) at a density of 4.17 nm ⁻²	126
Figure 4.7	Final HDT ^H SAM model on Au(111) surface after 3 000 000 velocity quenching optimisation steps -----	129
Figure 4.8	Ligand tilt and precession angles vs 300 K MD simulation time for the final HDT ^H SAM model on Au(111) surface for selected charge-damping factors -----	130
Figure 5.1	Nomenclature and NTOs for the S ₀ → S ₁ , HOMO-LUMO electronic transitions of selected BODIPYS -----	137
Figure 5.2	Calculated and experimental VUV spectra of CO, H ₂ O, O ₂ , and N ₂ O	141
Figure 5.3	Effect of cluster size on calculated VUV spectra of H ₂ O and α-O ₂ ----	142
Figure 5.4	Orbital analysis for CO (point group C _{∞v}) and H ₂ O (point group C _{2v}) electronic transitions on the isolated molecules and the clusters	144
Figure 5.5	Orbital analysis for N ₂ O (point group C _{∞v}) and O ₂ (point group D _{∞h}) electronic transitions on the isolated molecules and the clusters ----	146
Figure 5.6	Relaxed initial geometry of the square C ₂₉₆ graphene nanoflake used as the collision target-----	151
Figure 5.7	Representative structural outcomes obtained from collision-driven transformations towards the armchair edge of C ₂₉₆ graphene nanoflakes, illustrating selected metastable morphologies with distinct topologies -----	153
Figure 5.8	Probability maps for successful transformation to nanotube-like structures, P _{CNT} , as a function of collision energy and incidence angle for armchair and zigzag edge-aimed collisions to the C ₂₉₆ graphene nanoflake -----	155

Figure 5.9	Mechanism of edge-mediated topological closure of a graphene nanoflake from a fullerene collision aimed at the armchair edge of a C_{296} graphene nanoflake following ballistic impact -----	157
Figure 6.1	Representative PACVD precursor PECs fitted with Morse potentials for rCHARMM FF parametrisation and two views of a dummy-atom model of the Ru–diene bond in 3COT -----	164
Figure A.1	Calculated spectra for intact 3COT and its diene-containing fragments	212
Figure A.2	Calculated spectra for intact 3BUD and its diene-containing fragments	212
Figure A.3	Calculated spectra for intact 3CBUD and its diene-containing fragments	213
Figure A.4	Calculated spectra for $Ru(CO)_n$ ($n = 3, 2, 1$) fragments -----	213
Figure A.5	Main NTO components for all electronic transitions in 3COT as presented in Table 3.6 -----	214
Figure A.6	Main NTO components for all electronic transitions in pristine precursors other than 3COT as presented in Table 3.6 -----	215
Figure A.7	Rigid scans for Ru–CO dissociation in 3COT and its fragments -----	216
Figure A.8	Rigid scans and NEB MEPS for Ru–COT dissociation in 3COT and its fragments -----	217
Figure A.9	Schematic representation of the MEP obtained by a NEB calculation superimposed on a bidimensional GS PES slice in which the diene is simultaneously dissociated from the metal and distorted from its bonded geometry to its isolated relaxed geometry -----	218
Figure A.10	Rigid scans for Ru–CHD and Ru–CO dissociation in 3CHD -----	218
Figure A.11	Rigid scans for Ru–CO dissociation in 3BUD and its fragments -----	219
Figure A.12	Rigid scans for Ru–MBUD and Ru–CO dissociation in 3MBUD -----	220
Figure A.13	Rigid scans for Ru–CO dissociation in 3CBUD and its fragments -----	220
Figure A.14	Rigid scans and NEB MEPS for Ru–CBUD dissociation in 3CBUD and its fragments -----	221
Figure A.15	Rigid scans for Ru–CO dissociation in $Ru(CO)_n$ ($n = 3, 2, 1$) -----	222
Figure B.1	Energy decomposition analysis as a function of ligand tilt angle for HDT^{COOH} on Au(100) with a density of 4.73 nm^{-2} -----	238
Figure B.2	Energy decomposition analysis as a function of ligand tilt angle for HDT^H on Au(100) with a density of 4.73 nm^{-2} -----	238
Figure B.3	Energy decomposition analysis as a function of ligand tilt angle for HDT^{OH} on Au(100) with a density of 4.73 nm^{-2} -----	239
Figure B.4	Energy decomposition analysis as a function of ligand tilt angle for HDT^{COOH} on Au(100) with a density of 4.17 nm^{-2} -----	239
Figure B.5	Energy decomposition analysis as a function of ligand tilt angle for HDT^H on Au(100) with a density of 4.17 nm^{-2} -----	240

Figure B.6	Energy decomposition analysis as a function of ligand tilt angle for HDT ^{OH} on Au(100) with a density of 4.17 nm ⁻² -----	240
Figure B.7	Energy decomposition analysis as a function of ligand tilt angle for HDT ^{COOH} on Au(111) with a density of 4.67 nm ⁻² -----	241
Figure B.8	Energy decomposition analysis as a function of ligand tilt angle for HDT ^H on Au(111) with a density of 4.67 nm ⁻² -----	241
Figure B.9	Energy decomposition analysis as a function of ligand tilt angle for HDT ^{OH} on Au(111) with a density of 4.67 nm ⁻² -----	242
Figure B.10	Energy decomposition analysis as a function of ligand tilt angle for HDT ^{COOH} on Au(111) with a density of 4.21 nm ⁻² -----	242
Figure B.11	Energy decomposition analysis as a function of ligand tilt angle for HDT ^H on Au(111) with a density of 4.21 nm ⁻² -----	243
Figure B.12	Energy decomposition analysis as a function of ligand tilt angle for HDT ^{OH} on Au(111) with a density of 4.21 nm ⁻² -----	243
Figure B.13	Ligand tilt angle analysis for HDT ^{COOH} on Au(100) at a density of 4.73 nm ⁻² -----	244
Figure B.14	Ligand tilt angle analysis for HDT ^H on Au(100) at a density of 4.73 nm ⁻² -----	245
Figure B.15	Ligand tilt angle analysis for HDT ^{OH} on Au(100) at a density of 4.73 nm ⁻² -----	246
Figure B.16	Ligand tilt angle analysis for HDT ^{COOH} on Au(100) at a density of 4.17 nm ⁻² -----	247
Figure B.17	Ligand tilt angle analysis for HDT ^H on Au(100) at a density of 4.17 nm ⁻² -----	248
Figure B.18	Ligand tilt angle analysis for HDT ^{OH} on Au(100) at a density of 4.17 nm ⁻² -----	249
Figure B.19	Ligand tilt angle analysis for HDT ^{COOH} on Au(111) at a density of 4.67 nm ⁻² -----	250
Figure B.20	Ligand tilt angle analysis for HDT ^H on Au(111) at a density of 4.67 nm ⁻² -----	251
Figure B.21	Ligand tilt angle analysis for HDT ^{OH} on Au(111) at a density of 4.67 nm ⁻² -----	252
Figure B.22	Ligand tilt angle analysis for HDT ^{COOH} on Au(111) at a density of 4.21 nm ⁻² -----	253
Figure B.23	Ligand tilt angle analysis for HDT ^H on Au(111) at a density of 4.21 nm ⁻² -----	254
Figure B.24	Ligand tilt angle analysis for HDT ^{OH} on Au(111) at a density of 4.21 nm ⁻² -----	255
Figure B.25	Final HDT ^{COOH} SAM model on Au(111) surface after 3 000 000 optimisation steps -----	256
Figure B.26	Final HDT ^H SAM model on Au(111) surface after 3 000 000 optimisation steps -----	257
Figure B.27	Final HDT ^{OH} SAM model on Au(111) surface after 3 000 000 optimisation steps -----	258
Figure B.28	Atom types for the different ligands as defined in the CGenFF -----	259

LIST OF TABLES

Table 3.1	Calculated SCF singlet–triplet gaps and triplet $\langle S^2 \rangle$, for various diene-containing molecules other than 3COT and their fragments-----	88
Table 3.2	Calculated relative SCF energies and $\langle S^2 \rangle$ (for triplets), for the various geometries and electronic multiplicities of $M(\text{CO})_n$ fragments ($M = \text{Ru}, \text{Fe}; n = 3, 2, 1$)-----	89
Table 3.3	EDA-NOCV orbital interaction energies for the pristine precursors decomposed in the diene and $\text{Ru}(\text{CO})_3$ moieties with different charge and multiplicity combinations-----	92
Table 3.4	HOMO–LUMO gaps for the isolated diene ligands in their bonded geometries and in their relaxed equilibrium geometries, and the gap for their pristine complexes-----	93
Table 3.5	EDA-NOCV results for the pristine precursors decomposed in the diene and $\text{Ru}(\text{CO})_3$ moieties in their most favourable description-----	94
Table 3.6	Summary of relevant excitations for the pristine precursors considered in this work-----	96
Table 3.7	Selected bond dissociation energies (BDE)s for all fragmentation pathways investigated in this work-----	98
Table 4.1	Nomenclature and composition of the different force field sets tested in this work-----	115
Table 4.2	Optimisation steps sampled for tilt angle scans analysis-----	117
Table 4.3	Comparison between MM- and DFT-optimised geometries as coordinates RMSD (Å) for each FF set for the three ligands (as thiyl radicals) considered in this work-----	120
Table 5.1	TDDFT and STEOM-DLPNO-CCSD $S_0 \rightarrow S_1$ vertical excitation absorption wavelengths and energies compared with experimental values, and the Kohn–Sham frontier molecular orbital energies, of 1a , 1h , 3aa , and 3ha	136
Table B.1	CGenFF and NBO partial charges (in Coulomb) for all ligand atoms---	259
Table B.2	Relevant files utilised in the various MD simulations described in this work-----	260

LIST OF ABBREVIATIONS

A ₂ C	approximate two-component
ABCcluster	artificial bee colony algorithm for cluster global optimization
ADF	Amsterdam Density Functional
AMBER	assisted model building with energy refinement
AMS	Amsterdam Modeling Suite
ASD	area-selective deposition
BDE	bond dissociation energy
BJ	Becke–Johnson damping
BO	Born–Oppenheimer
BODIPY	boron-dipyrromethene
BuD	butadiene
CAHRMM	Chemistry at Harvard Macromolecular Mechanics
CBuD	cyclobutadiene
CC	coupled-cluster
CCSD	coupled-cluster singles and doubles
CCSD(T)	coupled-cluster singles and doubles with perturbative triples
CEQPAS	Centennial of Quantum Theory: Progress in Atomic and Molecular Structure
CGenFF	CHARMM general force field
CHD	cyclohexadiene
CI	configuration interaction
CID	configuration interaction doubles
CIS	configuration interaction singles
CISD	configuration interaction singles and doubles
CISDT	configuration interaction singles, doubles, and triples
CISDTQ	configuration interaction singles, doubles, triples, and quadruples
COD	Crystallography Open Database
COMB	charge-optimized many-body

COPCA	Collisions Physics and Chemistry and their Applications
COST	European Cooperation in Science and Technology
COT	cyclooctatetraene
CPCM	conductor-like polarizable continuum model
CVD	chemical vapour deposition
DCM	dichloromethane
DF	Dirac–Fock
DFT	density functional theory
DKH	Douglas–Kroll–Hess
DLPNO	domain-based local pair natural orbital
DySoN	Dynamics of Systems on the Nanoscale
ECP	effective core potential
EDA	energy decomposition analysis
EDA-NOCV	energy decomposition analysis with natural orbitals for chemical valence
EOM	equation of motion
EPSRC	Engineering and Physical Sciences Research Council
fcc	face-centred cubic
FDT	fluctuation-dissipation theorem
FEBID	focused electron beam–induced deposition
FF	force field
FFT	fast Fourier transform
FORA	first-order regular approximation
GEA	gradient expansion approximation
GGA	generalized gradient approximation
GN	graphene nanoflake
GS	ground state
GTO	Gaussian-type orbital
HDT	hexadecanethiol
HF	Hartree–Fock
HOMO	highest occupied molecular orbital
HPC	high-performance computing
IC	internal conversion
IDMD	irradiation-driven molecular dynamics

INDICO	Innovative Digital Control for 3D Nanoprinting
IPM	independent particle model
IR	infrared
ISACC	International Symposium Atomic Cluster Collisions
KS	Kohn–Sham
LANL2DZ	Los Alamos National Laboratory 2 double zeta
LCAO	linear combination of atomic orbitals
LDA	local density approximation
LJ	Lennard–Jones
LLCT	ligand-to-ligand charge transfer
LMCT	ligand-to-metal charge transfer
LRT	linear response theory
LUMO	lowest unoccupied molecular orbital
MBN	Meso-Bio-Nano
MBuD	isoprene or 2-methyl-1,3-butadiene
MC	metal centred
MD	molecular dynamics
MEP	minimum energy path
ML	metal-ligand
MLCT	metal-to-ligand charge transfer
MLIP	machine-learned interatomic potentials
MM	molecular mechanics
MMFF	Merck molecular force field
MO	molecular orbital
MOLESs	Molecular Excited State Spectroscopy
MultIChem	Multiscale Irradiation and Chemistry Driven Processes and Related Technologies
NBO	natural bond orbital
NEB	nudged elastic band
NOCV	natural orbitals for chemical valence
NTO	natural transition orbital
OPLS	optimized potentials for liquid simulations
P ₃ ME	particle-particle particle-mesh Ewald
PACVD	photoassisted chemical vapour deposition

PBC	periodic boundary condition
PDB	protein data bank
PEC	potential energy curve
PEF	potential energy function
PES	potential energy surface
PME	particle-mesh Ewald
PNO	pair natural orbital
PSF	protein structure file
QED	quantum electrodynamics
QFT	quantum field theory
QM	quantum mechanics
QUITEL	International Congress of Theoretical Chemists of Latin Expression
RAP	Roundtable on Astroscience and Planetary Analogues
RMSD	root-mean-square deviation
RPA	random phase approximation
SAM	self-assembled monolayer
SCF	self-consistent field
SCGVB	spin-coupled generalized valence bond
SE	Schrödinger equation
SNAP	spectral neighbour analysis potential
SOC	spin-orbit coupling
SOS	sum-over-states
SPME	smooth particle-mesh Ewald
STEOM	similarity transformed equation of motion
STO	Slater-type orbital
TDA	Tamm–Dancoff approximation
TDDFT	time-dependent density functional theory
TDHF	time-dependent Hartree–Fock
TDKS	time-dependent Kohn–Sham
TDSE	time-dependent Schrödinger equation
TheoDORE	Theoretical Density, Orbital Relaxation and Exciton analysis
TISE	time-independent Schrödinger equation
TS	transition state
UFF	universal force field

UV	ultraviolet
VUV	vacuum-ultraviolet
X ₂ C	exact two-component
XC	exchange-correlation
ZORA	zeroth-order regular approximation
ZPE	zero-point energy

CHAPTER 1

CONTEXT AND SCOPE

CONTENTS

1.1	ON THE MULTISCALE APPROACH-----	2
1.2	PROJECT DEFINITION AND AIMS-----	6
1.2.1	GENERAL OBJECTIVES-----	9

1.1 ON THE MULTISCALE APPROACH

THE HISTORY OF SCIENCE IS marked by the profound success of the reductionist approach as the dominant framework to investigate and interpret nature. This epistemological choice gained weight through landmark achievements, most notably Newtonian mechanics and the development of atomic theory, which together reinforced a methodology of isolating variables and seeking fundamental laws. In parallel to this way of thinking came a tendency to compartmentalise knowledge into increasingly fragmented disciplines, leading to the creation of specialised research communities that persist today.

The gains from this path have been enormous. Isolating variables, reducing complexity, and simplifying models proved extraordinarily productive. Dealing with one well-defined problem at a time became a deeply ingrained feature of scientific practice. Many scientists, particularly in the physical sciences, developed a scepticism of complexity, as the infamous tale of the spherical cow in a vacuum humorously illustrates. Explaining natural phenomena as the consequence of the movement and interactions of indivisible entities revolutionised our predictive power and ultimately defined the modern scientific worldview. Through this development we codified fundamental particles, forces, and laws, and the resulting technological advances powered the industrial and technological revolutions.

However, as even Aristotle observed, “the whole is more than the sum of its parts.” Despite the tremendous success of reductionism, a countervailing perception has always existed: that a purely reductionist focus might be insufficient for understanding certain classes of phenomena. The case of entropy is arguably one of the most important examples. It demonstrates how a fundamental property of the macroscopic world is not apparent in the time-symmetrical laws governing elementary constituents, but instead emerges as a collective, statistical consequence of their behaviour—a phenomenon now known as *emergence*. Until the statistical nature of entropy was understood, we struggled to explain the observed directionality of spontaneous processes, such as the diffusive mixing of miscible liquids (as opposed to its spontaneous unmixing) in contrast to the fundamentally time-symmetrical microphysical laws.

Today, the scientific enterprise is increasingly embracing this complexity. We recognise the need to integrate insights from the macro and the collective, and to bridge the gaps between disciplinary silos to build a more complete view of reality. This recognition has spurred the growth of fields such as systems theory [1, 2], complexity theory [3–5], and network science [6, 7], among others. It is within this evolving intellectual landscape that the work of this thesis is situated. The future of science—and the central theme of this work—is inherently multidisciplinary and multiscale.

THIS IS NOT TO SAY THAT REDUCTIONISM is inherently flawed, even though some authors will insist on saying so [8–13]. Although the reductionism–antireductionism debate is extremely complex [14–19], it is possible to see the methodological reductionist approach as a necessary

movement towards the micro, guided by the widely held and extraordinarily successful working hypothesis that reality has an ontological aspect of reductionism; that is, it appears to be built upon elementary particles governed by fundamental forces. But that alone does not tell the whole story and we should make the movement back to the macro, being careful to consider that, in changing scales, our methodological and epistemological approach makes the necessary adjustments, not only out of practical limitations, but as a fundamental necessity [20–26].

Let us consider more carefully the case of entropy. A certain reductionist methodology would assume that the macroscopic world, since composed of elementary particles—or some more complex discrete units such as atoms or molecules—that interact via a set of elementary forces, can be completely understood on the basis of such conceptual and material entities. However, one would be confronted by the reality that, although the laws of motion, momentum, forces, kinetic and potential energies are all time-symmetrical in the microscopic level, certain observations in the macroscopic level clearly imply that there is a preferential spontaneous direction as time passes. For instance, when a drop of ink is thrown into a glass of pure water, the ink will soon diffuse into the solvent and colour its whole content. The opposite—ink initially spread out in a solvent concentrating into a small spot—is never observed in reality. Yet, there is nothing in the fundamental laws of motion at the microscopic level that directly explain this fact.

We are here considering the case of irreversibility. The explanatory basis for this aspect of reality, now known as the second law of thermodynamics, was developed during the beginnings of the nineteenth century from studies at the macroscopic level [27]. In that context, it was clear that the fundamental forces and Newtonian mechanics were not sufficient to explain irreversible process, at least not straightforwardly. It was by the end of that same century that a connection between the microscopic mechanics and the thermodynamic laws began to be made via statistical thermodynamics, most notably in the work of Ludwig Boltzmann. Today we know that the arrow of time—the fact that the entropy of an isolated system always increases—can be explained on the basis of the probabilistic distribution of microstates in a system [20, 28–30]. Such microstates can indeed be accounted for on the basis of the usual laws of physics at the microscopic level. We say then that the concept of entropy and its increase *emerge* from the physics of the microscopic world. Thus, instead of saying that “the whole is nothing more than the sum of its parts” we could say that “the whole is composed entirely of its parts, but will have properties none of its parts have”.

The fact that a fundamental law of nature is not apparent from its elementary constituents, even though we can connect the elementary and the collective statistically, leads to a tension between reductionism in the one hand and holism in the other hand. It is indeed the case that the whole is more than the sum of its parts, but the properties of its parts define the higher level properties of the whole. That is the core of emergentism. In that sense, a methodological

reductionism is always at the service of the holistic view, in the sense that, structurally, lower level properties are always essential for giving rise to higher level¹ features; reductionism leads only to a part of the story. Therefore, reductionism and holism should not really be taken as conflicting, exclusive perspectives, but as complementary approaches to probe reality.

Some criticism can be applied to the view just posed above. A more thorough discussion of all the aspects involved in this debate is outside the scope of this text (see references above), but we can nevertheless offer some nuance into that perspective in order to be more precise. Some authors will make a distinction between *weak* and *strong* emergentism [31–37]. The former refers to properties that emerge in the higher level but can be explained on the basis of the interactions of the system’s components and properties at the lower level, although the explanation may not be obvious or simple. This is precisely the case we have discussed above. Strong emergentism, on the other hand, refers to emergent properties entirely new in a higher level, that cannot be reduced to properties of the lower level constituents of a system. While it is still considered that the properties arise from the parts, they are not fully determined by them, but they are autonomous and, more than that, they can exert influence onto the system’s parts—a phenomenon called *downward causation*. In summary, weak emergence is in the *epistemological* realm, while strong emergence is in the *ontological* level. Although there is currently no physical phenomenon unmistakably recognised as an instance of strong emergence, some would consider consciousness as an example [38, 39]. Our knowledge about consciousness is so limited, however, that any such claims are at least precipitate. In fact, any argument in favour of a strong emergentist stance seems precipitate and sprung out of the knowledge gap connecting the different levels of complexity. Thankfully, for the context of this work, one can remain agnostic in relation to strong emergence, and assume only the weak kind is justifiable and necessary.

IT HAS BEEN POINTED OUT THAT weak emergent phenomena can be observed by computer simulations of large scale systems with input variables informed by the elementary properties and entities at a lower level. As Mark Bedau argues, some weak emergent properties are characterised by explanatory incompressibility, ie, they cannot be predicted without simulating the underlying micro-level interactions [31, 32]. This makes computer simulation not merely a practical tool but an epistemological necessity for observing and understanding such phenomena [40]. A remarkable example is the cellular automata devised by Stephen Wolfram. He shows that complex macro-level patterns arise from simple micro-level rules, and their behaviour can only be discovered through simulation [41–43]. Complexity science has thus

¹*Note on terminology:* in the current context, we are using lower and higher levels to refer to the level of complexity. Thus, lower level refer to more fundamental scales; smaller spatial and often temporal scales, closer to elementary particles and forces. Higher level refer to greater level of organisation, where ensembles of more fundamental parts and more complex interplay between forces occur. Atoms are at a lower level than molecules, but at a higher level than subatomic particles.

adopted computer simulation as a core method for investigating emergent phenomena [44, 45].

One way simulation models can be thought of is as a layered process in which smaller scale elements and properties of a system are applied to the above layer at a larger spatial, temporal, and energetic scale, often incorporating approximations and abstraction of variables. This can be carried on layer by layer as one goes upscale. This *methodological* framework is akin to the *theory* framework in the very heart of some of the modern problems in physics, particularly when we go downscale. For example, general relativity is successful at explaining the gravitational interaction of matter at the larger cosmological scales (galaxies, stars, planets) and even at human scales. However, as one approaches the quantum scale, eg, in the interiors of black holes, its application leads to a breakdown of predictability, manifested in the prediction of spacetime singularities where classical concepts cease to be valid [46–48]. This implies that there should be a more fundamental theory of gravity for which general relativity is an *effective field theory* [49–51]. This *theory reduction* has happened before in the history of science. Trying to explain the spectrum of black-body radiation using the classical electromagnetic theory led to the prediction of infinite energy emission towards the ultraviolet (UV) region. Quantum theory then provided the answer, showing that the prevailing classical theories were good approximations at lower energies, but not at higher energies [52–55]. In fact, by analogy with this episode, physicists now refer to theories operating at smaller scales as UV theories, while those at higher scales are referred to as infrared (IR) theories. In this conceptual setting, as we move through different scales, different theories operate optimally. The higher level theory can be shown to be compatible with the lower level one, the latter being a generalisation. In the case of classical mechanics and quantum mechanics the equivalence is shown by the Ehrenfest theorem [56–60].

The method and theory reductionism concepts are applied in the multiscale simulation framework known as the *hierarchical multiscale approach*. In this strategy, knowledge gained about components of a system at smaller scales, using more refined theories, is fed into higher scale models, usually based on higher level theories, in a bottom-up, constructivist fashion. This method was originally devised out of practical necessity, as increasing the size of the system or the temporal span of the simulation demanded unattainable computational capacity. By abstracting out variables and/or components of the system and approximating the physical theory, higher level models become less computationally demanding, allowing for increase in scale at reasonable computational cost. Despite the practical origin of multiscale methods, from the discussion above, we now understand that the use of higher level theory and models is epistemologically called for, since often higher level phenomena need their own set of concepts—its own language if you will—to be adequately conceptualised and explained.

In this work, the lowest organisational scale (the level of atoms and molecules) is treated by quantum mechanical methods (see § 2.1). The next step up the scale is accounted for by means of molecular mechanic (MM) and molecular dynamics (MD) methods (see § 2.2). At higher temporal and spatial dimensions, in which MM/MD methods become impractical, one often resorts to stochastic or Monte Carlo methods. Although we make reference to an stochastic approach in this text (see § 2.3), the goal is not to climb the scale ladder, but rather to simplify the computationally demanding tasks of treating irradiation-driven process even at the molecular level. In various inherently multiscale processes, irradiation and its aftermath play central role [61], and this is the main interest of this thesis.

Besides the hierarchical approach, there is the *concurrent multiscale approach*, which was not used in this work. In this strategy, rather than connecting various methods at progressively higher scale simulations, a large scale system is broken down into different domains in which different scale methods are employed simultaneously. The goal is to simplify the model as much as possible in order to gain computational efficiency in domains of the system where exactness is less of a concern (using MM/MD, for example), while maintaining a finer description of regions where a higher level of detail and exactness is necessary (with QM methods, for example). If MM/MD and QM methods are coupled in such a fashion, we are using the QM/MM approach. A myriad of other ways of devising multiscale methodologies exist and serve multiple research fields. A more detailed discussion of the approach used in this work can be found in [62–64]. A broader and more comprehensive treatment, including numerical methods, can be found in [65–67].

1.2 PROJECT DEFINITION AND AIMS

WITH THIS GROUND PREPARED, we are now in a position to lay out this work’s structure. The discussion presented in the subsequent chapters is built around the framework of a multiscale simulation of the photoassisted chemical vapour deposition (PACVD) process [68–72]. This is an innovative variation of the traditional chemical vapour deposition (CVD) [73]. Both of these techniques are used to controllably form thin films or coatings on a substrate through the chemical reaction of vapour-phase precursors resulting in a solid deposit and volatile by-products. The difference is that, while in traditional CVD the substrates are thermally activated, often under hundreds of degrees Celsius, in PACVD the activation happens by photon irradiation, often near room temperature.

Conventional CVD of metals and metal-containing compounds is widely employed in microelectronics, semiconductors, optoelectronics, and protective coatings [74–77], where substrates can tolerate the high pyrolytic temperatures typically required to activate precursors. However, many emerging technologies, including organic photovoltaics [78], chemical sensors [79], and related electronic devices [80, 81], rely on thermally sensitive polymeric thin films

or self-assembled monolayers (SAMs). As such substrates cannot withstand conventional CVD conditions, PACVD offers an attractive alternative, enabling lower-temperature processing with improved selectivity and energy efficiency.

The PACVD process consists in controllably introducing precursor molecules in the gas phase into a reaction chamber containing the substrate to be coated. The precursor is contained in a separate vessel, often as a solid or liquid, from which it is sourced and volatilised before injection into the reaction chamber by a flow-control valve. A high-energy light source, typically a laser or UV lamp, provides the necessary photoactivation. The light is usually directed toward the substrate surface, either through a transparent window in the chamber or from a source positioned inside it. If the substrate is photosensitive, the light beam can be oriented parallel to the surface, activating the precursor in the head space before it lands on the surface. Although this technique allows for room-temperature deposition, heat can still be applied to the substrate if needed. In many settings, the reaction chamber can be evacuated, although it is not always necessary (Figure 1.1).

In the particular experiment that inspired this work [72], alkanethiol SAMs on gold, meant to be a model for organic thin films, were used as substrates. $(\eta^4\text{-diene})\text{Ru}(\text{CO})_3$ precursors were then employed for the deposition of ruthenium onto the substrate. The reaction chamber was kept under moderate vacuum and at room temperature. The light source, oriented parallel to the substrate's surface through a transparent window, was a 500 W Hg arc UV lamp. The essential elements to be considered in the simulation of this process are the alkanethiol SAM substrates, the various Ru-based precursors, the photodissociation reactivity of these molecules under the photon energy range of the light source, and the reaction between precursor fragments and the substrate's surface. As already anticipated, the computational model was devised in the hierarchical multiscale perspective. Therefore, in a bottom-up fashion, QM methods (§ 2.1) were employed to investigate the molecular structures, reactivity properties, and the processes happening at the lowest level of organisation; in this case the single-molecule level. Information gathered at this stage then informed the selection of parameters for MD simulations of larger scale systems (§ 2.2), including the irradiation-driven molecular dynamics (IDMD) strategy to simulate the photodissociation events of the PACVD precursors (§ 2.3). This stage of the simulation was performed using the MESOBIONANO EXPLORER (MBN EXPLORER) software package [82] (more on § 2.2).

The subsequent material is organised in the following way. **Chapter 2** discusses in depth the QM and MM/MD methods utilised in this work, offering insight into the method selection, their advantages and limitations. **Chapter 3** presents the QM investigation of the various pertinent properties of the Ru precursors, with focus on the geometries, electronic absorption spectra, and photodissociation reactivity of the intact molecules and their fragments. The results obtained in this investigation provide geometrical parameters for the development of an MM model of the precursors and help estimate stochastic parameters and reaction

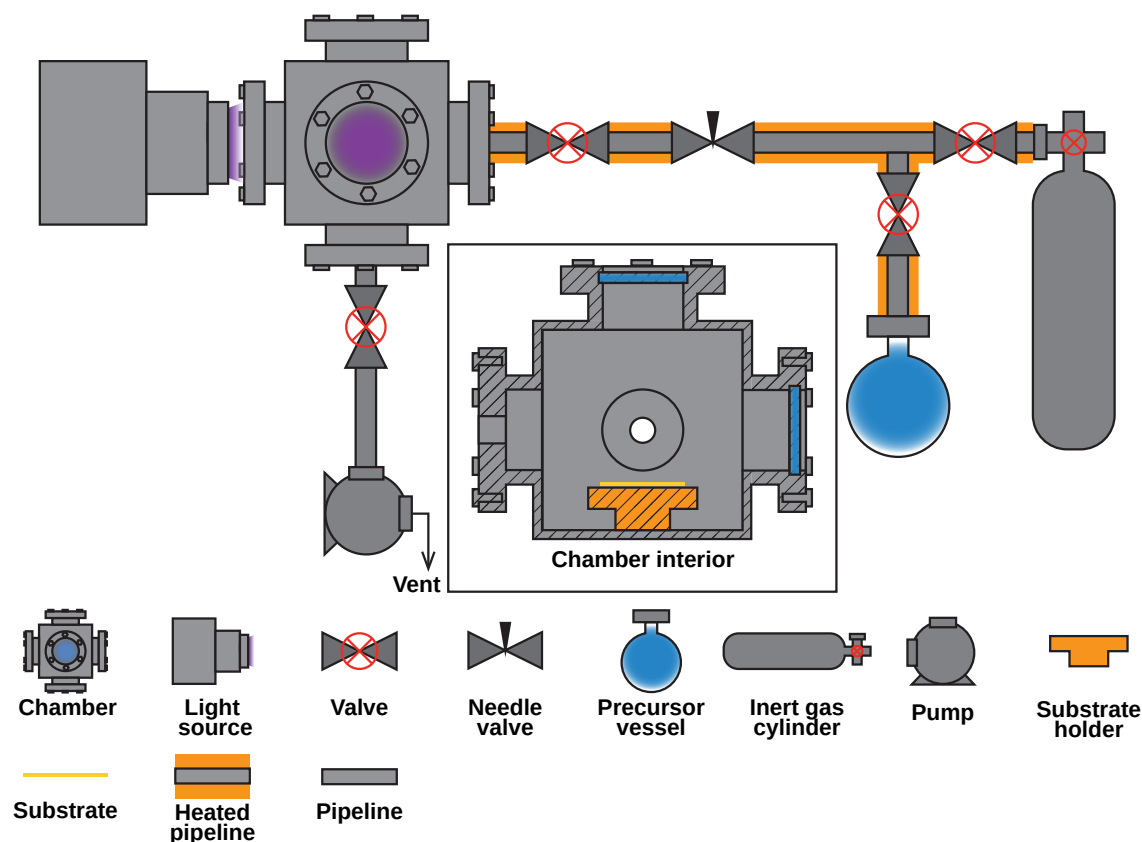


FIGURE 1.1 – Schematic representation of a simple PACVD apparatus. The chamber is connected to an inlet line through which the precursor is introduced from a (possibly heated) vessel by an inert gas flow and controlled by a dosing needle valve. If the precursor is not air-sensitive, the carrying gas can be atmospheric air introduced by a rotary pump, as it was done in the setup in [72]. An outlet line connects the chamber to a turbo pump that evacuates its interior and vent out the gas residues generated in the process. The pump outlet can be connected to a gas washing or adsorption system in case toxic volatiles are released. A light source shines light through a window in one face of the chamber. Alternatively, a light source can be installed inside the chamber. A substrate holder with heating and temperature control is positioned inside the chamber.

channels for the IDMD photodissociation model. The information gathered in this stage of the investigation is not limited to parametrisation of the next-level simulations, but stand on its own as important information about the photochemistry of these molecules, and is showcased in dialogue with experimental results. In **Chapter 4** we present the development of a model of alkanethiol SAMs on gold. In this chapter, moving to the next organisational level comes with the shift from the QM level of theory to a less detailed MM/MD setting in order to simulate an extended, multi-molecule system. Self-assembled systems are particularly interesting for the theme of emergence. They are highly organised dynamical systems that arise and are sustained purely by thermodynamic laws and intermolecular forces. Their macroscopic features are emergent but fully explainable by the underlying-level atomistic

properties. Our discussion will focus particularly on the definition and refinement of MM force field (FF) parameters capable of describing the high level of geometrical organisation and the dynamic stability of these systems. Once again, although in the context of this work this model is developed as one step towards the simulation of a PACVD process, the results of this study are independent and can be further utilised in the investigation of various properties of alkanethiol SAMs.

Before addressing the assembly of the results of Chapter 3 and Chapter 4 into the deposition simulation, we expand on the methods applied so far by considering a few case-studies **Chapter 5**. Case Study 1 (§ 5.2) compares the ability of a TDDFT method in describing the electronic transitions of a series of boron-dipyrromethene against DLPNO-EOM-CCSD—a linear-scaling coupled-cluster method—offering insight on the strengths and weaknesses of the method. Case Study 2 (§ 5.3) discusses a few notable examples where TDDFT can be utilised to predict and interpret the vacuum-UV spectra of molecular ices of astrochemical interest. The results show the possibility of approaching scales beyond the molecular level even at such detailed and demanding level of theory. This in turn demonstrate that a theory shift is not always needed when changing scales, although some caveats exist. Case Study 3 (§ 5.4) moves to the MD level to show the capabilities of reactive MD (§ 2.2.1.2) in a study of the collision-induced allotropic transformation of carbon nanoflakes into nanotubes. The exemplary studies are laid out as short-format, continuous text and are meant to expand on the methodological discussion in the context of multiscale excited-state modeling.

To conclude, **Chapter 6** integrates the findings from Chapter 3 and Chapter 4 into a proof-of-concept methodology for the simulation of a PACVD process. This chapter establishes the conceptual framework, detailing its core features and construction, and discusses what is required for its future validation against experimental data. By critically assessing the current scope and inherent limitations of the model, we contextualise the present achievements while laying the groundwork for its future evolution towards a complete simulation of the full process. We then chart a clear course forwards, outlining sophisticated enhancements that will further refine the methodology in future works.

1.2.1 GENERAL OBJECTIVES

THE OVERARCHING OBJECTIVE of this thesis is to develop a proof-of-concept multiscale model for the photoassisted chemical vapour deposition of ruthenium onto alkanethiol SAMs on gold from $(\eta^4\text{-diene})\text{Ru}(\text{CO})_3$ precursors. This goal is achieved through three integrated tasks:

- i To investigate the geometrical properties, excited states, and photodissociation reactivity of $(\eta^4\text{-diene})\text{Ru}(\text{CO})_3$ precursors using electronic structure methods. These

data provide the foundation for developing the IDMD and reactive FF parameters essential for large-scale dynamics simulations (Chapter 3).

- ii To construct a MM/MD model of alkanethiol SAMs on gold that accurately reproduce known experimental geometrical, energetic and dynamical properties, thereby establishing a realistic substrate for the multiscale model (Chapter 4).
- iii To integrate the precursors reactivity data (i) and the substrate model (ii) into a unified multiscale framework for the simulation of the PACVD of ruthenium onto substrates consisting of alkanethiol SAMs on gold (Chapter 6).

Collectively, these objectives establish a novel computational framework to predict and understand the fundamental physical chemistry governing a technologically relevant deposition process. The model is based on the unique combination of the IDMD approach with the reactive CHARMM force field implemented in MBN EXPLORER. The result is a unified model spanning from the fast, local irradiation events to the large spacial and temporal scales of the post-irradiation relaxation and deposition processes involved in PACVD.

CHAPTER 2

FOUNDATIONS

FEATURED WORK

C P Souza and F Fantuzzi, “Computational strategies for modelling excited states in organometallic chemistry”, in *Organometallic Chemistry*, ed C Bakewell, G R Owen, N Costa and R Musgrave, Royal Society of Chemistry, London, 2024, vol 45, chap 9, pp 271–316, DOI: 10.1039/9781837676200-00271.



CONTENTS

2.1	QUANTUM MECHANICAL METHODS -----	12
2.1.1	HARTREE–FOCK AND POST-HARTREE–FOCK METHODS -----	18
2.1.2	DENSITY FUNCTIONAL THEORY-----	24
2.1.3	RELATIVISTIC CORRECTIONS -----	30
2.1.4	THE TIME-DEPENDENT EXTENSIONS FOR EXCITED STATES -----	31
2.2	CLASSICAL MOLECULAR MECHANICS AND DYNAMICS -----	44
2.2.1	STANDARD AND REACTIVE FORCE FIELDS -----	46
2.2.2	MOLECULAR DYNAMICS ALGORITHMS -----	70
2.3	IRRADIATION-DRIVEN MOLECULAR DYNAMICS AND THE MBN EXPLORER PACKAGE -----	78

2.1 QUANTUM MECHANICAL METHODS

NONRELATIVISTIC QUANTUM mechanical methods, particularly density functional theory (DFT), were utilised to investigate the smallest scales in this work. This is the most detailed (higher in hierarchy) level of theory¹ we will employ here. Adding to the theory reduction discussion above, QM can be viewed as an effective field theory of a more general quantum field theory (QFT) below the speed of light and high energy limits. Indeed, a QFT currently accounts for all known fundamental particles and forces (the standard model) in the universe except for gravity. For most chemical phenomena, QM is sufficient for an accurate treatment, though. Despite starting with an essentially nonrelativistic formalism, we will use relativistic corrections when needed. Our discussion in this section will briefly describe the most important aspects of the two classes of QM methods employed in our calculations, namely, wavefunction-based and density functional-based methods, and introduce the time-dependent approaches applicable to both of them in order to calculate excited-state properties. More details can be found in [83] and references thereof. Additional references are included below.

IN THE NONRELATIVISTIC QM framework, we usually start with the Schrödinger equation (SE) and the accompanying standard collection of postulates as the foundation of our model [84]. This would be all we need to develop a model of any molecular system described by the atom's nuclei and their surrounding electrons (an electronic structure method), except we would be missing a very important property, one that guarantees the stability of atoms and allows us to talk about an electronic structure in the first place: the *spin*. The spin, a fundamentally relativistic quantity, cannot be derived from a nonrelativistic treatment of QM—although it is featured in a more general relativistic model such as Dirac's [85, 86]—and must come as an *ad hoc* addition.

The general equation for the framework considered here is the full (or time-dependent) Schrödinger equation (TDSE) given by

$$\mathcal{H}(\mathbf{r}, \mathbf{R}, t)\Psi(\mathbf{r}, \mathbf{R}, t) = i\hbar \frac{\partial \Psi(\mathbf{r}, \mathbf{R}, t)}{\partial t}, \quad (2.1)$$

where $\mathcal{H}(\mathbf{r}, \mathbf{R}, t) = \mathcal{K}(\mathbf{r}, \mathbf{R}) + \mathcal{V}(\mathbf{r}, \mathbf{R}, t)$ is the Hamiltonian operator composed of the kinetic ($\mathcal{K}$) and potential ($\mathcal{V}$) energy operators for the system; $\mathbf{r}$ and $\mathbf{R}$ are the electronic and nuclear position vectors, respectively, and t is the time. For a time-independent potential $\mathcal{V}(\mathbf{r}, \mathbf{R}, t) = \mathcal{V}(\mathbf{r}, \mathbf{R})$ (such as the nuclear potential in atoms and molecule), the wavefunction

¹*Note on terminology:* do not confuse hierarchical level of theory with level of complexity (see n 1). A theory is in a higher hierarchical level than another if it is more fundamental and general. For example, QM is a higher level of theory than classical mechanics. Higher level theories are often better at explaining phenomena at lower levels of complexity.

can be separated into the product of a time-dependent and a time-independent part as

$$\Psi(\mathbf{r}, \mathbf{R}, t) = f(t)\psi(\mathbf{r}, \mathbf{R}), \quad (2.2)$$

leading to the time-independent Schrödinger equation (TISE)

$$\mathcal{H}(\mathbf{r}, \mathbf{R})\psi_i(\mathbf{r}, \mathbf{R}) = E_i\psi_i(\mathbf{r}, \mathbf{R}) \quad (2.3)$$

and a time-dependent part

$$f(t) = e^{-iE_it/\hbar}, \quad (2.4)$$

when Equation 2.2 is inserted into Equation 2.1 and the resulting equation is solved for t .

The solution of Equation 2.3 yields a complete set of state wavefunctions $\{\psi_i\}$ and their respective energies $\{E_i\}$. Each wavefunction contains all possible information about a state and can be used with suitable operators to obtain the expected values of any observable. In other words, all that can be known about the system is encoded in $\{\psi_i\}$. However, this optimistic picture is complicated even for simple atomic systems containing more than one electron. To understand why, let us consider in more detail the standard nonrelativistic Hamiltonian for a system that contains N electrons and M nuclei, and is devoid of external potential interactions. It can be written as

$$\mathcal{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \frac{1}{2} \sum_{A=1}^M \frac{1}{M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^M \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{A>B}^M \frac{Z_A Z_B}{R_{AB}}, \quad (2.5)$$

where M_A and Z_A are the mass and the total charge of nucleus A , respectively; and r_{iA} , r_{ij} , and R_{AB} are the distances between electron i and nucleus A , electrons i and j , and nuclei A and B , respectively.² This Hamiltonian is written in atomic units.³ The first two terms are the kinetic energy of the electrons and nuclei, respectively; the last three terms describe the electron-nucleus, the electron-electron, and the nucleus-nucleus Coulomb interactions, respectively.

If we consider atomic systems, for which the second and last terms in Equation 2.5 are void, the TISE has exact analytic solution only for hydrogenic atoms.⁴ This is because the

²*Note on mathematical notation:* in Equation 2.5 R_{AB} and r_{ij} are the moduli of the distance vectors, while in Equation 2.1, $\mathbf{R}$ and $\mathbf{r}$ are the distance vectors themselves. In this text, scalars are set in regular type, and vectors are set in bold weight. Variables are italicised while constants are written as Roman (upright) characters. Calligraphic characters are reserved for operators.

³In this system of units, physical constants or combinations thereof are utilised as units of measurement. Eg, the electron mass m_e , the absolute value of its charge $|e|$, Planck's constant divided by 2π , $\hbar$, and $4\pi\epsilon_0$ (where ϵ_0 is the electric permittivity of free space) are all set to unity.

⁴There is, however, an accurate numerical solution for the helium atom and heliogenic species, first developed by Egil Hylleraas [87–90]. These solutions are systematically improvable, ie, the error can be made arbitrarily small by including more terms in the wavefunction expansion, but they are not closed-form solutions. In this sense, they provide a numerically exact result for practical purposes, with a quantifiable error bound.

pairwise electron-electron interaction is impossible to solve exactly in multielectronic systems. An approximation that remedies this complication is discussed in detail in § 2.1.1 below, but it is worth advancing the concept here. The idea is to approximate the electron-electron interaction term $\mathcal{J}_{ij} = \frac{1}{r_{ij}}$ in the many-electron Hamiltonian by replacing it with a spatially- and spin-averaged effective potential $v_i(\mathbf{r})$. This potential v_i represents the average repulsive field generated by the remaining $N - 1$ electrons. Substituting v_i for the full $\sum_{i=1}^N \sum_{j>i}^M \frac{1}{r_{ij}}$ term yields a one-electron Hamiltonian. Solving the corresponding one-electron Schrödinger equation produces a set of one-electron wavefunctions ϕ_i , ie, *orbitals*. Finally, an *ansatz* for the total N -electron wavefunction is constructed from these orbitals (eg, a single Slater determinant for Hartree–Fock, § 2.1.1). Any electronic structure method that follows this logic is called an *independent particle model* (IPM).

If we move further in complexity to molecular systems, an additional complication arises: because nuclei can also move relative to one another, accounting for the dynamic electron-nucleus interactions becomes complicated. That leads to another key approximation often made in quantum chemical models for molecules: the Born–Oppenheimer (BO) approximation, which we briefly discuss now. The key idea in the BO approximation is to devise a way of decoupling the electronic motion from that of the nuclei. From Equation 2.5, we can define an *electronic* Hamiltonian $\mathcal{H}_{el}$ by neglecting the nuclear kinetic energy term $\mathcal{K}_n = -\frac{1}{2} \sum_{A=1}^M \frac{1}{M_A} \nabla_A^2$ and fixing all the nuclear positions $\mathbf{R}$, essentially transforming them into parameters. This change makes the last term in the equation a constant that contributes only to the *energy* of the states, and not to their *wavefunctions*. We can now seek a solution for the TISE (Equation 2.3) using $\mathcal{H}_{el}$ as

$$\mathcal{H}_{el} \Phi_i(\mathbf{r}; \mathbf{R}) = V_i(\mathbf{R}) \Phi_i(\mathbf{r}; \mathbf{R}). \quad (2.6)$$

In this equation, the eigenvalues $V_i(\mathbf{R})$ are the energies of the electronic levels Φ_i , which depend *only parametrically* on the nuclear positions $\mathbf{R}$. $V_i(\mathbf{R})$ is referred to as a potential energy surface (PES). Since the Hamiltonian is a Hermitian operator, the solutions $\{\Phi_i\}$ constitute a complete basis set, allowing the total wavefunction ψ to be expressed as a linear combination of Φ_i such that

$$\psi(\mathbf{r}, \mathbf{R}) = \sum_i \chi_i(\mathbf{R}) \Phi_i(\mathbf{r}; \mathbf{R}). \quad (2.7)$$

Note that in this last equation, $\psi(\mathbf{r}, \mathbf{R})$ recovers the full dynamic dependence in the nuclear coordinates through the nuclear coefficients $\chi_i(\mathbf{R})$. Equation 2.7 is called the Born representation of the wavefunction.

Up to this point, no approximation has been made. We have only encountered a more convenient representation of the time-independent wavefunction which is completely equiva-

lent to the ψ in Equation 2.2. Inserting the *multiconfigurational ansatz* given by Equation 2.7 into Equation 2.3, multiplying by the complex conjugate of an electronic wavefunction Φ_j^* , and integrating over all electronic coordinates, we obtain

$$[\mathcal{K}_n + V_j] \chi_j - \sum_i \hat{\Lambda}_{ij} \chi_i = E_j \chi_j. \quad (2.8)$$

The matrix elements $\hat{\Lambda}_{ij}$ are the nonadiabatic coupling operators, given by⁵

$$\hat{\Lambda}_{ij} = \delta_{ij} \mathcal{K}_n - \langle \Phi_j | \mathcal{K}_n | \Phi_i \rangle. \quad (2.9)$$

These operators are a consequence of the nuclear kinetic energy operator's action on the electronic wavefunctions. Therefore, they describe the coupled movement of electrons and nuclei. Expressing $\nabla^2 = \nabla \cdot \nabla$ in the nuclear kinetic energy operator $\mathcal{K}_n$, we can write Equation 2.9 as

$$\hat{\Lambda}_{ij} = \frac{1}{2M_A} (2\mathbf{F}_{ij} \cdot \nabla + G_{ij}), \quad (2.10)$$

where

$$\mathbf{F}_{ij} = \langle \Phi_i | \nabla \Phi_j \rangle \quad (2.11)$$

is the derivative coupling vector and

$$G_{ij} = \langle \Phi_i | \nabla^2 \Phi_j \rangle \quad (2.12)$$

is the scalar coupling. In this and subsequent equations, the ∇ operator acts only on nuclear coordinates.

The impossibility of a closed exact solution to the multinuclear and multielectronic problem is a direct consequence of the coupling of the electronic and nuclear movement discussed above. The BO approximation is obtained if we use the simple product for a single electronic state Φ_i [92]

$$\psi(\mathbf{r}, \mathbf{R}) = \chi_i(\mathbf{R}) \Phi_i(\mathbf{r}; \mathbf{R}). \quad (2.13)$$

Inserting it into Equation 2.3 and following the same procedure that resulted in Equation 2.8, we obtain

$$[\mathcal{K}_n + V_i - \hat{\Lambda}] \chi_i(\mathbf{R}) = E_i(\mathbf{r}; \mathbf{R}) \chi_i(\mathbf{R}), \quad (2.14)$$

where $\hat{\Lambda} = \hat{\Lambda}_{ii}$ is the diagonal nonadiabatic coupling operator for the state of interest. Equation 2.8 with the null off-diagonal terms results in an infinite set of independent equations similar to Equation 2.14. We can further approximate this solution if we completely ignore

⁵From now on, we will make use of the bra-ket notation for the integrals over electronic coordinates as this greatly simplifies the notation and readability. The reader unfamiliar with such notation can consult § 1.1.4 of [91].

the term $\hat{\Lambda}$. We then obtain

$$[\mathcal{H}_n + V_i] \chi_i(\mathbf{R}) = E_i(\mathbf{r}; \mathbf{R}) \chi_i(\mathbf{R}). \quad (2.15)$$

This last equation is the *adiabatic approximation* as all the nonadiabatic coupling terms are absent.

We can now interpret the results of the approximations made here. Equation 2.10 shows that the factors $\hat{\Lambda}_{ij}$ are the less significant the greater the nuclear masses M_A . Hence the usual justification for BO approximation's validity being that electrons adapt themselves to changes in nuclear configuration by virtue of their much smaller mass in relation to that of the nuclei. This reasoning is made by Oppenheimer himself via perturbation theory [93].⁶ Applying the operator ∇ to Equation 2.6 and using Equation 2.11 we obtain the analogous of the Hellmann–Feynman theorem for the off-diagonal elements

$$\mathbf{F}_{ij} = \frac{\langle \Phi_i | \nabla \mathcal{H}_{el} | \Phi_j \rangle}{V_j - V_i}, \quad i \neq j, \quad (2.16)$$

the diagonal elements ($i = j$) being all null. Equation 2.16 implies that, in the vicinity of a degeneracy between states ($V_i = V_j$), the derivative coupling grows fast, invalidating the BO approximation. This happens when two PESs cross or touch each other. For states well separated in energy, though, the approximation is excellent. These characteristics of the approximation suggest that we can utilise an *ansatz* intermediate to Equation 2.7 and Equation 2.13 by expanding ψ in groups that contains only the states with appreciable nonadiabatic couplings. This is the *group adiabatic approximation*. In this case we end up with a finite sum of terms in place of the original infinite one in Equation 2.7, impossible to be used in practice.

The basis set of the electronic wavefunctions $\{\Phi_i\}$ obtained as solutions to Equation 2.6 and utilised in the Born representation of the total wavefunction (Equation 2.7) is called an *adiabatic basis*. The origin of this name is probably linked to the common property of the adiabatic states' PESs not crossing one another.⁷ The so-called noncrossing rule or Neumann–Wigner theorem offers an explanation to the phenomenon [94] (a demonstration can be found in § 79 of [95]). However, O'Malley [96] argues that this theorem is not a physical property but rather a mathematical construct valid only for representations in which the Hamiltonian

⁶An English translation can be accessed at <http://elib.bsu.by/handle/123456789/154381>

⁷The term *adiabatic* comes from the Greek ἀδιαβατικός (adiabatikós), a variation of ἀδιάβατος (adiábatos), composed by the negative prepositive particle α- (a-) + the preposition διά (diá; through) + the verb βαίνω (baínō; to go, to walk, to move, to pass) adjectivised by the suffix -τος (-tos), meaning that which “cannot be transposed”; impassable, impermeable. In the current context it refers to the noncrossing property of the PESs of electronic states. With this definition, the words *nonadiabatic* and *diabatic* should be clear. The word should not be confused with the same term applied in the context of adiabatic thermodynamic processes. In that case, the term qualifies the system's boundaries, impermeable to matter and energy.

matrix is diagonal—precisely the case of the adiabatic representations. Moreover, conical intersections are a property that indeed demonstrate that crossings between PESs not only exist but are fairly common (see, for example, [92]).

The adiabatic representation contains terms of the type F_{ij} and G_{ij} over electronic states even in the group BO approximation. It is possible to select a set of basis functions in which these terms vanish. Such set is called a *diabatic basis* for the system (see § 12.2.2 of [97], § 2.2 of [98] and § 5.3 of [92] for more details). The exact basis transformation to a diabatic basis is possible only for diatomic molecules but transformations in which nonadiabatic couplings become negligible (the so-called quasidiabatic transformations) are generally possible.

An interesting consequence of the BO approximation is the concept of an *equilibrium geometry* for a multinuclear system. Equation 2.6 defines a PES $V_i(\mathbf{R})$ for each electronic state Φ_i of a system. One can look for the set of nuclear coordinates $\mathbf{R}$ that minimises the energy $V_i(\mathbf{R})$ of the systems electronic ground state for example, and call it an equilibrium geometry. The PES for an electronic state exist independent of the BO approximation and is an exact mathematical object within the theory. However, it does not correspond to any *observable*. The total wavefunction for the system is given by the Born representation (Equation 2.13) that mixes all the states. The “geometry” that can be associated with a given state of a system is the expectation values of the nuclear wavefunctions $\chi_i(\mathbf{R})$, which is a quantum mechanical quantity depending dynamically on $\mathbf{R}$. However, by eliminating the nonadiabatic coupling vectors and therefore decoupling the electronic states and their nuclear wavefunctions (Equation 2.15), the BO approximation essentially equates the minimum of $V_i(\mathbf{R})$ with the expectation value of $\chi_i(\mathbf{R})$ for a given state. When the BO approximation is valid, the nuclear configuration $\mathbf{R}$ that minimises $V_i(\mathbf{R})$ can then indeed be reasonably defined as an equilibrium geometry and be associated with a stable configuration of a multinuclear system that can be “observed in reality”. The procedure by which it is obtained is called *geometry optimisation*. Various minimisation algorithms exist to perform such procedure [99–101]. It is important to remember, however, that, even in conditions in which the BO approximation is valid, the nuclei are still quantum mechanical objects subject to Heisenberg’s uncertainty principle and their position and momentum can never be defined simultaneously; nuclei are always delocalised.

In this text, we will reserve the upper-case psi (Ψ) for the total time-dependent wavefunction, the lower-case psi (ψ) for the total time-independent wavefunction, the upper-case phi (Φ) for the electronic wavefunctions, and later on, the lower-case straight phi (ϕ) for spatial orbitals (or one-electron wavefunctions) and the lower-case cursive phi (φ) for spin-orbitals. With this definition, we will omit the electronic Hamiltonian subscript as it becomes superfluous.

IN GOING FROM A MODEL OF the simplest atom to a multielectronic atom to a molecular system, we have essentially made two key approximations to the more fundamental nonrelativistic

QM theory: the IPM and the BO approximation. These are not just convenient approximations to facilitate calculations. They are necessary if we want to describe many-body systems for which there is no exact solution of the Schrödinger equation. There is no practical quantum chemical theory without them. More than that, each of these approximations introduces epistemological keystones for modern chemistry that permeate the very language we use: the concept of *electronic orbitals* and the concept of *equilibrium geometry*. Neither of these entities correspond to physical reality, ie, they are not observables within the QM framework. They are useful fictions, spawned from approximations, that we created to rationalise complicated aspects of reality, and this should be always kept in mind. Yet, they are epistemologically necessary both to allow us a model of the molecular world—since without them we would be limited to hydrogenic atoms—and to provide us with a language with which we can rationalise chemical concepts, as we started discussing in § 1.1. This is one instance of higher level conceptual structures that arise when we move up the complexity scale. Therefore, the naïve idea that one could explain the world at the highest level of complexity *ab initio* breaks down even at the atomic and molecular levels.

2.1.1 HARTREE–FOCK AND POST-HARTREE–FOCK METHODS

WE ARE NOW IN A POSITION TO start discussing in more detail how to model the electronic structure of atomic and molecular systems. As anticipated above, the natural way to develop such a model is by means of an independent particle model. The Hartree–Fock (HF) method is the historical IPM of choice. Here we offer a superficial treatment of the method and improvements upon it, sufficient to inform the remaining of our discussion. More details can be found in [91].

We begin by associating a *spin-orbital*—a product of a spin function with a spatial one-electron wavefunction—to each electron in the system. As discussed above, being a relativistic property, the spin must be an *ad hoc* addition to the model. Fermions—of which the electron is one example—have half-integer spins that assume $\pm 1/2$ values. We can define two spin functions $\alpha(\omega)$ and $\beta(\omega)$ associated with each possible spin values for an electron. With this definition, an spin-orbital can be written as

$$\varphi(\mathbf{x}) = \begin{cases} \alpha(\omega)\phi(\mathbf{r}) \\ \text{or} \\ \beta(\omega)\phi(\mathbf{r}) \end{cases}, \quad (2.17)$$

where $\mathbf{x}$ is now the combined spatial ($\mathbf{r}$) and spin (ω) vectors. A spin-orbital is a solution to the one-electron TISE.

Each spin-orbital is typically expressed as a linear combination of a set of atomic basis functions, of which there are a few types [100, 102]. Two traditional types of atomic basis

functions are Slater-type orbitals (STOs) and Gaussian-type orbitals (GTOs). Although GTOs are not solutions for the hydrogenic atom problem, they make up a complete basis set that can describe any arbitrary function inside the Hilbert space and they are more tractable computationally than the exponential functions that are solutions to the one-electron problem. A complete basis set would include an infinite number of these functions. Thus, in practice, truncated basis sets must be used. The number and types of functions included in the basis set will directly impact the quality of the system's description.

When describing molecules in the molecular orbital (MO) picture, the spin-orbitals are taken to be molecular orbitals built from a set of atomic basis functions centred in the various atoms composing the molecule. This is known as *linear combination of atomic orbitals* (LCAO). In the HF model, the one-electron effective Hamiltonian is the Fock operator

$$\mathcal{F}(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} + v^{HF}(i) = h(i) + v^{HF}(i). \quad (2.18)$$

Spin-orbitals are then obtained as solution of the HF eigenvalue equation

$$\mathcal{F}(i) |\varphi_i(x)\rangle = \epsilon_i |\varphi_i(x)\rangle, \quad (2.19)$$

where ϵ_i is the orbital energy for orbital φ_i . The set $\{ |\varphi_i\rangle \}$ are one-electron solutions for a given molecule. From a basis set containing $K \geq N$ spatial orbitals, one can construct $2K$ unique spin-orbitals. To build an N -electron wavefunction $\Phi(\mathbf{r})$, we make use of the fact that the multielectron Fock operator is simply the sum of N $\mathcal{F}(i)$ operators, and that the solution of the corresponding eigenvalue equation is a product of N φ_i spin-orbitals with the total energy corresponding to the sum of the ϵ_i orbital energies. The N lowest energy φ_i spin-orbitals are the *occupied* orbitals describing the N electrons of the system, while the remaining $2K - N$ are *virtual* orbitals.

A simple product of N φ_i is called a Hartree product. However, this solution breaks an important property of the quantum behaviour of fermions: the antisymmetry principle. According to this principle, the total wavefunction of an electronic system must be antisymmetrical (the wavefunction must change signs) with respect to the exchange of coordinates of any pair of electrons. One way of achieving a wavefunction built as a product of spin-orbitals that satisfies this principle is the use of a Slater determinant of the form

$$|\Phi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(\mathbf{x}_1) & \varphi_2(\mathbf{x}_1) & \cdots & \varphi_N(\mathbf{x}_1) \\ \varphi_1(\mathbf{x}_2) & \varphi_2(\mathbf{x}_2) & \cdots & \varphi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_1(\mathbf{x}_N) & \varphi_2(\mathbf{x}_N) & \cdots & \varphi_N(\mathbf{x}_N) \end{vmatrix}. \quad (2.20)$$

While the antisymmetry condition is necessary for a correct description of the wavefunction, it is not sufficient. In fact, a correct wavefunction must also transform as an irreducible representation of the symmetric group S_N (where N is the number of electrons), reflecting the permutation symmetry of the Hamiltonian (Equation 2.5), which is completely symmetric under any permutation of the *spatial coordinates*. A single Slater determinant does transform as an irreducible representation of S_N —specifically, the totally antisymmetric one—but its spatial and spin factors are not independently symmetry-adapted. This means that the Slater determinant *ansatz* is unable to describe the independent spatial and spin permutation symmetries required for a correct treatment of electron correlation, and is therefore a limited choice from the beginning. More details on that can be found in [103–106].⁸

Equation 2.19 is a pseudo-eigenvalue equation because the effective HF potential $v^{HF}(i)$, being an averaged potential over $N - 1$ electrons, depends on all the orbitals in the system. This nonlinear characteristic of the equation leads to a solution procedure called the *self-consistent field* (SCF). The basis is the quantum variational principle, according to which, for a given Hamiltonian $\mathcal{H}$, the energy of a trial wavefunction $|\Phi\rangle$ is always greater than or equal to the true energy E_0 of the system; equality holding if, and only if, $|\Phi\rangle$ is the true wavefunction for the system. Mathematically,

$$\frac{\langle\Phi|\mathcal{H}|\Phi\rangle}{\langle\Phi|\Phi\rangle} \geq E_0. \quad (2.21)$$

In the SCF method, in principle, one starts with an initial guess for the wavefunction composed as the Slater determinant of spin-orbitals. By a combination of Equation 2.19 and the variational principle, the HF equation is solved, yielding a new set of orbitals (see Chapter 3 of [91] for the details). These new orbitals are then utilised to solve the HF equation again. This iterative procedure is repeated until the resulting orbitals converge and are virtually indistinguishable from those of the previous iteration. The flexibility of the wavefunction $|\Phi\rangle$ is in the choice of spin-orbitals and the coefficients of the basis set expansion of them. This direct SCF algorithm has a slow and unstable convergence. *In practice*, more sophisticated SCF algorithms are implemented. One example is the direct inversion in the iterative subspace (DIIS), which keeps track of a collection of previous iterations (and the associated error in energy), and utilises a linear combination of them that minimises the error for the next guesses. Details on this implementation can be found in [114–116].

THE HF WAVEFUNCTION obtained by the procedure described above, coming from an IPM, does not include the effect of the instantaneous electron-electron interactions. We say, then, that HF lacks electronic correlation or is an uncorrelated method. The HF method can

⁸A wavefunction-based method that starts from a correctly constructed wavefunction is given by the spin-coupled generalised valence bond (SCGVB) theory [103, 107–113].

be extended to include electron correlation by a procedure called *configuration interaction* (CI). In fact, the exact nonrelativistic wavefunction can be obtained *in principle* from the CI approach. This is a direct consequence of the fact that the set of spin-orbitals $\{\varphi_i(\mathbf{x})\}$, being the solution of an eigenvalue problem of a Hermitian operator, forms a complete set. Thus, any arbitrary function of the $\mathbf{x}$ variable can be expressed as a linear combination of the form $f(\mathbf{x}) = \sum_i a_i \varphi_i(\mathbf{x})$. A function of N variables such as $\Phi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ can in turn be expressed as a linear combination of products of N $\varphi_i(\mathbf{x})$ functions. Requiring that this function be antisymmetric then turns this expansion into the combination of all unique N -function determinants that can be constructed from the complete set $\{\varphi_i(\mathbf{x})\}$ of one-variable functions (see § 2.2.7 of [91] for a demonstration).

All possible determinants in the expansion can be constructed with reference to the HF determinant $|\Phi\rangle$. To make it easier to visualise, we can define *excited determinants* from this reference by exchanging occupied and virtual orbitals. The set of all determinants for which only one such exchange is made (singly-excited determinants) we call singles (s). Analogously, doubles (D), triples (T), quadruples (Q), ... are sets of determinants constructed by two, three, four, ... exchanges of occupied to virtual orbitals. The number of exchanges goes up to the number N of electrons in the system. The CI wavefunction *ansatz* can be written as

$$\Phi_{\text{CI}} = a_0 \Phi_{\text{HF}} + \sum_{\text{S}} a_{\text{S}} \Phi_{\text{S}} + \sum_{\text{D}} a_{\text{D}} \Phi_{\text{D}} + \sum_{\text{T}} a_{\text{T}} \Phi_{\text{T}} + \dots, \quad (2.22)$$

where each of the S, D, T, ... terms correspond to summation over all possible singles, doubles, triples, ... elements in the sets of determinants, respectively. The coefficients of the determinants are determined using the variational principle and orthonormalisation condition analogous to Equation 2.21. The result of a CI calculation is a series of eigenvalues and eigenfunctions, which can be viewed as the outcome of diagonalising the CI matrix. The smallest eigenvalue is the ground state energy, with its corresponding eigenfunction being the ground state wavefunction. The second lowest eigenvalue and its associated wavefunction correspond to the first excited state, and so on.

The exact wavefunction in principle will, naturally, include an infinite number of determinants since the complete basis set has an infinite number of virtual orbitals. The truncated basis set used in practice will define the maximum number of possible determinants in the expansion. One can easily perceive that a full CI calculation, even with a small basis set, is unfeasible but for the smallest systems. In fact, given a basis set with $2K$ spin-orbitals for a system of N electrons, there are

$$\binom{2K}{N} = \frac{(2K)!}{N! (2K - N)!} \quad (2.23)$$

possible Slater determinants. Essentially, this calculates how many different ways we can arrange N electrons into $2K$ available spin-orbitals. As $2K$ increase (provided $|N - K| \ll K$), the number of possible configurations increases rapidly, in a combinatorial explosion.

A common approximation for chemical purposes is to consider only the excited determinants arising from valence electrons, a procedure known as the *frozen core approximation*. The absolute error in energy by introducing such a procedure is not small. Core and core-valence correlation have large contributions to the total energy of multielectron systems. However, since core electrons respond weakly to chemical changes, this leads to good relative energies due to error cancellation. In addition to the frozen core approximation, CI calculations are typically performed using a truncated expansion, which limits the inclusion of excited determinants based on their order. Including only single excitations (CIS) does not improve the HF wavefunction because integrals involving singly excited determinants and the HF reference are zero because of orthogonality. Thus, the smallest improvement can be achieved by considering doubly excited determinants, either alone (CID) or with singles (CISD). The latter offers a slight improvement because the overlap between singles and doubles is nonzero. Further improvements can be made by including triply (CISDT) and quadruply (CISDTQ) excited determinants. The latter often approaches sufficiently close the full CI energy for many systems, but it becomes extremely computationally costly for large molecules and basis sets.

It is common to define the electronic correlation energy of a system as

$$E_{\text{corr}} = E_{\text{CI}} - E_{\text{HF/CBS}} \quad (2.24)$$

where E_{CI} is the exact nonrelativistic energy taken as the full CI energy and $E_{\text{HF/CBS}}$ is the (restricted) HF energy in the limit of a complete basis set. Such a definition assumes that the only effect separating the exact nonrelativistic energy from the HF energy is electronic correlation effects. It is also common practice to partition correlation into a *static* (or *non-dynamic*) and a *dynamic* part. Static correlation is a denomination to the effect of some systems being only correctly described by a combination of different near-degenerate configurations, which the single-reference HF wavefunction cannot account for. Dynamic correlation is then the effect of the instantaneous correlated movement of the electrons. Both this partition and the choice of the HF reference in Equation 2.24 is shown to be flawed by the fact that a Slater determinant is not the best form for the wavefunction as discussed previously. What is missing from the HF energy is not only due to correlation but also due to the lack of proper S_N permutation symmetry. In other words, static correlation is simply an effect of the incorrect HF wavefunction's symmetry.

ONE SIGNIFICANT PROBLEM WITH any truncated CI-based method is their lack of size consistency and extensivity. *Size consistency* refers to a method's ability to correctly describe

the energy of a collection of noninteracting particles. A size consistent method should predict that the energy of N noninteracting particles is exactly N times the energy of a single particle. *Size extensivity*, on the other hand, refers to systems of interacting particles and requires that the method correctly scales the energy in *proportion* to the number of particles. Although the full CI is both size consistent and extensive, as an exact theory should be, this is not the case for any truncated CI method. Consequently, these methods are not suitable for describing macroscopic effects, both due to computational cost and size inconsistency, or for large molecular systems, as their accuracy deteriorates with increasing number of particles (size extensivity). For a detailed explanation of that, see § 4.6 of [91].

Thankfully, there are ways to truncate the exact solution described by the CI Equation 2.22 in a way that preserves its size consistency and extensivity. This can be achieved by coupled-pair theories, with the gold standard being the *coupled-cluster* (CC) method (also known as *coupled-pair many-electron theory*). The trade-off is that these methods are not variational, meaning that CC energies can sometimes be lower than the exact energy, and there is no definitive upper or lower bound against which to measure their accuracy.

At the core of such theories is the so-called cluster expansion of the wavefunction. A motivation for the method we will now describe, that shows the intuition behind the formalism, can be found in § 5.2 of [91]. To offer a summary of the formalism, consider the excitation operator

$$\mathcal{T} = \mathcal{T}_1 + \mathcal{T}_2 + \mathcal{T}_3 + \cdots + \mathcal{T}_N, \quad (2.25)$$

where N is the number of electrons in the system. The effect of the $\mathcal{T}_i$ operator on a given reference wavefunction is to generate all i th excited determinants. To write the full CI expansion, one only needs to apply $(1 + \mathcal{T})$ to the HF reference and normalise accordingly. In the CC approach, however, one instead uses the exponential *ansatz*

$$\Phi_{\text{CC}} = e^{\mathcal{T}} \Phi_{\text{HF}}. \quad (2.26)$$

Note that both the CI and CC expansions are exact since they include all excited determinants, thereby covering the entire Hilbert space generated by the Hamiltonian. The difference lies in how these approaches group the contributions of each excitation. If one expands $e^{\mathcal{T}}$ in a Taylor series, it yields

$$\begin{aligned} e^{\mathcal{T}} &= 1 + \mathcal{T} + \frac{1}{2}\mathcal{T}^2 + \frac{1}{6}\mathcal{T}^3 + \cdots = \sum_{k=0}^{\infty} \frac{1}{k!} \mathcal{T}^k \\ &= 1 + \mathcal{T}_1 + \left(\mathcal{T}_2 + \frac{1}{2}\mathcal{T}_1^2 \right) \\ &\quad + \left(\mathcal{T}_3 + \mathcal{T}_2\mathcal{T}_1 + \frac{1}{6}\mathcal{T}_1^3 \right) \\ &\quad + \left(\mathcal{T}_4 + \mathcal{T}_3\mathcal{T}_1 + \frac{1}{2}\mathcal{T}_2^2 + \frac{1}{2}\mathcal{T}_2\mathcal{T}_1^2 + \frac{1}{24}\mathcal{T}_1^4 \right) + \cdots \end{aligned} \quad (2.27)$$

The right-most side of the equation can be interpreted as follows: the first term returns the reference wavefunction, the second term includes all singly-excited determinants, the third term (first in parentheses) includes the doubly-excited determinants, the fourth term includes the triply-excited determinants, and so on. Note that, at each excitation level, terms arising from combinations of lower-order excitations are present. The major advantage of this approach becomes evident when we truncate the operator $\mathcal{T}$ at a certain excitation level. For instance, if we consider a CC with only singles and doubles (CCSD), Equation 2.27 then becomes

$$e^{\mathcal{T}_1+\mathcal{T}_2} = 1 + \mathcal{T}_1 + \left(\mathcal{T}_2 + \frac{1}{2}\mathcal{T}_1^2\right) + \left(\mathcal{T}_2 + \frac{1}{6}\mathcal{T}_1^3\right) + \left(\frac{1}{2}\mathcal{T}_2^2 + \frac{1}{2}\mathcal{T}_2\mathcal{T}_1^2 + \frac{1}{24}\mathcal{T}_1^4\right) + \dots \quad (2.28)$$

By projecting the CCSD wavefunction against different singly excited determinants, one can obtain the coefficients for the various contributions in the expansion of the wavefunction. Noteworthy, contributions from higher than doubly excited determinants appear, even though the operator $\mathcal{T}$ is truncated at the doubles level. For example, the term $\mathcal{T}_2^2$ will generate quadruply excited determinants. This feature is what ultimately makes CC methods more accurate, as well as size consistent and extensive. However, it also introduces nonlinearity, leading to the nonvariational nature of the method. The method has also a much higher computational cost than a CI of the same order, say CCSD versus CISD.

2.1.2 DENSITY FUNCTIONAL THEORY

THE COMMON FEATURE OF the electronic structure methods discussed so far was the central role of the wavefunction. However, arguably the most used routine quantum chemical calculations do not use wavefunction methods. *Density functional theory* offers a class of conceptually different approaches that have proven exceptionally effective for many computational tasks at a fraction of the cost of, and with comparable or even superior accuracy to, many post-HF counterparts. Instead of solving the Schrödinger equation for the full wavefunction of a system and its corresponding energies, DFT exploit the fact that there is a univocal correspondence between the energy of a quantum system and its one-electron density.

The mathematical foundation of DFT is the Hohenberg–Kohn theorems [117]. The one-electron density $\rho(\mathbf{r})$ of an electronic system described by the wavefunction $|\Phi\rangle$ is defined as

$$\rho(\mathbf{r}) = N \iint \dots \int |\Phi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 d\omega_1 d\mathbf{x}_2 \dots d\mathbf{x}_N, \quad (2.29)$$

where the integrals run over all electron's spin coordinates and the spatial coordinates of $N - 1$ electrons. Thus, $\rho(\mathbf{r})$ is a function of the spatial coordinates of a single electron. Since electrons are indistinguishable, the function represents the spatial probability density of any one of the N electrons with an arbitrary spin, while the remaining electrons have arbitrary

positions and spins. The integral of the density is $\int \rho(\mathbf{r}) d\mathbf{r} = N$. We say that a density of the form of Equation 2.29 is N -representable, provided that $\Phi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ is antisymmetric.

The first Hohenberg–Kohn theorem is a proof of existence. It states that the external potential $V_{\text{ext}}(\mathbf{r})$ —the potential caused by the nuclei in the context of molecules—is, up to a constant, a univocal functional of $\rho(\mathbf{r})$ and, since $V_{\text{ext}}(\mathbf{r})$ fixes the Hamiltonian $\mathcal{H}$, the complete ground state (GS) of the system is also a univocal functional of $\rho(\mathbf{r})$. Thus, the existence of a functional of the one-electron density $E_0[\rho(\mathbf{r})]$ that determines the system’s GS is demonstrated.

The second theorem establishes a variational principle for the GS energy. According to it, the density functional $E[\tilde{\rho}(\mathbf{r})]$ for a defined external potential among all possible N -representable trial densities $\tilde{\rho}(\mathbf{r})$ will give the smallest energy for the system if, and only if, the density $\tilde{\rho}(\mathbf{r}) = \rho_0(\mathbf{r})$, where ρ_0 is the GS density. More formally,

$$E_0 = E[\rho_0] \leq E[\tilde{\rho}] \quad \forall \tilde{\rho}. \quad (2.30)$$

In this way, $E[\tilde{\rho}]$ is an upper bound to the real GS energy E_0 .

In the BO approximation, it is convenient to write the density functional of the energy as

$$E_0[\rho_0] = T[\rho_0] + E_{ee}[\rho_0] + E_{ne}[\rho_0], \quad (2.31)$$

where T is the electron’s kinetic energy component and E_{ee} and E_{ne} are the electron-electron and nucleus-electron interaction components, respectively. We can separate out the system-dependent component $E_{ne}[\rho_0] = \int \rho_0(\mathbf{r}) V_{\text{ext}} d\mathbf{r}$ from the part that do not depend on N , $\mathbf{R}_A$ and Z_A . The functional becomes

$$E_0[\rho_0] = \int \rho_0(\mathbf{r}) V_{\text{ext}} d\mathbf{r} + F_{\text{HK}}[\rho_0], \quad (2.32)$$

where the system-independent factors are collected into the Hohenberg–Kohn functional $F_{\text{HK}}[\rho_0] = T[\rho_0] + E_{ee}[\rho_0]$. This is usually referred to as the universal functional since it does not depend on the nuclei nor on the total number of electrons in the system. The Hohenberg–Kohn theorems are only true for the exact density functional. However, we unfortunately do not know the exact form of $F_{\text{HK}}[\rho_0]$.

What Hohenberg & Kohn are promising us is almost a miracle. Somehow, the GS of a system represented by a complicated function of $3N$ variables, that grows in complexity with the system’s size (see Equation 2.22, for instance), can be completely and exactly represented by a functional of only the three spatial variables, regardless of the system’s size. In DFT, in principle, it is as easy to represent the electronic structure of a hydrogen atom as it is to do so for a whole living creature. Of course, V_{ext} will still be as complex as the system is and in practice we still have to represent this information by a basis set expansion and/or a numerical

grid and store it. Nevertheless, this is still a remarkable conceptual shift. For multiscale simulations, it means we can assess larger and larger scales with the same computational level, making comparison between scales much more reliable and smooth than if we had to resort to less detailed and more approximate methods as scale grows. If we only knew the exact form of $F_{\text{HK}}[\rho_0] \dots$

CURRENTLY, OUR ONLY OPTION is to approximate the density functional the best we can. At DFT's onset, simple approximate functionals that utilised the electronic density directly were devised, one of the most famous being the Thomas–Fermi model, based on the model of an electron gas [118–121] (see § 3.1 of [122]). These methods are not suitable for modelling molecules, however. Their description of the electron's kinetic energy is so poor that they are incapable of describing the chemical bond. The only successful version of DFT for chemical systems was offered by Walter Kohn and Lu Jeu Sham. The main idea of the Kohn–Sham (KS) method is the realisation that an N -particle Slater determinant, such as the one used in the HF model (Equation 2.20), is the exact wavefunction of a system of N noninteracting fermions, ie, electrons without electric charge but still obeying the antisymmetry and Pauli exclusion principles, moving in an effective field whose Hamiltonian is

$$\mathcal{H}_S = -\frac{1}{2} \sum_i^N \nabla_i^2 + \sum_i^N V_{\text{ext}}(\mathbf{r}_i). \quad (2.33)$$

The spin-orbitals are determined by an equation similar to Equation 2.19

$$\mathcal{F}_{\text{KS}}(i) |\varphi_i(\mathbf{x})\rangle = \epsilon_i |\varphi_i(\mathbf{x})\rangle, \quad (2.34)$$

where the one-electron KS operator is defined as

$$\mathcal{F}_{\text{KS}} = -\frac{1}{2} \nabla^2 + V_{\text{ext}}(\mathbf{r}). \quad (2.35)$$

The connection of the fictitious noninteracting system with the real one is made by choosing V_{ext} such that the electron density calculated from the KS spin-orbitals

$$\rho_{\text{KS}}(\mathbf{r}) = \sum_i^N \sum_{\omega} |\varphi_i(\mathbf{r}, \omega)|^2 = \rho_0(\mathbf{r}), \quad (2.36)$$

where $\rho_0(\mathbf{r})$ is the real system's ground state. The kinetic energy for the noninteracting system is

$$T_{\text{KS}} = -\frac{1}{2} \sum_i^N \langle \varphi_i | \nabla^2 | \varphi_i \rangle. \quad (2.37)$$

Although it is not the real system's kinetic energy, it is the best approximation that can be calculated exactly.

The universal functional can now be written as

$$F_{\text{HK}}[\rho(\mathbf{r})] = T_{\text{KS}}[\rho(\mathbf{r})] + J[\rho(\mathbf{r})] + E_{\text{xc}}[\rho(\mathbf{r})], \quad (2.38)$$

where the exchange-correlation (xc) energy E_{xc} contains the remaining kinetic energy not included in T_{KS} and the nonclassic electrostatic interaction contribution. In other words E_{xc} represents all that is unknown in the exact density functional.

To determine the V_{ext} that yields the Slater determinant whose electronic density is the same as that of the ground state, one needs to use Equation 2.36, Equation 2.37, and Equation 2.38 as well as the variational principle. The result is the equation (see [123] for the derivation)

$$\left[-\frac{1}{2}\nabla^2 + \left(\int \frac{\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 + V_{\text{xc}}(\mathbf{r}_1) - \sum_A^M \frac{Z_A}{r_{1A}} \right) \right] \varphi_i = \left[-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r}_1) \right] \varphi_i = \epsilon_i \varphi_i, \quad (2.39)$$

where V_{xc} is simply defined as

$$V_{\text{xc}} := \frac{\partial E_{\text{xc}}}{\partial \rho}. \quad (2.40)$$

Comparing Equation 2.34 with Equation 2.39 and taking the definition of the KS operator $\mathcal{F}_{\text{KS}}$ in Equation 2.35, we see that $V_{\text{ext}}(\mathbf{r}) \equiv V_{\text{eff}}(\mathbf{r})$. Thus, once we know the various contributions to $V_{\text{ext}}(\mathbf{r})$, we feed it into Equation 2.34, which determines the spin-orbitals and, therefore, the density and energy of the ground state via Equation 2.39. Since V_{eff} itself depends on the orbitals via the density, the KS equations must be solved iteratively as in the SCF method, with the spin-orbitals described by basis set functions just like in the HF method. Different from the latter, though, KS DFT includes electronic correlation through the approximate xc functional, and yields much better results than HF at a comparable computational cost.

THE ONLY UNKNOWN IN THE Kohn–Sham theory is the exchange-correlation functional $E_{\text{xc}}[\rho(\mathbf{r})]$. The simplest strategy to devise an approximate E_{xc} is the local density approximation (LDA). This model is based on a uniform electron gas—a model where electrons move in the field of a continuous positive charge distribution, in a way that the total system is neutral. The number N of electrons and the volume V of the system are infinite, while the electronic density N/V remains finite and constant throughout. The xc functional for such a system can be written as

$$E_{\text{xc}}^{\text{LDA}}[\rho(\mathbf{r})] = \int \rho(\mathbf{r}) \epsilon_{\text{xc}}(\rho(\mathbf{r})) d\mathbf{r}, \quad (2.41)$$

where $\epsilon_{\text{xc}}(\rho(\mathbf{r}))$ is the xc energy per particle of the electron gas.

An improvement over LDA is the generalised gradient approximation (GGA). In this approach, the information coming from the electron gas density is supplemented by the gradient of the density, $\nabla\rho(\mathbf{r})$. It considers the fact that the electronic density of a real electronic system, contrary to that of an electron gas, is not homogenous. This is achieved by recognising that LDA can be regarded as the first-order term of a Taylor expansion of E_{xc} in terms of the density. The gradient expansion approximation (GEA) can be written as

$$E_{\text{xc}}^{\text{GEA}}[\rho(\mathbf{r})] = \int \rho(\mathbf{r}) \epsilon_{\text{xc}}(\rho(\mathbf{r})) d\mathbf{r} + C_{\text{xc}}(\rho(\mathbf{r})) \int \frac{|\nabla\rho_{\sigma}(\mathbf{r})|^2}{\rho_{\sigma}(\mathbf{r})^{4/3}} d\mathbf{r} + \dots \quad (2.42)$$

GGA functionals are obtained from this expansion by certain manipulations to ensure that exchange-correlation hole properties are respected (see § 8.5 of [122] and §§ 2 and 6.5 of [124]). Such functionals are not derived entirely from first principles but include a series of parameters fitted to experimental data and/or higher level calculations, as is the case with the remaining functionals below.

Building on the Taylor expansion mentioned earlier, one can further improve on the GGA functional form by including the Laplacian of the density, $\nabla^2\rho(\mathbf{r})$. Functionals that incorporate this additional term, although not directly constructed by the simple addition of the Laplacian of the density, are known as meta-GGA functionals. They typically perform better than LDA and GGA functionals for molecular systems. More details on their implementation can be found in reference [125].

Another class of functional that generally outperforms GGAs, and often surpasses meta-GGAs, are the hybrid or hyper-GGA functionals. They leverage the fact that the exchange part of the xc energy can be computed exactly for a Slater determinant using the HF approach. One can thus use this parcel of the energy and only approximate the correlation part in the functional. Although this partition is a fictitious mathematical construct—the xc term is inherently a single entity—a careful partitioning scheme can yield effective xc functionals by mixing the HF exchange energy with LDA, GGA, or even meta-GGA xc energies. In fact, one of the most popular DFT functionals, B3LYP, is an example of this approach.

An even higher level of improvement is achieved with double-hybrid functionals. They not only use information from occupied orbitals in the form of the HF exchange energy but also incorporate information from all the KS orbitals. Specifically, they include a perturbative component of the energy obtained by applying the second order Møller–Plesset MP2 method (see § 1.5 of [83]) to the KS Slater determinant. These methods have a higher computational cost than the previous ones because of the extra computations required for the MP2 energy and the convergence difficulties associated with such a perturbative approach. Figure 2.1 presents a schematic hierarchy of DFT functional classes, commonly referred to as Jacob’s ladder [126].⁹

⁹Jacob’s ladder is a reference to the account given in the Book of Genesis 28: “Jacob left Beersheba and set out for Harran. When he reached a certain place, he stopped for the night because the sun had set. Taking one

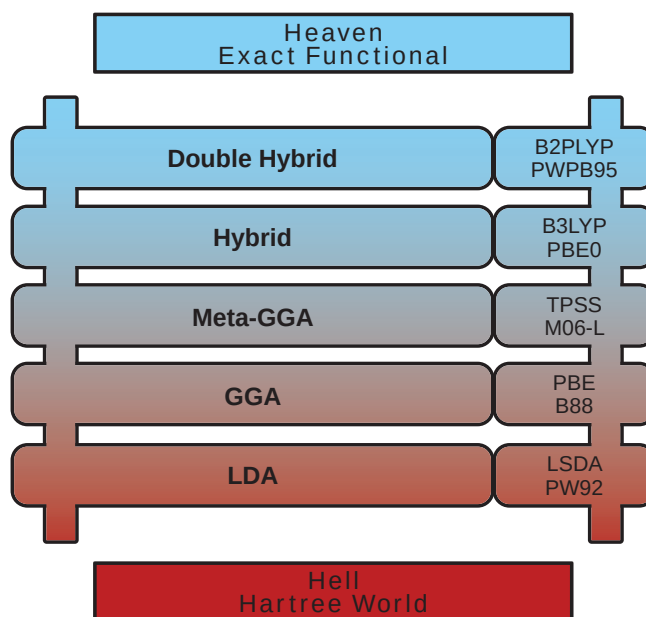


FIGURE 2.1 – Jacob's ladder representation of DFT functionals hierarchy.

When treating excited-states via time-dependent DFT (TDDFT) methods (see § 2.1.4), it has been observed that many functionals fail to accurately describe charge-transfer and Rydberg states. This issue arises partly because DFT tends to artificially favour delocalised systems over localised ones. Additionally, the long-range behaviour of the electronic energy is generally misrepresented due to an imbalance between the density-based Coulomb ($J[\rho(\mathbf{r})]$) and exchange (HF part in hybrid functionals) components and the approximate xc potential. A solution to this problem is brought by the class of range-separated functionals. In this strategy, the electron-electron Coulomb operator for the exchange energy (only) is split into short-range and long-range components, using different approaches for each. Typically, a density exchange functional is used for the short-range part, while the exact HF part is used for the long-range part. The two domains are interpolated using an ω parameter, which can be tuned for specific systems by applying Koopman's theorem [127]. The range-separated hybrid GGA functional ω B97X was chosen for the excited-state investigations in this work.

of the stones there, he put it under his head and lay down to sleep. He had a dream in which he saw a stairway resting on the earth, with its top reaching to heaven, and the angels of God were ascending and descending on it. There above it stood the Lord...". The original metaphor for the DFT xc functionals is Perdew's and Schmidt's [126]. They depict the ladder as going from "Hartree World" to "Chemical Accuracy". We make a slight change here, and a conceptual clarification. The biblical passage tells about a ladder going from earth towards heaven (there is no concept of hell in the Hebrew Bible, and even in the Greek Bible this is contested). We consider here that both the bottom and top references of our metaphor are disconnected to the xc approximation. So the best, unattainable target is the exact functional (not the attainable chemical accuracy). The worst is a Hartree picture, with no electronic correlation whatsoever, also far below the simplest type of xc functionals, thus a reference to hell, under the earth (to be a bit anachronistic in our metaphor).

Two of the major inaccuracies of DFT calculations are the self-interaction error and the absence of long-range correlation effects, responsible for London's dispersion forces. Although the omission of long-range correlation is an inherent limitation of DFT, it can now be easily addressed by applying several established dispersion correction methods. Prominent among these is Grimme's D3 method [128]—which can be applied using either the initial damping function, D3(0) [129], or the updated Becke–Johnson (BJ) damping function—or its more recent version D4 [130]. Dispersion correction is used throughout this work.

The reader interested in a more complete view of DFT will encounter a gentle introduction in [124], a more detailed treatment in [122] and a rigorous mathematical treatment in [125].

2.1.3 RELATIVISTIC CORRECTIONS

WE HAVE LIMITED THE scope of our QM methods discussion to the nonrelativistic case. However, reality cannot always be accurately approximated to fit this assumption without serious errors, even at the low energy molecular level. In fact, from the onset of our discussion we were forced to introduce a relativistic property, namely, the electron spin. The fundamental problem with the nonrelativistic treatment of a quantum system is that the Schrödinger equation (Equation 2.1) is not invariant under a Lorentz transformation of space-time coordinates—a fundamental requirement of special relativity. By imposing this property, the Dirac equation can be seen as a generalisation of the Schrödinger equation that also accounts for the fact that the mass of a particle increases with increasing velocity. This implies that an electron orbiting a heavier nucleus will have a higher velocity, and therefore a larger mass, compared to one orbiting a lighter nucleus. The outcome is either a contraction or an expansion of orbitals depending on their angular momentum. Another consequence of the Dirac equation is that the total angular momentum of an electronic system is no longer defined solely by the orbital angular momentum (L), but by a combination of this with the spin angular momentum (S), giving rise to a J term. In other words, the L and S operators do not commute with the Hamiltonian anymore, but J does. This is the spin-orbit coupling (SOC) phenomenon. As a result, orbitals (and the entire system) do not have well-defined spin states, and the pure s, p, d, etc nonrelativistic orbitals now mix. In the presence of an external electromagnetic field, other relativistic effects also arise.

Additionally, the use of a Coulomb potential to describe the electric interactions is no longer valid in the relativistic realm since such interactions are instantaneous and thus violate the universal speed limit of light. The correct treatment of electric interactions would have to start from a quantum electrodynamics (QED) perspective, but modifications of the Coulomb potential can be made through approximation schemes, such as the inclusion of a Breit operator (see Chapter 9 of [100]).

There are various ways to supplement or correct the methods discussed above to account for these relativistic effects. The simplest way is to employ effective core potentials (ECPs) to

the atomic basis set. Examples of basis sets with ECP available are the Los Alamos National Laboratory 2 double zeta (LANL2DZ) [131] and the Weigend and Ahlrichs def2 family of basis sets [132]. This correction accounts for the scalar relativistic effects arising from the change in orbital energies, sizes and shapes discussed above.

Another relatively straightforward approach is to approximate a relativistic Hamiltonian using methods such as the zeroth-order regular approximation (ZORA) or the first-order regular approximation (FORA) [133–139]. Besides the inclusion of scalar relativistic effects, these methods also include spin-orbit coupling. Given the presence of ruthenium—a heavy atom—in the precursors investigated in this work, we used ECP in the basis sets and ZORA to investigate the bonding situation (see § 3.2).

Perturbative operators have also been devised to include corrections to the nonrelativistic solution [100]. Since this strategy results in complicated equations, it is sometimes easier to directly solve the Dirac equation. Using *spinors* (relativistic spin-orbitals) in a Slater determinant, one can write a relativistic *ansatz* similar to the HF wavefunction for the Dirac equation, in what is known as the Dirac–Fock (DF) method.

The so-called two-component methods are also available. The reason for this name is that a relativistic wavefunction has four components, which can be separated into one pair called the large component, and another pair called the small component, which depend on one another. Two-component methods use unitary transformations to separate these component pairs, making them (quasi-)independent and allowing them to be solved separately. Examples of this approach include the exact two-component (X2C)¹⁰ [140–144] and Douglas–Kroll–Hess (DKH) methods [145, 146].

2.1.4 THE TIME-DEPENDENT EXTENSIONS FOR EXCITED STATES

WE STARTED OUR DISCUSSION with the fundamental TDSE (Equation 2.1) and right away we separated out the time component (Equation 2.2) and carried on with the time-independent factor (Equation 2.3), and that is where we have stayed so far. In other words, we have focused on a *static* treatment of quantum systems. This is a convenient, standard choice to make. Provided that the Hamiltonian does not contain a time-dependent potential, the TDSE has independent time ($i\hbar \frac{\partial}{\partial t}$) and spatial ($\mathcal{H}(\mathbf{r}, \mathbf{R})$) operators, and that is what makes the separation of variables in Equation 2.2 exactly valid. In the case of molecular systems in the absence of external time-varying potentials, the assumption of a time-independent Hamiltonian is correct. There are many cases, however, in which we would like to consider

¹⁰The name of the method was proposed by its cocreator Wenjian Liu, who tells the story in a note to a chapter in the Springer Handbook of Relativistic Quantum Chemistry [140]. Citing *verbatim*: “The acronym ‘X2C’ (pronounced as ecstasy) for exact two-component Hamiltonians was proposed by W Liu after intensive discussions with H J Aa Jensen, W Kutzelnigg, T Saue and L Visscher during the Twelfth International Conference on the Applications of Density Functional Theory (DFT-2007), Amsterdam, August 26–30, 2007. Note that the ‘exact’ here emphasises that all the solutions of the matrix Dirac equation can be reproduced up to machine accuracy. It is particularly meaningful when compared with the approximate two-component (A2C) Hamiltonians.”

a molecular system subject to an external potential that does vary with time, ie, we are interested in a *dynamic* treatment of quantum systems. The case we will consider extensively in this work is that of the impinging electromagnetic field of a photon onto matter (light-matter interaction).

A conceptual note is necessary. We will refer to such methods as dynamical because they deal with time-dependent properties. However, this should not be read as dynamical in the sense of dynamic simulations such as molecular dynamics or quantum (adiabatic or nonadiabatic) dynamics in which the explicit serial time evolution of the system is modelled. The general theory we will start our discussion with *can* be utilised to develop various types of QM dynamic models, but we will direct our formalism to methods that allow us to access the excited states of molecules and their properties as stationary states. Two main formalisms that achieve this goal were employed in this work, namely, linear response theory (LRT) and equation of motion (EOM) methods. Other options are discussed in [83] and references therein. Most of the treatment below is based on [97].

The case of electronic time-dependent methods is complicated by the fact that a general theory should consider the relativistic and quantum nature of both the photons and the molecular systems. This is what QED and, more generally, QFT do. Since routine methods at this level are not easily available for chemistry, we will use an approximate, semi-classical theory, which is standard in the computational chemistry practice. We will continue with the assumption of a nonrelativistic QM theory and we will treat light classically, as oscillations of an electromagnetic field. Since at low light intensity and nonrelativist velocity the effect of the magnetic component on the electrons is much smaller than that of the electric component (by a factor of v/c , where v is the electron's speed), we will disregard the former and use the dipole approximation (see below). As usual, we will be working within the BO approximation, although the models can be extended to account for non-BO effects. To simplify the notations in this portion of the text, we will condense all spatial and spin coordinates, including the nuclear coordinates (in the BO approximation, a parameter), into the variable $\mathbf{x}$.

2.1.4.1 SCHRÖDINGER AND HEISENBERG REPRESENTATIONS

LET US RETURN WITH MORE attention to the separation of time and spatial variables in Equation 2.2. By the same argument that led to Equation 2.4, we can implicitly separate variables, maintaining the action of the (time-independent) Hamiltonian unsolved, and solving the resulting differential equation for time as¹¹

$$\int_{\Psi(\mathbf{x},0)}^{\Psi(\mathbf{x},t)} \frac{d\Psi(\mathbf{x},t)}{\Psi(\mathbf{x},t)} = \int_{t_0}^t -\frac{1}{i\hbar} \mathcal{H}(\mathbf{x}) dt, \quad (2.43)$$

¹¹Note that, in the time-dependent treatment we discuss here, atomic units are not being used as was done in the electronic structure methods discussed above. Using atomic units here would only omit $\hbar$, set equal to unit. We prefer to preserve it in the equations since most texts will do so.

that leads to

$$\ln \frac{\Psi(\mathbf{x}, t)}{\Psi(\mathbf{x}, 0)} = -\frac{i}{\hbar} \mathcal{H}(\mathbf{x}) t, \quad (2.44)$$

from which

$$\Psi(\mathbf{x}, t) = e^{-\frac{i}{\hbar} \mathcal{H} t} \Psi(\mathbf{x}, 0). \quad (2.45)$$

We see then that the exponential operator on the right-hand side of Equation 2.45 maps the initial Ψ at time $t = 0$ to that at time t . This serves as a motivation to a more rigorous definition of an operator

$$\mathcal{U}(t) = e^{-\frac{i}{\hbar} \mathcal{H} t} \quad (2.46)$$

called the evolution operator or propagator. Differentiating $\mathcal{U}(t)$ with respect to time, we see that it satisfies the TDSE

$$i\hbar \frac{d\mathcal{U}(t)}{dt} = \mathcal{H} \mathcal{U}(t). \quad (2.47)$$

Equation 2.45 is strictly valid for a time-independent, self-adjoint Hamiltonian, but Equation 2.47 is valid even for a time-dependent one and is the more general definition of $\mathcal{U}(t)$ as the Green's function that solves the TDSE (see [147] for a detailed derivation).

In this context, consider now the expectation value of an operator $\mathcal{A}$ as a function of time

$$\langle \mathcal{A} \rangle_t = \langle \Psi(\mathbf{x}, t) | \mathcal{A} | \Psi(\mathbf{x}, t) \rangle = \left\langle e^{-\frac{i}{\hbar} \mathcal{H} t} \Psi(\mathbf{x}, 0) \left| \mathcal{A} \right| e^{-\frac{i}{\hbar} \mathcal{H} t} \Psi(\mathbf{x}, 0) \right\rangle. \quad (2.48)$$

This result is expressed in the *Schrödinger picture*, where the time dependence of the expectation value is included solely on the state vectors $|\Psi\rangle$, while the operators are stationary. One can define a different representation where the state vectors are kept constant in time, but the operators evolve with time. Such a representation is called the *Heisenberg picture*. It is accomplished by defining the Heisenberg-picture state vector $|\Psi_H\rangle$ in terms of the Schrödinger-picture state vector $|\Psi_S\rangle$ as

$$|\Psi_H(\mathbf{x}, t)\rangle = \left| e^{\frac{i}{\hbar} \mathcal{H} t} \Psi_S(\mathbf{x}, t) \right\rangle. \quad (2.49)$$

From Equation 2.45, we see that $|\Psi_H(\mathbf{x}, t)\rangle = |\Psi_S(\mathbf{x}, 0)\rangle = |\Psi_H(\mathbf{x}, 0)\rangle$, thus proving that $|\Psi_H(\mathbf{x}, t)\rangle$ is stationary in time. The connection between an operator $\mathcal{A}_S$ in the Schrödinger picture and its counterpart $\mathcal{A}_H$ in the Heisenberg picture is given by

$$\mathcal{A}_H = e^{\frac{i}{\hbar} \mathcal{H} t} \mathcal{A}_S e^{-\frac{i}{\hbar} \mathcal{H} t}. \quad (2.50)$$

The expectation value of $\mathcal{A}$ in any of the pictures is, of course, the same since they only differ in representation.

A somewhat intermediate representation between the Schrödinger and Heisenberg pictures is the *interaction picture*. Consider a partitioning of the full Hamiltonian as $\mathcal{H} = \mathcal{H}_0 + \mathcal{V}$, as

we shall see shortly when discussing perturbative methods, where $\mathcal{H}_0$ is a Hamiltonian for which the time evolutions are known. The interaction-picture wavefunction is defined by

$$|\Psi_I(\mathbf{x}, t)\rangle = \left| e^{\frac{i}{\hbar}\mathcal{H}_0 t} \Psi_S(\mathbf{x}, t) \right\rangle = \left| e^{\frac{i}{\hbar}\mathcal{H}_0 t} e^{-\frac{i}{\hbar}\mathcal{H} t} \Psi_S(\mathbf{x}, 0) \right\rangle. \quad (2.51)$$

If most of the time evolution is due to $\mathcal{H}_0$ (ie, $\mathcal{V}$ is considered a perturbation) then the forward propagation under $\mathcal{H}$ will be counteracted by the backward propagation due to $\mathcal{H}_0$. Thus, Ψ_I undergoes much less time evolution than Ψ_S in the same situation. These different representations of the TDSE can be used interchangeably but depending on the problem at hand, one will generally prove more adequate than the others, as we shall see below.

2.1.4.2 TIME-DEPENDENT PERTURBATION THEORY AND LINEAR RESPONSE THEORY

IN THE CONTEXT WE ARE currently working, arguably the most popular formalism is the perturbative, in which the effect of a time-dependent field over the initial state of a system is considered a perturbation to the initial Hamiltonian. More explicitly, consider a Hamiltonian partitioned as

$$\mathcal{H} = \mathcal{H}_0 + \lambda \mathcal{H}_1. \quad (2.52)$$

Here, $\mathcal{H}_0$ is a time-independent Hamiltonian for which we know at least an approximate solution for its time evolution. $\mathcal{H}_1$ is regarded as a perturbation, ie, the effect of $\mathcal{H}_1$ in the evolution of the system is much smaller than the effect of $\mathcal{H}_0$. The parameter λ is introduced as an ordering parameter and will ultimately be set to unity.

We proceed by expanding the wavefunction in a power series in λ as

$$\Psi(\mathbf{x}, t) = \Psi^{(0)}(\mathbf{x}, t) + \lambda \Psi^{(1)}(\mathbf{x}, t) + \lambda^2 \Psi^{(2)}(\mathbf{x}, t) + \dots = \sum_n \lambda^n \Psi^{(n)}(\mathbf{x}, t). \quad (2.53)$$

Substituting the expansion into the TDSE, and equating like powers of λ yields a series of equations for the different orders of perturbation corrections to the wavefunction. The first few corrections are

$$i\hbar \frac{\partial}{\partial t} \Psi^{(0)}(\mathbf{x}, t) = \mathcal{H}_0 \Psi^{(0)}(\mathbf{x}, t), \quad (2.54)$$

$$i\hbar \frac{\partial}{\partial t} \Psi^{(1)}(\mathbf{x}, t) = \mathcal{H}_0 \Psi^{(1)}(\mathbf{x}, t) + \mathcal{H}_1 \Psi^{(0)}(\mathbf{x}, t), \quad (2.55)$$

$$i\hbar \frac{\partial}{\partial t} \Psi^{(2)}(\mathbf{x}, t) = \mathcal{H}_0 \Psi^{(2)}(\mathbf{x}, t) + \mathcal{H}_1 \Psi^{(1)}(\mathbf{x}, t). \quad (2.56)$$

Solving the equations and performing some algebraic manipulations, one arrives at various expressions for the corrections to the wavefunction (see § 9.2.1 of [97]). The first- and

second-order solutions are

$$\Psi^{(1)}(\mathbf{x}, t) = \frac{1}{i\hbar} \int_{t_0}^t dt' e^{-\frac{i}{\hbar} \mathcal{H}_0(t-t')} \mathcal{H}_1(t') e^{-\frac{i}{\hbar} \mathcal{H}_0(t'-t_0)} \Psi^{(0)}(\mathbf{x}, t_0), \quad (2.57)$$

$$\Psi^{(2)}(\mathbf{x}, t) = \frac{1}{(i\hbar)^2} \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' e^{-\frac{i}{\hbar} \mathcal{H}_0(t-t')} \mathcal{H}_1(t') e^{-\frac{i}{\hbar} \mathcal{H}_0(t'-t'')} \mathcal{H}_1(t'') e^{-\frac{i}{\hbar} \mathcal{H}_0(t''-t_0)} \Psi^{(0)}(\mathbf{x}, t_0), \quad (2.58)$$

where Equation 2.57 was utilised to expand the solution to second order. Further corrections can be derived, although the expressions become increasingly complex to integrate. However, the core idea of a perturbative correction is that it is a small effect. Therefore, higher order corrections should be irrelevant to the problem, or the initial perturbative assumption is not valid. Here, we have assumed that $\Psi(\mathbf{x}, t_0) = \Psi^{(0)}(\mathbf{x}, t_0)$, ie, the total wavefunction at the initial time is the unperturbed wavefunction under the effect of $\mathcal{H}_0$ only. If the perturbation is finite in time, such as the case of a laser pulse (eg, pump-probe experiments), we can set $t_0 = 0$, where the origin of time is set before the perturbation takes effect. If one is treating a prolonged exposure to an electric field (eg, regular UV-vis spectroscopy), it is better to consider the perturbation as always-existing or steady-state. In this case, we set $t_0 \rightarrow -\infty$.

A different approach to perturbation theory can be taken. Above, we found a perturbative correction to the wavefunction in the Schrödinger picture. Alternatively, one can also use the interaction picture to search for corrections to the Schrödinger picture propagator $\mathcal{U}(t, t_0)$, since in this representation the perturbation is entirely due to the perturbation operator. For this, we define the zeroth-order propagator $\mathcal{U}^{(0)}(t, t_0)$, associated with $\mathcal{H}_0$, which satisfies the TDSE as

$$i\hbar \frac{\partial}{\partial t} \mathcal{U}^{(0)}(t, t_0) = \mathcal{H}_0 \mathcal{U}^{(0)}(t, t_0). \quad (2.59)$$

We can then define an interaction picture propagator (see the definition of the interaction picture wavefunction, Equation 2.51)

$$\mathcal{U}_I(t, t_0) = e^{\frac{i}{\hbar} \mathcal{H}_0(t-t_0)} e^{-\frac{i}{\hbar} \mathcal{H}_0(t-t_0)} = \mathcal{U}^{(0)\dagger}(t, t_0) \mathcal{U}(t, t_0) \quad (2.60)$$

which satisfies the TDSE

$$i\hbar \frac{\partial}{\partial t} \mathcal{U}_I(t, t_0) = \mathcal{H}_I(t) \mathcal{U}_I(t, t_0), \quad (2.61)$$

where

$$\mathcal{H}_I(t) = e^{\frac{i}{\hbar} \mathcal{H}_0(t)} \mathcal{H}_1(t) e^{-\frac{i}{\hbar} \mathcal{H}_0(t)} \quad (2.62)$$

is the interaction picture Hamiltonian. Equation 2.61 can be iteratively solved exactly to arrive at

$$\mathcal{U}_I(t, t_0) = 1 + \sum_{n=1}^{\infty} \mathcal{U}_I^{(n)}(t, t_0), \quad (2.63)$$

where

$$\mathcal{U}_I^{(n)}(t, t_0) = \frac{1}{(i\hbar)^n} \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 \mathcal{H}_1(\tau_n) \mathcal{H}_1(\tau_{n-1}) \cdots \mathcal{H}_1(\tau_1) \mathcal{U}_I(t, t_0). \quad (2.64)$$

The causality constraint $t > \tau_n > \tau_{n-1} > \cdots > \tau_1 > t_0$ is applied. By setting $\mathcal{U}_I(\tau_1, t_0) = 1$, which amounts to setting $\mathcal{H} = \mathcal{H}_0$, and replacing in Equation 2.63 and Equation 2.62, one can use Equation 2.60 to derive the perturbation expansion for the Schrödinger picture propagator

$$\mathcal{U}(t, t_0) = \mathcal{U}^{(0)}(t, t_0) + \sum_{n=1}^{\infty} \mathcal{U}^{(n)}(t, t_0) \quad (2.65)$$

where

$$\begin{aligned} \mathcal{U}^{(n)}(t, t_0) &= \frac{1}{(i\hbar)^n} \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 \\ &\times \mathcal{U}^{(0)}(t, \tau_n) \mathcal{H}_1(\tau_n) \mathcal{U}^{(0)}(\tau_n, \tau_{n-1}) \mathcal{H}_1(\tau_{n-1}) \cdots \\ &\times \mathcal{U}^{(0)}(\tau_2, \tau_1) \mathcal{H}_1(\tau_1) \mathcal{U}^{(0)}(\tau_1, t_0) \end{aligned} \quad (2.66)$$

If we substitute $\mathcal{U}^{(0)}(t, t') = e^{-i/\hbar \mathcal{H}_0(t-t')}$ into Equation 2.65 and Equation 2.66 and apply the results to $\Psi^{(0)}(t_0)$, we arrive at the same expressions in Equation 2.57 and Equation 2.58 for the time-dependent corrections to the wavefunction. Notice that each of the approaches just described arrive at the same result, which is a correction to the total wavefunction in terms of an unperturbed wavefunction $\Psi^{(0)}$. In practice, we do not have an exact solution of the TDSE for $\Psi^{(0)}$. Therefore, our corrections will be applied on an imperfect reference. Since the time-dependent $\Psi^{(0)}$ will always be represented by a time-independent imperfect reference (such as a HF or CI wavefunction), perturbative methods will exacerbate the flaws of this reference, demanding care in its application.

THE GENERAL FORMALISM just described can be applied to many time-dependent problems, provided the initial assumption of the perturbative regime is valid. The focus of interest in this work is the simulation of one-photon absorption and emission spectroscopies. We provide here a sketch of the theory. More details can be found in [97, 148]. We assume the BO approximation and describe our system as composed of two states: the initial state with Hamiltonian $\mathcal{H}_a$, which can be considered the ground state but does not necessarily have to be, and the final excited state after absorption of a photon with Hamiltonian $\mathcal{H}_b$. In the dipolar approximation, the interaction of matter with light is considered independent of position, and the potential due to the light is $-\mu \cdot \varepsilon(t)$, where μ is the molecular dipole moment and $\varepsilon(t)$ is the electric component of the radiation.

Here, we will consider a continuous wave, such that $\varepsilon(t) = \varepsilon_0 \cos(\omega t) = \frac{1}{2}\varepsilon_0(e^{i\omega t} + e^{-i\omega t})$. We momentarily disregard the vectorial nature of μ and ε . We can then define, in the perturbation regime, $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1$ such that

$$\mathcal{H}_0 = \begin{pmatrix} \mathcal{H}_a & 0 \\ 0 & \mathcal{H}_b \end{pmatrix} \quad (2.67)$$

and

$$H_1 = \begin{pmatrix} 0 & -\frac{1}{2}\mu\varepsilon_I e^{-i\omega t} \\ -\frac{1}{2}\mu\varepsilon_S e^{i\omega t} & 0 \end{pmatrix}. \quad (2.68)$$

Here, $-\frac{1}{2}\mu\varepsilon_S e^{i\omega t}$ is related to the emission (scattering) process, while $-\frac{1}{2}\mu\varepsilon_I e^{-i\omega t}$ is related to the absorption of the incident light. If we assume that before excitation there is no amplitude in the excited state, we can write the zeroth-order wavefunction as

$$\Psi^{(0)}(\mathbf{x}, 0) = \begin{pmatrix} \Psi_a \\ 0 \end{pmatrix}. \quad (2.69)$$

Substituting the equations above into our result for the first-order correction to the wavefunction (Equation 2.57) and solving, one arrives at the following result (omitting a phase factor; see [97] for details)

$$\Psi^{(1)}(\mathbf{x}, t) = \frac{1}{2i\hbar} \int_{-\infty}^t e^{-\frac{i}{\hbar}\mathcal{H}_b(t-t')} (\mu \cdot \varepsilon_I e^{-i\omega_I t'}) e^{-\frac{i}{\hbar}E_I t'} \Psi_i(\mathbf{x}, -\infty) dt', \quad (2.70)$$

where $\Psi_i(\mathbf{x}, -\infty)$ is an eigenfunction of the ground state Hamiltonian $\mathcal{H}_a$ with the corresponding energy E_i . Now, the absorption spectrum can be defined as the ratio of the number of photons absorbed per unit time to the number of incident photons per unit area per unit time. The number of photons absorbed per unit time is equal to the rate of change of the excited state population, which, in the perturbative limit, is given by the time derivative of $\langle \Psi^{(1)}(\mathbf{x}, t) | \Psi^{(1)}(\mathbf{x}, t) \rangle$. Using Equation 2.70 and differentiating this definition with respect to t , we arrive at the expression for the time derivative of the upper state population. We then divide the result by the number of incident photons per unit area per unit time, perform rotational averaging of the light field (now remembering its vectorial nature), and obtain the absorption cross section¹²

$$\begin{aligned} \sigma(\omega_I) &= \frac{2\hbar\omega_I}{\varepsilon_0\varepsilon_I^2 c} \frac{d}{dt} \langle \Psi^{(1)}(\mathbf{x}, t) | \Psi^{(1)}(\mathbf{x}, t) \rangle \\ &= \frac{\omega_I}{6\varepsilon_0\hbar c} \int_{-\infty}^{\infty} \langle \Psi_i(\mathbf{x}, -\infty) | \mu e^{-i\mathcal{H}_B t/\hbar} \mu | \Psi_i(\mathbf{x}, -\infty) \rangle e^{i\tilde{\omega} t} dt, \end{aligned} \quad (2.71)$$

¹²Notice that [97] uses Gaussian units. Thus, a factor of $1/4\pi\varepsilon_0$ is omitted from the equivalent equations.

where ϵ_0 is the permittivity of free space, c is the speed of light, and we defined $\tilde{\omega} = E_i/\hbar + \omega_I$. If we consider a complete set of excited eigenfunctions, obtained, for example, as a solution of the unperturbed Hamiltonian, we can expand our total wavefunction in this set and insert in Equation 2.71, thus obtaining the popular energy frame formula for the electronic absorption (UV–vis) spectrum in the Franck–Condon regime

$$\sigma(\omega_I) = \frac{\pi\omega_I}{3\epsilon_0\hbar c} \sum_n |\langle \Psi_n | \mu | \Psi_i \rangle|^2 \delta(\tilde{\omega}_I - \omega_n). \quad (2.72)$$

It is often the case that oscillator strength (f) is used as a measure of transition intensity or probability. Since

$$f_{ni} = \frac{2m_e\omega_I}{3e^2\hbar} |\langle \Psi_n | \mu | \Psi_i \rangle|^2, \quad (2.73)$$

where m_e is the electron mass and e is the elementary charge, Equation 2.72 can also be expressed as

$$\sigma(\omega_I) = \frac{\pi e^2}{2\epsilon_0 m_e c} \sum_n f_{ni} \delta(\tilde{\omega}_I - \omega_n). \quad (2.74)$$

Before we discuss the significance and interpretation of Equation 2.72, it is important to say that Equation 2.71 and Equation 2.72 can be obtained from a different approach, called linear response theory [97, 100]. In general, LRT is concerned with finding an approximation for the expectation value $\langle \Psi | \mathcal{A} | \Psi \rangle$ of an operator $\mathcal{A}$ in the perturbative regime if one considers only the first order in perturbation (thus, linear response). This is attained by expanding $\langle \Psi | \mathcal{A} | \Psi \rangle$ into a Taylor series in terms of the perturbation $\mathcal{A}_1$. Each term will be related to a different molecular property.

In the case of molecular absorption, the interaction of light with matter generates a dipole (polarisation). In a general formulation, the polarisation P will be expanded in a power series of the field strength ϵ . To linear approximation, we can keep the first term $P = \chi\epsilon$ only, where χ is the macroscopic susceptibility. In the microscopic level, this is related to the polarisation $\langle \Psi | \mu | \Psi \rangle$. Expanding this in terms of the field perturbation, one can compare the terms to the expansion of Ψ and arrive at terms $P_{nm} = \langle \Psi^{(n)} | \mu | \Psi^{(m)} \rangle$, called coherences. If we consider the coherence $P_{01}(t) = \langle \Psi^{(0)} | \mu | \Psi^{(1)} \rangle$, using the definition of $\Psi^{(1)}$ (Equation 2.57), we arrive at

$$P_{01}(t) = \frac{i}{\hbar} \int_0^\infty \left\langle \Psi^{(0)} \left| \mu e^{-\frac{i\mathcal{H}_b t}{\hbar}} \mu \right| \Psi^{(0)} \right\rangle \epsilon(t - \tau) d\tau. \quad (2.75)$$

The quantity $C_{00} = \left\langle \Psi^{(0)} \left| \mu e^{-\frac{i\mathcal{H}_b t}{\hbar}} \mu \right| \Psi^{(0)} \right\rangle$ is called the wavepacket correlation function. We see that $P_{01}(t)$ can be written as a convolution of $C_{00}(t)$ with a contribution of the field. $C_{00}(t)$ is the response function in this case. By applying a Fourier transform to Equation 2.75 and using the definition of the absorption spectrum, one can arrive at Equation 2.71 and then

Equation 2.72. With this formulation, we can thus interpret the absorption spectrum as the Fourier transform of the wavepacket correlation function.

Equation 2.72 is the workhorse of one-photon spectroscopy calculations. This formulation of the excitation spectrum is sometimes referred to as the sum-over-states (SOS) approach, since the summation in the formula runs through each of the eigenvectors of the reference wavefunction. The quantity under the summation is the average dynamic polarisability in the frequency space $\langle\alpha\rangle_\omega$ and is sometimes equivalently expressed as

$$\langle\alpha\rangle_\omega = \sum_n \frac{|\langle\Psi_n|\mu|\Psi_i\rangle|^2}{\tilde{\omega}_I - \omega_n} \quad (2.76)$$

or

$$\langle\alpha\rangle_\omega = \sum_n \left\{ \frac{|\langle\Psi_n|\mu|\Psi_i\rangle|^2}{\tilde{\omega}_I - \omega_n} - \frac{|\langle\Psi_n|\mu|\Psi_i\rangle|^2}{\tilde{\omega}_I + \omega_n} \right\}. \quad (2.77)$$

From LRT, one can interpret the perturbative absorption spectrum as arising from the response of the dynamic polarisability of a system to the radiation field. The spectrum is obtained by finding the poles of the polarisability function, ie, the points where $\omega_i = \omega_n$, which makes the value of $\langle\alpha\rangle_\omega \rightarrow \infty$. In such points, the photon frequency is in “resonance” with the energy difference between states, resulting in electronic transition by absorption of the photon. The probability of each transition is proportional to the numerator $|\langle\Psi_n|\mu|\Psi_i\rangle|^2$ —these matrix elements being the transition dipole moment—and can be used in different measures (eg, oscillator strength, Einstein coefficients, etc) to calculate the intensity of the absorptions [149]. The result of such a calculation is a stick-like spectrum with positive amplitudes at each absorption frequency. These are called vertical or Frank–Condon excitations, and do not consider the vibrational levels, which one can include by adding vibrational Hamiltonian matrix elements in the formulation [148]. The vibronic coupling accounts for most of the band shape in electronic spectra. The temperature and solvent polarisation are also contributors and can be included through a variety of approaches, although it is not straightforward [150–159]. For simple qualitative comparison of simulated and experimental spectra, arbitrary Gaussian or Lorentzian functions can be fitted to each vertical transition to compose the spectra (see § 3.2 for more details).

To apply the polarisability-based approach above, one only needs to know the set of ground and excited states wavefunctions. We recall once again that such an approach carries all the usual problems related to the choice of the reference wavefunction, and a complete set of Ψ_n is unattainable, demanding the use of an approximate basis set. LRT approaches are available in most software packages applied to a variety of electronic models such as HF, DFT, CI. LRT applied to CC methods are possible (eg, LR-CC2), but the expressions derived in this section are not suitable for nonvariational wavefunctions. The poles of the polarisability matrix are still a measure of excitation energies in such cases, but the expression must be

formulated in terms of the derivative of the action Lagrangian. LR-CC formulations suffer from many problems, including lack of size extensivity and consistency. Notice that this procedure is primarily meant to obtain frequencies and intensities of transitions (properties), rather than attaining to calculate the wavefunctions and excited state dynamics, although some qualitative characterisation of the wavefunctions are possible through the consideration of the transition dipole moments.

THE FORMALISM DESCRIBED above is quite general. However, Equation 2.72 (or Equation 2.76, or Equation 2.77) is not suitable for direct implementation in computer algorithms. The methods termed time-dependent Hartree–Fock (TDHF) (and its derivatives) and TDDFT implemented in available computational chemistry codes cast the perturbative LRT approach into eigenvalue problems that can be easily implemented with the usual machinery utilised in GS electronic structure calculations. Below we offer a glimpse on these implementations and provide references for further reading. Although the mathematical formalism is not much complicated, it is sufficiently lengthy to prevent their full reproduction here.

Within the linear response regime, both TDHF and TDDFT lead to a generalised non-Hermitian eigenvalue problem of the form

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}, \quad (2.78)$$

where the eigenvectors $(\mathbf{X}, \mathbf{Y})$ represent the amplitudes of electron–hole pair excitations and de-excitations that mix to form the true excited state. The eigenvalues ω are the excitation energies; the poles of the dynamic polarisability occur exactly at these eigenvalues. The matrices $\mathbf{A}$ and $\mathbf{B}$ contain orbital energy differences and coupling terms between electron–hole pairs. The specific content of these matrices distinguishes TDHF from TDDFT, but both theories share a core concept: the expansion of the first-order response wavefunction (Equation 2.57) in the basis of (HF or KS) occupied-virtual orbital products.

The extension of HF theory to the time-dependent case is relatively direct. Within linear response, one obtains the eigenvalue problem in Equation 2.78 with $\mathbf{A}$ and $\mathbf{B}$ constructed from the exact, nonlocal HF exchange potential. This formulation, often termed the random phase approximation (RPA) in quantum chemistry [160], predates its density-functional counterpart. The matrices are given explicitly by¹³

$$\mathbf{A}_{ia,jb}^{\text{TDHF}} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + (ia|jb) - (ib|ja), \quad (2.79)$$

$$\mathbf{B}_{ia,jb}^{\text{TDHF}} = (ia|bj) - (ij|ba), \quad (2.80)$$

¹³These are the forms for a closed-shell singlet ground state, working with spatial orbitals for singlet excitations.

where

$$(pq|rs) = \iint \phi_p^*(\mathbf{r}_1) \phi_q(\mathbf{r}_1) \frac{1}{r_{12}} \phi_r^*(\mathbf{r}_2) \phi_s(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (2.81)$$

denotes the two-electron Coulomb integral over molecular orbitals, ϵ_p are orbital energies, and indices i, j (a, b) label occupied (virtual) orbitals.

For the less direct time-dependent extension of DFT, we recall that the Hohenberg–Kohn theorems are what enables one to obtain the GS energy and properties of a system from the knowledge of its one-electron density, and it is only valid for the GS. The critical question to be answered before a TDDFT approach can be devised is: does the time-dependent one-electron density $\rho(\mathbf{r}, t)$ of a system uniquely determines the time-dependent external potential $V_{\text{ext}}(\mathbf{r}, t)$ and therefore its time-dependent Hamiltonian? The affirmative answer was provided by Erich Runge and Eberhard Gross in 1984 [161]. Their proof, now known as the Runge–Gross theorem, establishes a one-to-one correspondence between the time-dependent potential $V_{\text{ext}}(\mathbf{r}, t)$ and the time-dependent density $\rho(\mathbf{r}, t)$ of a system *evolving from a fixed initial state* Ψ_0 , *provided the external potential is analytic (Taylor-expandable) in time around* $t = t_0$. Subsequent work by Gross and Kohn [162], and by Ghosh and Dhara [163], refined the proof and clarified its domain of applicability.

A practical TDDFT formulation for quantum chemistry—as is the case with the GS version—is built within the KS model. Both the Hohenberg-Kohn and the Runge–Gross theorems are proof of uniqueness, but a proof of existence is missing. For the GS, the existence of a one-electron density that arises from a given external potential is not guaranteed. This is the v -representability problem, and is carried on to the time-dependent formulation, ie, it is not guaranteed that there exists a one-electron time-dependent density corresponding to the time evolution of a given scalar potential. In the KS theory, assuming there is a v -representable density for the real system, one still needs to answer the noninteraction v -representability problem: can the density for an interacting system, representing an interacting external potential, be exactly reproduced by a noninteracting system? Besides that, it is desirable to have a variational principle such as the second Hohenberg–Kohn theorem for the time-dependent case.

Therefore, for a TDDFT formulation in the KS model (TDKS), two additional foundational results are required. First, van Leeuwen proved that a time-dependent density arising from an interacting system can be reproduced exactly by a noninteracting system, solving the noninteracting v -representability problem [164]. Second, van Leeuwen also resolved the causality problem identified by Gross, Dobson, and Petersilka [165], which had plagued earlier attempts to formulate a variational principle for the time-dependent action [166].

Apart from the v -representability problem and the lack of an exact functional, the mathematical foundation for a TDDFT formulation is sound. Casida derived a linear-response formalism for TDDFT analogous to the RPA approach above [167]. The linear response

equations become a non-Hermitian eigenvalue problem in the form of Equation 2.78. The key difference lies in the definition of $\mathbf{A}$ and $\mathbf{B}$: in TDDFT, the two-electron integrals involve the Coulomb kernel plus the xc kernel f_{xc} . In the adiabatic approximation—invoked in almost all practical implementations— f_{xc} becomes frequency-independent and is evaluated using the GS functional. The matrices then take the form

$$A_{ia,jb}^{\text{TDDFT}} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + (ia|jb) + (ia|f_{\text{xc}}|jb), \quad (2.82)$$

$$B_{ia,jb}^{\text{TDDFT}} = (ia|bj) + (ia|f_{\text{xc}}|bj), \quad (2.83)$$

where

$$(pq|f_{\text{xc}}|rs) = \iint \phi_p^*(\mathbf{r}_1) \phi_q(\mathbf{r}_1) f_{\text{xc}}(\mathbf{r}_1, \mathbf{r}_2) \phi_r^*(\mathbf{r}_2) \phi_s(\mathbf{r}_2) d^3r_1 d^3r_2, \quad (2.84)$$

denotes the integral of the xc kernel over the indicated orbital products and

$$f_{\text{xc}}(\mathbf{r}_1, \mathbf{r}_2) = \left. \frac{\delta V_{\text{xc}}[\rho(\mathbf{r}_1)]}{\delta \rho(\mathbf{r}_2)} \right|_{\rho_0} \quad (2.85)$$

is the ground state exchange-correlation kernel evaluated at the ground state density ρ_0 . The details of the derivation is discussed in the original reference above as well as in [168].

Since the TDDFT method is the most popular among the two—TDHF rarely applied to any practical problem—the formulation in Equation 2.78 is usually called the Casida equation, even outside the TDDFT context. The Tamm–Dancoff approximation (TDA) is often applied in calculations, where the $\mathbf{B}$ matrix is neglected, yielding the Hermitian eigenvalue problem

$$\mathbf{A}\mathbf{X} = \omega\mathbf{X}, \quad (2.86)$$

which is computationally simpler and avoids problems such as triplet instabilities. The effect of neglecting the $\mathbf{B}$ matrix is to remove de-excitation contributions to excitations and vice versa, ie, the coupling between the $\mathbf{X}$ and $\mathbf{Y}$ matrices is removed. Such couplings accounts for excited state correlations which usually decrease the excitation energies. The difference is often negligible, however, and Rydberg and charge-transfer states are better described in the TDA approximation with DFT [169–173]. In the TDHF case, the problem in Equation 2.86 is equivalent to the CIS method (see § 2.1.1).

2.1.4.3 PROPAGATORS AND EQUATION-OF-MOTION METHODS

WE HAVE COME ACROSS THE definition of an evolution operator or propagator above, as an operator which maps $\Psi(\mathbf{x}, t_0) \rightarrow \Psi(\mathbf{x}, t_1)$. After defining our perturbed Hamiltonian for light-matter interaction, we arrived at an expression which maps a wavefunction $\Psi_i(\mathbf{x}, -\infty)$ into the first order correction to the wavefunction $\Psi^{(1)}(\mathbf{x}, t)$ (Equation 2.70). The quantity multiplying $\Psi_i(\mathbf{x}, -\infty)$ is, therefore, a propagator. When discussing LRT, we have seen that

this quantity leads to the correlation function, whose Fourier transform can be interpreted as the absorption spectrum. Furthermore, we have seen that this is equivalent to the response of the average polarisability in the frequency domain $\langle\alpha\rangle_\omega$ plus constants. From this, we can see that there is a close connection between the properties of a propagator and time-dependent molecular properties such as the polarisability, which leads to excitation energies. Writing the TDSE in the Heisenberg picture, one can in fact work directly with propagators, without any need to consider expansions of the time-dependent wavefunction. If we Taylor-expand the expectation value of the dipole moment operator $\langle\Psi|\mu|\Psi\rangle$ in terms of the perturbation $\mathcal{H}_1$ as defined in Equation 2.68, we arrive at a propagator-based expansion. It can be shown that the first order term is the frequency dependent polarisability which we are already familiar with. Propagators can be used in a broader way for a variety of time-dependent formulations, going beyond perturbation theory or variational approximations and even considering QFT formulations. For this, one considers the calculation of the general propagators as solution to their equation-of-motion (eg, Equation 2.61), thus avoiding the costly calculation of corrections to the wavefunction. In this context it is common to refer to the propagators as Green's functions, since they are essentially the solutions to differential equations involving a linear differential operator [174]. Such a treatment is beyond the scope of this text, but [97, 100, 175] discuss some propagator approaches in more detail.

A different approach to the calculation of excited states is what is conventionally called equation-of-motion methods. In this approach, one starts from the assumption that an excited state wavefunction Ψ_n is produced from the GS wavefunction Ψ_0 by an excitation operator $\mathcal{O}_n^\dagger$ (with a corresponding de-excitation operator $\mathcal{O}_n$). Defining a Hamiltonian superoperator $\mathcal{H}$ (or Liouvillian) as an object that, when operating on an operator $\mathcal{A}$, generates the commutator with the Hamiltonian, ie,

$$\mathcal{H}\mathcal{A} = [\mathcal{H}, \mathcal{A}], \quad (2.87)$$

one can see that, for exact state eigenfunctions, we have

$$\mathcal{H}\mathcal{O}_n^\dagger|\Psi_0\rangle = \mathcal{H}\mathcal{O}_n^\dagger|\Psi_0\rangle - \mathcal{O}_n^\dagger\mathcal{H}|\Psi_0\rangle = (E_n - E_0)\mathcal{O}_n^\dagger|\Psi_0\rangle. \quad (2.88)$$

Thus, when acting on the exact ground state wavefunction, $\mathcal{H}\mathcal{O}_n^\dagger$ returns the excitation energy. Equation 2.88 means that $\mathcal{O}_n^\dagger$ is an eigenoperator of $\mathcal{H}$ with eigenvalue equal to the exact excitation energy. By seeking (approximate) solutions to the eigenvalue equation above, eg, by using an operator basis to expand $\mathcal{O}_n^\dagger$, one can formulate a general theory based on these quantities and calculate excitation energies without the need to bother about approximations to the time-dependent wavefunction. Although no explicit mention of the equation-of-motion was made, the commutation relations arising from such formulations resemble those found when applying the equation-of-motion to operators in the Heisenberg picture, as discussed in the paragraph above.

The EOM technique can be applied to CC wavefunctions with a suitable expansion of the excitation operators $\mathcal{O}_n^\dagger$ for a given cluster exponential operator. This is generally done by a similarity transform of the Hamiltonian such that it commutes with the approximate $\mathcal{O}_n^\dagger$ operator. To perform this, a CIS matrix is used as an initial guess for the singles and doubles space Hamiltonian. Currently, EOM-CCSD is the highest level of this approach since reliable implementations for EOM-CCSD(T) or EOM-CCSDT have not been developed. EOM-CC methods are costly, but an alternative similarity transformed EOM (STEOM) approach exists [176]. In this version, a second similarity transform to the Hamiltonian further compresses the space to the CIS space only, thus decreasing the computational cost. Multireference formulations of this approach are also available. Another implementation that greatly improves the scalability (to near linearity) of CC methods is the domain-based local pair natural orbital (DLPNO) transformation. This approach first localises the occupied orbitals and then, for each pair of localised occupied orbitals, applies a transformation to the virtual orbitals to generate a compact set of pair natural orbitals (PNOs). These PNOs span only the most important virtual space for excitations from that pair. The less important excitations are either ignored or treated at a less costly level [177–180]. A word of caution regarding STEOM-CC methods is that they are not size consistent or extensive.

Except for the CC method discussed above, when applied to other reference wavefunctions at the usual level of approximation considered here, EOM, propagator, perturbative and variational methods all lead to the same working equations for discussing electronic excitations. For example, with a one-determinant closed-shell reference function and a single excitation manifold, all methods yield the standard LRT equations [175].

2.2 CLASSICAL MOLECULAR MECHANICS AND DYNAMICS

EVEN WITH THE SEVERAL approximations introduced to the *ab initio* QM methods discussed above and widely utilised in problems of interest for chemistry, these methods are the most accurate we have for the description of molecular properties and processes. However, such accuracy comes with a high computational demand that forbids their application to very large systems or long time scales in the current technological stage. DFT methods—among the most efficient QM methods available—scales as $O(N^3)$, where N is the number of basis functions, and is limited to systems with a few hundred atoms for routine calculations in high-performance computing (HPC) clusters. Although there are pure QM-based approaches to improve scalability and stretch these limits, such as approximate algorithms for linear scaling HF and DFT [181–186], and quantum fragmentation [187–189] and embedding [190–192] methods (QM/QM), massive improvement on system size and time scale can only be achieved by simplifying the model and abstracting variables. The best alternative is to resort to MM or MD methods, sometimes generically called force field methods. This can also be done

with embedded or fragmentation techniques sometimes called QM/MM methods [193–197], or in the hierarchical approach utilised in this work, in which QM data is first obtained for smaller components of the system (molecules and atoms) and then fed to the coarser force field models for the simulation of the larger system (see § 1.1). The gain in computational efficiency by MM/MD methods is basically due to two simplifications: (1) the abstraction of the electrons by representing the system only as the $3N$ Cartesian coordinates of the N nuclei, therefore massively decreasing the size of the coordinate space; and (2) the simplification of the mathematical model, leading to more tractable and efficient calculation steps in general. In this section we discuss the machinery and formalism of MM/MD methods.¹⁴

The MM/MD approach is a substantially coarse approximation of the physics at the molecular level when compared with the *ab initio* QM methods discussed above. Oftentimes, the approximations are not rigorously justified and usually come with known severe unphysical effects and errors. As such, the validity of such methods are always constrained to a definite domain of applicability and must be properly validated if the results are to be used for any modelling and prediction of reality at all. There are, however, a few physical and mathematical justifications that underpin the choice of model, the most important and general of them we discuss here, and more being discussed as necessary alongside the detailed discussion below. This section covers the general idea of MM/MD methods. § 2.2.1 discusses the form of the most common FFS describing the interatomic interactions in molecular systems, including an approach that allows for the description of chemical reactions. In doing that, we discuss the definition of the system’s geometry and topology, simulation boxes and boundary conditions, and algorithms to tackle the most expensive aspect of the potential energy calculation: the treatment of long-range nonbonded interactions. § 2.2.2 concerns the setup of MD simulations, the underlying mathematical models and specific numerical algorithms, and geometry optimisation techniques. We focus on the implementation available in the MBN EXPLORER software package utilised in the MM/MD calculations in this work (Chapter 4).

We have already met the core concept that ultimately allows us to routinely perform *in silico* molecular simulations: the BO approximation (§ 2.1, p 14). This concept is also important here. It is only because we can reasonably treat the movement of the nuclei separated from that of the electrons, and therefore utilise the concept of a potential energy surface that governs the nuclear movement in a certain electronic state of the system (see Equation 2.6 and the discussion on p 17), that we can come up with the idea of abstracting electrons out of the model. In MM models, the complicated multidimensional description

¹⁴*Note on terminology:* it is customary to separate the MM and MD concepts. In general, MM refers to the modelling of molecular systems based on geometry and interactions to compute the potential energy as a function of nuclear coordinates and derived properties, typically without intrinsic time evolution, though geometry optimisation (see below) involves iterative coordinate changes, sometimes with explicit dynamics. MD applies to the time-dependent calculations of such systems, propagating atomic motion over time, governed by MM force fields, to compute properties dependent on the generated trajectories of positions and velocities such as conformational changes, thermal fluctuations, and transport properties.

of the electronic structure of a system as function of the parametric nuclear coordinates is substituted by a collection of simplified effective potential functions that can locally and approximately describe the PES. This set of functions is called a force field. The dynamic evolution of the system is then obtained by assuming the nuclei move governed by this set of functions in the classical regime, ie, following Newton's law of motion. In QM reasoning, under the BO approximation, it is indeed already the case that we make the underlying assumption of classical motion of the nuclei in various instances, eg, when thinking about geometry optimisation, reaction coordinates, and conformational changes. However, depending on what properties we need, we can always resort to the actual quantum nature of the nuclei via the nuclear wavefunction $\chi_i(\mathbf{R})$ (Equation 2.7). Here we take it a big step forwards in that direction: everything is classical, and the quantum nature of molecules is gone for good.

2.2.1 STANDARD AND REACTIVE FORCE FIELDS

WE THEREFORE NEED TO devise an approximate way to describe the PES. A recurrent theme we will see with MM/MD is that of expanding functions in a suitable series of basis functions and (overly) truncating it at the first few terms. In fact, we have already met such strategy in QM methods in several moments, eg, in the truncated basis set for the Hilbert space of electronic orbitals, in the truncated CI method (of which HF is the lowest-order approximation), and in the linear approximation to the response function of a system to the radiation field (LRT). Since MM was initially built for properties of molecular systems near equilibrium structures, making local approximations to the PES seem like a good choice. Therefore, often the strategy is to expand the $3N+1$ -dimensional PES of a system of N particles by a suitable series at an equilibrium geometry (a local minimum on the PES), and truncate the series. The most simplified FF will make the approximations up to second order. We do not attempt to approximate all degrees of freedom homogeneously, though. Using the QM knowledge we have of molecular movements, how restrict they are, and how the slice of the PES along each mode looks like, we carefully select suitable functional forms depending on their nature. We see here already the feature of the more fundamental description informing the higher level, more approximate model, as discussed in § 1.1.

Before we continue, some housekeeping is necessary. Since we are shifting our attention to a whole new class of models in this section—in fact, based on a fully classical framework as opposed to the quantum one—it is better we reset the mathematical conventions we have been using. For the remaining of this chapter, we will now use the notation previously applied to electrons to refer to the most fundamental particles in the current model. Usually these are the atoms in the system, but some models will group atoms into one elementary particle. The *united atom model* will group carbon atoms and their bonded hydrogens and *coarse-grained models* will group molecular functional groups, monomer of a polymer, or even whole molecules, into single units. However, we need not consider such approaches here

since in all simulations discussed in Chapter 4, an *all-atom model* was utilised. Therefore, N is now the total number of atoms. $\mathbf{x}_i$ and m_i are the position vector and the mass of the i th atom, respectively (all lowercase indices). The purely mathematical notations (see n 2) remain the same. Other notations will be introduced as we carry on.

Of the initial $3N$ degrees of freedom for a molecular system, three are related to the translation of the whole system along each Cartesian axis, and other three—two if the molecule is linear—to the rotation around each axis. The energy of the molecule is unchanged by these movements and therefore we exclude these degrees of freedom from the description of the PES. Therefore, the PES is a function of the $3N - 6$ ($3N - 5$ if linear) internal coordinates of the molecule. In molecular FFs, the interactions between the various atoms can be classified in bonded and nonbonded. Bonded interactions are those affecting only atoms covalently bonded together, while nonbonded interactions affect all atoms in the system, and are the only interactions between atoms in separate molecules (or isolated atoms). A fairly standard FF will have three types of bonded potential energy functions (PEFs), usually termed bond stretch (E^{bond}), angle bend (E^{bend}), and dihedral angle torsion or bond torsion (E^{torsion}); and two nonbonded PEFs, one for the electrostatic interactions (E^{elec}) and one for the van der Waals interactions (E^{vdW}). The total potential energy of a molecular system under such FF is then given by

$$E^{\text{FF}} = E^{\text{bond}} + E^{\text{bend}} + E^{\text{torsion}} + E^{\text{elec}} + E^{\text{vdW}}. \quad (2.89)$$

We now discuss each term in turn. Figure 2.2 is a schematic summary of the ensuing discussion.

Bond stretch. The potential energy curve (PEC) as a function of the distance between two bonded atoms—usually called the bond stretch PEC in the context of molecular FFs—has a typical shape, as can be seen, for example, in the bond scans discussed in Chapter 3. An empirical functional form that fits well to such curves is the Morse potential, suggested by Philip M Morse in the context of the quantum-mechanical calculation of vibrations in diatomic molecules [198], and given by

$$E^{\text{Morse}}(x_{ij}) = D_{ij} \left[1 - e^{-a_{ij}(x_{ij} - x_{ij}^{(0)})} \right]^2, \quad (2.90)$$

where x_{ij} and $x_{ij}^{(0)}$ are the bond distance variable and the bond reference distance between atoms i and j , respectively; D_{ij} is the bond dissociations energy (BDE); and a_{ij} is a parameter controlling the width of the potential well, which will be better described below. We are here following Andrew Leach [101] in calling $x_{ij}^{(0)}$ the *reference bond distance*, as opposed to the equilibrium bond distance used in other texts. The reason is that, for a molecule described by a complex FF, $x_{ij}^{(0)}$ will not in general be the distance displayed between the atoms i and j at the equilibrium geometry, even though $\min [E^{\text{Morse}}(x_{ij})] = E^{\text{Morse}}(x_{ij}^{(0)}) = 0$. This is

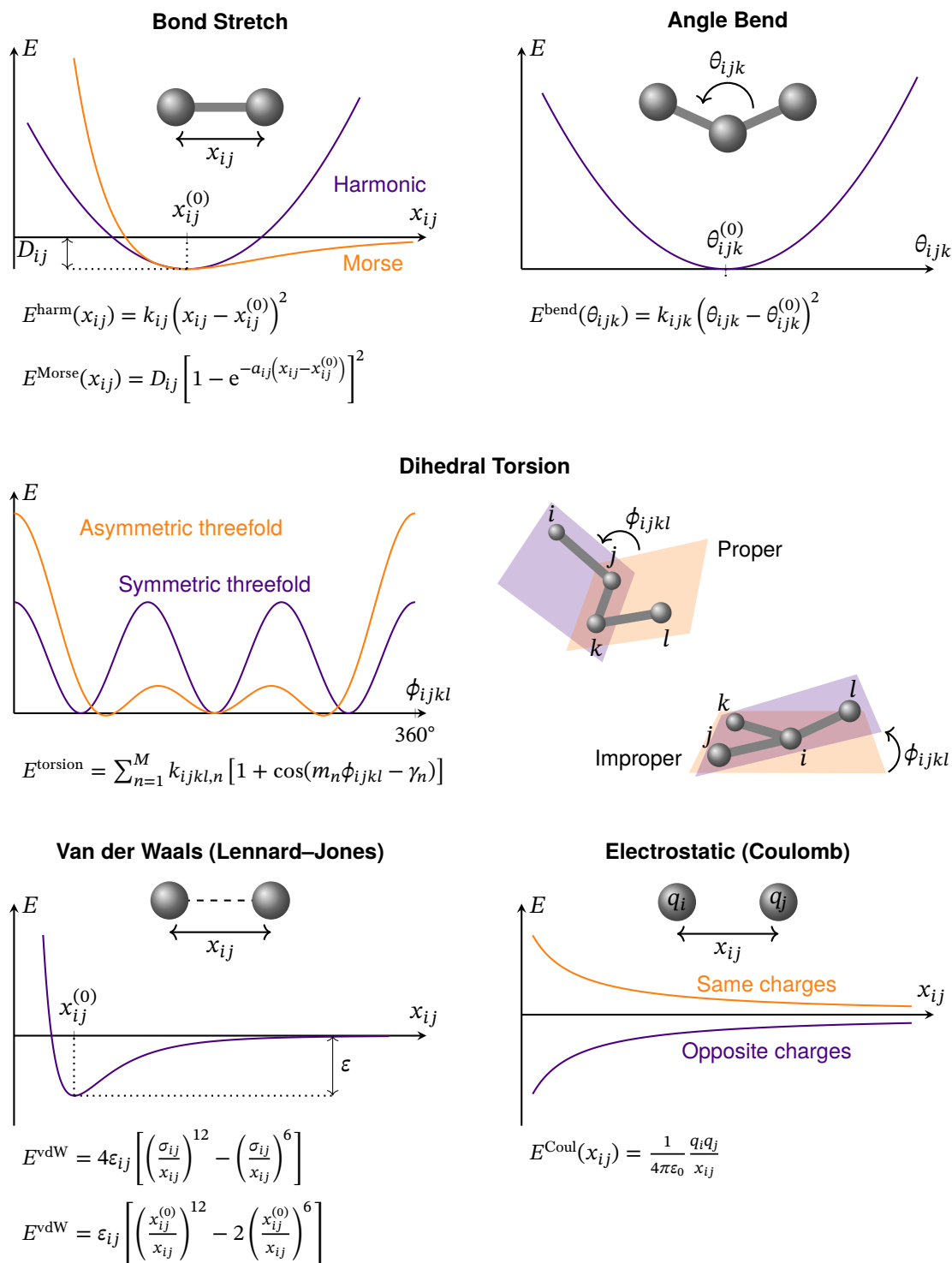


FIGURE 2.2 – Schematic representation of the potential energy terms in a typical molecular force field. See text for definitions and discussion. All axes cross at (0,0).

because all the other interactions will contribute to the overall potential that is minimised in the geometry optimisation of the system. This is true for all reference parameters we will encounter in the subsequent potentials in this text.

The Morse potential is not an exact representation of the real bond stretching potential. In fact, Morse himself put four conditions that a good functional form should obey: (1) it should asymptotically approach a finite value as $x_{ij} \rightarrow \infty$ (as interactions cease to exist); (2) it should have a unique minimum point at $x_{ij} = x_{ij}^{(0)}$; (3) it should approach infinity as $r \rightarrow 0$ (as nuclear and Pauli repulsions increase); and (4) it should exactly give the vibrational energy levels according to the polynomial $W(n) = -D + \hbar\omega_0[(n + 1/2) - x(n + 1/2)^2]$ plus a small constant error factor (we need not worry about the interpretation of the coefficients here). Equation 2.90 satisfies all but condition (3). An exact function do not exist in this case, although various (infinite) series expansions have been proposed. The Morse potential, however, gets close enough and is simple enough that it became the standard functional form for this type of potential. We will come back to the Morse potential when we discuss reactive FF below.

The majority of the available FFs will employ the simplest harmonic potential to describe bond stretching. We can think of the Morse potential as being the “accurate” description, and we can expand it as a Taylor series around $x_{ij} = x_{ij}^{(0)}$ as

$$E^{\text{Morse}}(x_{ij}) = Da^2(x_{ij} - x_{ij}^{(0)})^2 - Da^3(x_{ij} - x_{ij}^{(0)})^3 + \frac{7}{12}Da^4(x_{ij} - x_{ij}^{(0)})^4 - \dots \quad (2.91)$$

Thus, the simplest approximation is to truncate the expansion at the first, quadratic term. This is simply the harmonic potential

$$E^{\text{harm}}(x_{ij}) = \frac{1}{2}k_{ij}(x_{ij} - x_{ij}^{(0)})^2 \quad (2.92)$$

given by Hook’s law for a restorative force. This is the picture of a bond being represented by a spring of force constant k . If we compare Equation 2.92 with the quadratic term in Equation 2.91, we see that

$$a_{ij} = \sqrt{\frac{k_{ij}}{2D_{ij}}} = \omega_{ij}\sqrt{\frac{\mu_{ij}}{2D_{ij}}}, \quad (2.93)$$

where $\mu_{ij} = (m_i m_j)/(m_i + m_j)$ is the reduced mass of the atoms and ω_{ij} is the angular frequency of the harmonic motion under the restorative force, approximating the bond vibrational frequency. Describing bond stretch by the harmonic potential means that the accuracy of the potential sharply decreases as the bond distance is displaced from its reference value (see comparison in Figure 2.2). In fact, from the four criteria imposed by Morse for an accurate function, Equation 2.92 only satisfies (2). This approximate potential will only perform well if the geometry of the system do not deviate too much from equilibrium, and will never be

able to describe bond dissociation. As we mentioned above, however, most molecular FFs were designed for exactly this scenario, and therefore we usually have

$$E^{\text{bond}} = \sum_{ij(\text{bonded})} k_{ij} \left(x_{ij} - x_{ij}^{(0)} \right)^2, \quad (2.94)$$

where the summation extends over all bonded i, j atom pairs. The functional form in Equation 2.94 absorbs the $1/2$ factor into k_{ij} and is the form used in the Chemistry at Harvard Macromolecular Mechanics (CHARMM) FF [199–202], which was utilised in all MM/MD calculations in this work (see Chapter 4).

Angle bend. Three atoms i, j , and k bonded together will form an angle between the two bonds. Moving this angle away from an equilibrium value will cause the atoms at the extremes to repel and/or the bonds to destabilise, increasing the energy. There is no defined functional form that can describe the angle bend potential. However, if we restrict the bond angle such that $0^\circ \leq \theta_{ijk} \leq 180^\circ$, then we can write a general local power series expansion of the PEC around $\theta_{ijk} = \theta_{ijk}^{(0)}$ as

$$E(\theta_{ijk}) = k \left(\theta_{ijk} - \theta_{ijk}^{(0)} \right) + k' \left(\theta_{ijk} - \theta_{ijk}^{(0)} \right)^2 + k'' \left(\theta_{ijk} - \theta_{ijk}^{(0)} \right)^3 + \dots \quad (2.95)$$

where $k, k', k'', \dots$ are constants and $\theta_{ijk}^{(0)}$ is the reference bend angle such that $E(\theta_{ijk}^{(0)}) = 0$. The restriction in the angle range is done so that the function is not periodic, and it is not actually restrictive in the physical standpoint since large deviations from the reference angle requires a large amount of energy, as with the case of bond stretching.

Of course, such an infinite series is impractical for calculations and, as the reader will have anticipated, it is truncated at the first term in most molecular FFs. This yields

$$E^{\text{bend}} = \sum_{ijk(\text{bonded})} k_{ijk} \left(\theta_{ijk} - \theta_{ijk}^{(0)} \right)^2. \quad (2.96)$$

This is the analogue harmonic potential for bond bending. k can also be interpreted as a “force constant” for the bending, although it is not directly tied to any molecular property. It is better to consider it as a generic parameter of the FF, as we should do with any of the parameters for that matter (more on that below). Other FFs will employ correction terms or other functional forms to account for anharmonicity. In the CHARMM FF, Equation 2.96 is the form employed for the angle bend potential. However, for some bonds, there is an optional Urey–Bradley term available. This has the form of the harmonic bond stretch potential (Equation 2.92) and applies to atoms i and k at the extremities of the bonded triad, as if they were connected. The use of such device makes Equation 2.96 become

$$E^{\text{bend+UB}} = \sum_{ijk(\text{bonded})} k_{ijk} \left(\theta_{ijk} - \theta_{ijk}^{(0)} \right)^2 + k_{ik} \left(x_{ik} - x_{ik}^{(UB)} \right)^2. \quad (2.97)$$

Such addition includes some degree of anharmonicity to the bending potential, prevents too much distortion of the bending angle, and weakly couples bending and stretching of the bonds.

Dihedral torsion. Now consider four atoms i, j, k , and l bonded in sequence. i, j , and k lie in a plane while j, k , and l is in another (possibly coplanar) one (see Figure 2.2). Torsion of their configuration about the central j, k bond defines a variable dihedral angle ϕ_{ijkl} that can range between 0° and 360° . Repulsion between atoms i and l (and possibly other atoms bonded to them) will establish a characteristic PEC, usually with multiple local minima. If we think of a simple ethane molecule, torsion around the C–C bond results in a PEC with three maxima at the angles where the hydrogens are aligned (eclipsed conformation) and three minima at the angles where they are the farthest apart (staggered conformation). The number of minima or maxima in the potential is called the multiplicity m . Since this is a periodic potential, the most general way to represent it is via a Fourier series

$$E(\phi_{ijkl}) = C_0 + \sum_{n=1}^{\infty} [A_n \cos(n\phi_{ijkl}) + B_n \sin(n\phi_{ijkl})] = \sum_{n=1}^{\infty} \frac{V_n}{2} [1 + \cos(n\phi_{ijkl} - \gamma_n)], \quad (2.98)$$

where A_n, B_n, C_0 , and V_n are constants and γ_n is a phase factor. The second equality is a consequence of the sum formula $\cos(\phi - \delta) = \cos \delta \cos \phi + \sin \delta \sin \phi$. In practice, only a few terms are included in FFS. The approximate functional form for the torsion potential is thus

$$E(\phi_{ijkl}) = \sum_{n=1}^M \frac{V_n}{2} [1 + \cos(m_n \phi_{ijkl} - \gamma_n)]. \quad (2.99)$$

Note that in Equation 2.99 the number of terms M and the multiplicity of the cosine function m_n are independent of each other. In other words, one can use as many terms as needed, of whatever multiplicity each. That is not the case in Equation 2.98, where there exists always one term of each and every multiplicity in the complete set of functions. Many texts (including [101]) will make $n = m_n$ in a misleading notation.

With this definition, the torsion factor in a typical molecular FF is given by

$$E^{\text{torsion}} = \sum_{ijkl(\text{bonded})} \sum_{n=1}^M k_{ijkl,n} [1 + \cos(m_n \phi_{ijkl} - \gamma_n)]. \quad (2.100)$$

This is the form adopted by the CHARMM FF, with the $1/2$ factor absorbed into the constants, as we have already seen for bond stretch. Not all molecular FF will include a torsion potential. Some will prefer to describe the interactions by means of the nonbonded potentials between the i and l atoms at the extremities of each tetrad of bonded atoms.

In some FFS, as is the case with CHARMM, the same functional form in Equation 2.100 will be employed as an **improper dihedral** to ensure planarity of a set of four atoms not

bonded in sequence, but one being the central atom to which the other three are connected (see Figure 2.2). If i is the central atom, we can define two planes, one containing i , j , and k and another containing j , k , and l . If the atoms are to be planar, the dihedral angle of these two planes must be enforced to 0° . This can be done by assigning the potential $E(\phi_{ijkl}) = k_{ijkl} [1 + \cos(2\phi_{ijkl})]$ to the atoms, with a high enough k_{ijkl} barrier and the correct initial geometry.

Nonbonded interactions. With the potentials defined above, we are able to describe the equilibrium geometry of a single isolated molecule fairly well. We are not able, however, to describe intermolecular interaction or even intramolecular nonbonded interactions. Therefore, our FF needs more potentials to account for them.

In real molecules, there is a series of possible nonbonded interactions resulting from net charges or nonspherical charge distributions. In chemistry, it is usual to separate them into two categories: electrostatic (or ionic) interactions, existing between two charged particles only, and van der Waals interactions including all of those weak, short range interactions that do not arise from a net charged system. The electrostatic interactions are described by an electric potential that falls with $1/x$, a Coulomb potential. The van der Waals interactions have the common feature that, at not very short distances, the potential falls with $1/x^6$. This encompasses (1) *London dispersion forces*, arising from dynamic inhomogeneous electron density distributions in the atoms or molecules—a quantum dynamical effect that creates multipole fluctuations that induce corresponding fluctuations in neighbouring atoms or molecules; (2) *Keesom forces*, that are interactions between rotationally averaged permanent electric dipoles; and (3) *Debye forces* or dipole-induced dipole interactions.

Such picture is in fact useful and captures most of the effects, as will become clear shortly, but it is not complete. For example, the interaction between two molecules with permanent dipoles and fixed spatial orientation is neither of a Coulomb nor of a van der Waals type as the potential falls with $1/x^3$. Besides that, a homonuclear diatomic molecule do not posses net charge nor permanent electric dipole moment, but it does have a permanent electric quadrupole moment that produces an interaction potential falling with $1/x^5$. In general, every molecule will have a permanent electric multipole of some order since they are never a perfectly neutral spherical distribution of charges. Any multipole will create some electric field that will allow for interactions at fixed orientations (in solids or at low temperatures) or spatially averaged ones (in liquids and gases at higher temperatures).

As often happens with real complex systems, the charge distribution of a real molecule will produce a complicated electric field that cannot be described by a simple mathematical closed form. Consider the electric field at a certain distance from a molecule where orbital overlap is negligible. We can model such field as being generated by an instantaneous charge distribution on the surface of a sphere enclosing the molecule. The average field strength outside the sphere will be a function of the distance r from the centre of the sphere and will

have a complicated dependence on the spherical azimuthal (θ) and polar (φ) angles, arising from the various electronic effects discussed above. Such a field can be described by a series expansion on the spherical harmonic functions, called a Laplace or multipole expansion—the three-dimensional equivalent of a Fourier expansion—plus a radial part. This description comes as the direct general solution of the Poisson equation for the electric potential Φ of a continuous charge distributions ρ given by¹⁵

$$\nabla^2 \Phi(\mathbf{x}) = -\frac{\rho(\mathbf{x})}{\epsilon_0}. \quad (2.101)$$

Outside the charge distribution, ρ is identically zero and the equation simplifies to the homogeneous case (Laplace equation)

$$\nabla^2 \Phi(\mathbf{x}) = 0. \quad (2.102)$$

Writing the Laplace operator ∇^2 in spherical coordinates, it becomes possible to separate the three spherical variables. This is done by writing the solution to Equation 2.102 as a product *ansatz* of three functions, one for each of the spherical coordinates r , θ and φ . Each function can then be determined separately by invoking adequate boundary conditions. The development is fairly lengthy so we refer the interested reader to Chapters 1, 2, and 3 of [203]. The solution of Equation 2.102 obtained in such a way is

$$\Phi(\mathbf{x}) = \frac{1}{4\pi\epsilon_0} \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} g_{lm} \frac{Y_{lm}(\theta, \varphi)}{r^{l+1}}, \quad (2.103)$$

where

$$Y_{lm}(\theta, \varphi) = \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} P_l^m(\cos \theta) e^{im\varphi} \quad (2.104)$$

are the spherical harmonics, combining the solutions of the Laplace equations in φ and in θ , where $P_l^m(\cos \theta)$ are the associated Legendre functions. The coefficients g_{lm} can be determined by the form of the charge distribution $\rho(\mathbf{x})$ inside the sphere and are obtained as solution to the inhomogeneous problem (Equation 2.103). The result is

$$g_{lm} = \int Y_{lm}^*(\theta', \varphi') r'^l \rho(\mathbf{x}') d^3x', \quad (2.105)$$

where the integration is over the whole space and the prime indicates coordinate of the source charge distribution internal to the sphere. The coefficients are called multipole moments of

¹⁵We are using $\mathbf{x}$ for the position vector in general to avoid confusion with the polar radial coordinate r .

the charge distribution. $l = 1$ defines a monopole, $l = 2$ a dipole, $l = 3$ a quadrupole, $l = 4$ an octupole, $l = 5$ an hexadecapole, and so on.¹⁶

We need not worry about the detailed form of the functions above for the point we want to make. It is sufficiently enlightening to look at the expansion of $\Phi(\mathbf{x})$ in Cartesian coordinates

$$\Phi(\mathbf{x}) = \frac{1}{4\pi\epsilon_0} \left[\frac{q}{r} + \frac{\mathbf{p} \cdot \hat{\mathbf{x}}}{r^2} + \frac{1}{2} \sum_{i,j} Q_{ij} \frac{\hat{x}_i \hat{x}_j}{r^3} + \frac{1}{6} \sum_{i,j,k} O_{ijk} \frac{\hat{x}_i \hat{x}_j \hat{x}_k}{r^4} + \dots \right] \quad (2.106)$$

where the hat sign indicates unit vectors and $\hat{x}_i$ is the i th Cartesian component of the unit vector $\hat{\mathbf{x}}$. The summations run over all combinations of the three Cartesian components. Each of the terms inside square brackets are the monopole, dipole, quadrupole, octupole, ... terms. q is the total charge of the system. $\mathbf{p} = \int \rho(\mathbf{x}') \mathbf{x}' d^3x'$ is the dipole moment vector. $Q_{ij} = \int \rho(\mathbf{x}') (3x'_i x'_j - r'^2 \delta_{ij}) d^3x'$ are the components of the quadrupole moment rank-2 tensor. $O_{ijk} = \int \rho(\mathbf{x}') [15x'_i x'_j x'_k - 3r'^2 (x'_i \delta_{jk} + x'_j \delta_{ik} + x'_k \delta_{ij})] d^3x'$ are the components of the traceless octupole moment rank-3 tensor.

If a system has a net charge, the first term in Equation 2.106 will be the monopole. For a neutral system with a dipole moment, eg, a heteronuclear diatomic molecule, the monopole vanishes and the leading term is the dipole. For a homonuclear diatomic molecule, as anticipated above, there is no permanent dipole moment but there is a quadrupole moment as a consequence of the axial symmetry, and therefore the leading term is the quadrupole. There are molecules whose first permanent multipole moment is the octupole, all lower-order ones vanishing. This is the case of methane, for example. In general, for a given molecular system, there will be one leading term of some order, followed by the subsequent higher order terms. The important thing to take from Equation 2.106 is the fact that, at each step up in order of the multipole moments, there is a multiplication of a $1/r$ factor. Therefore, the contribution of the higher order terms decreases much quicker with distance than that of the leading term. That means that it is a reasonable first approximation to define the interactions by the leading term only, particularly at large enough distances from the source.

With this general picture in mind, let us go back to our initial approximate classification of nonbonded interactions into electrostatic and van der Waals. The full description in Equation 2.103 will account for all permanent (static) multipole effects, and if the molecular orientation is allowed to evolve in time in a MD fashion, can naturally cover the spatially averaged cases. Therefore, the electrostatic Coulomb interactions between charged particles as well as the Keesom and Debye forces are included. The only effects left out are the quantum dynamical electron density fluctuations (London dispersion), the formation of induced dipoles (polarisability), and the repulsions arising from orbital superposition at close distances (a quantum effect). While the quantum effects cannot be described by a

¹⁶These types of functions are similar to those obtained in the solution of the TISE (Equation 2.3) for the hydrogen atom and that define the atomic orbitals s, p, d, f, etc.

purely classical theory, by definition, polarisability effects can be included by introducing dynamical multipole polarisability terms in the expansion and considering the full set of Maxwell's equations [203]. However, Equation 2.103 is already much more complicated than most MM/MD implementation ever consider, even when truncated to the first several terms.

Some advanced molecular FF will include dynamic polarisability effects [204, 205] including extensions of the standard CHARMM FF with Drude polarisation (CHARMM-Drude) [206] or fluctuating charges (CHARMM-FQ) [207, 208]. Some other will include various multipolar contributions [209]. However, first-generation simplified FFs such as CHARMM will account for all nonbonded interactions via a combination of real-valued atomic charges (partial or formal) evaluated from a Coulomb potential and a Lennard-Jones (LJ) potential for van der Waals interactions. We briefly discuss them now.

Electrostatic interactions. As discussed above, the leading term in a multipole expansion for a charged system is the monopole, the subsequent terms having diminishing contributions as the distance to the source increases. A coulomb term is thus a good approximation for approximately spherical systems with a formal charge. More often than not, however, molecular systems of interest for MM modelling are neutral. Yet, the only electrostatic potential included in simple FF such as CHARMM is the pairwise coulomb potential

$$E^{\text{elec}} = \sum_{i=1}^N \sum_{j>i}^{N-1} \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{x_{ij}}. \quad (2.107)$$

This choice of functional form can never account for the correct fall-off of the higher order multipoles. But by allowing the atomic charges to assume any real value multiple of the elementary charge, some flexibility is added. An approximation to the spatial charge distribution of a molecule can be made that, at far enough distances, is better than nothing. The fact that the potential's decay is limited to the $1/x$ rate can be partially compensated by tuning the values of partial charges and by the interplay of all other FF parameters, particularly the LJ parameter discussed below.

There is one additional problem with this choice of representation. Assigning charges only to the atoms does not allow for charged poles outside atomic positions, which would help in the description of lone electron pairs or conjugated π electron clouds. This can be remedied by allowing the placement of off-atom charges (sometimes called lone-pair charges) or by including dummy atoms in the description. The CHARMM FF offers these two options. A classical example where this representation is made is in the various multisite water models such as the transferable intermolecular potential n point (TIPnP) representations for $n > 3$ [210].

Van der Waals interactions. Not all nonbonded interactions in molecular systems arise from permanent electric multipole as already discussed. Neutral atoms in the gas phase such

as noble gases can be liquefied. That is only possible because some interaction exists between them. The role of the nonbonded interactions not accounted for by the electrostatic model in Equation 2.103 and (highly) approximated by the electrostatic interaction model discussed above is modelled by a phenomenological potential, the most famous being the LJ potential

$$E^{\text{vdW}} = \sum_{i=1}^N \sum_{j>i}^{N-1} 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{x_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{x_{ij}} \right)^6 \right], \quad (2.108)$$

where ε_{ij} is the depth of the potential well and σ_{ij} is the distance for which the potential is zero, sometime called collision diameter. An alternative form of the potential in terms of the reference distance $x_{ij}^{(0)}$ at which the potential is a minimum can also be written as

$$E^{\text{vdW}} = \sum_{i=1}^N \sum_{j>i}^{N-1} \varepsilon_{ij} \left[\left(\frac{x_{ij}^{(0)}}{x_{ij}} \right)^{12} - 2 \left(\frac{x_{ij}^{(0)}}{x_{ij}} \right)^6 \right]. \quad (2.109)$$

Comparing the derivatives of the general terms in Equation 2.108 and in Equation 2.109 at $x_{ij} = x_{ij}^{(0)}$ we see that $x_{ij}^{(0)} = 2^{1/6}\sigma$.

The power-six factor in the LJ potential describes the van der Waals attractive part while the power-twelve part describes the steep repulsive part. This repulsive term is meant to model the Pauli repulsion at short distances, but is clearly much worse at that than the Morse potential (see discussion above). This choice for the repulsive part is purely practical since the power-twelve factor can be computed simply by squaring the power-six term. A generalisation of the LJ potential can be made by allowing the powers to assume any real value, adding two more parameter to the FF. Better choices of van der Waals potentials exist but since they have not been used in this work, we will not cover them here. More details can be found in [101, 209].

The nonbonded interactions must be summed over every unique pair of atoms in the system. For the LJ potential that means that parameters ε_{ij} and σ_{ij} (or $x_{ij}^{(0)}$) would have to be defined for each pair. To simplify this description, the interaction parameters for pairs of different atoms are obtained from same-atom parameters by

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) \quad (2.110)$$

or

$$x_{ij}^{(0)} = \frac{1}{2}(x_{ii}^{(0)} + x_{jj}^{(0)}) \quad (2.111)$$

and

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}. \quad (2.112)$$

This is called the Lorentz–Berthelot mixing rule. The reference or collision distance parameters are obtained by the arithmetic mean while the well depth are calculated from the geometric mean of the respective same-atom parameters.

In principle, the sum of the Coulomb and LJ contributions in Equation 2.107 and Equation 2.108 should run over all unique pairs of atoms in the system. However, two exceptions are often made. The first one is the use of a cutoff distance beyond which two particles will not interact via the nonbonded potential. Since the LJ potential falls quickly with distance, that is a reasonable choice that will greatly decrease computational cost for large systems and will introduce a very small error if properly setup. The Coulomb potential, however, is significant at a much larger range so that the introduction of a cutoff will either cause too much error or not be much effective unless the dimensions of the system are very large. The second exception is regarding bonded atoms at 1,2; 1,3; and 1,4 relative positions in a molecule. All nonbonded interactions for the first two cases are completely excluded in most force fields because their interactions are already set by the bond stretch and bond bend potentials. Moreover, they are often too close that the wrong form of the LJ repulsive part would cause large errors. For atoms at the 1,4 positions, that are at the extremities of a bond torsion configuration as we have seen above, the nonbonded interactions will affect the torsion potential. Thus, they are often excluded, damped, or set to special values.

BEFORE WE MOVE ON TO SOME specificities about the machinery of FFs in actual applications, a critical assessment of the choice of model discussed above is important. As we stressed multiple times, the simplifications and approximations made to the molecular physics FF methods are design to describe are extreme. Although there are much more complicated, new-generation FFs available, the CHARMM FF is one of the simplest models possible. The first simplifying assumption it makes, right at the outset in Equation 2.89, is that the combination of the various contributions to the total potential is additive, and the terms are all independent. In reality, there are coupling effects between all the contributions that are excluded from the description. A similar issue is the definition of the nonbonded interactions only as pairwise potentials. In reality, these are many-body interactions, ie, every particle in the system are affecting every nonbonded interaction. Treating that at the many-body level would require self-consistent iterations in every energy evaluation step. That would overwhelmingly increase the computational cost.

Fortunately, the large parameter space in a FF setup is enough to accommodate for most of the deviation with proper parametrisation. The consequence is that the potentials defined as above are actually effective potentials, and we should abandon the idea that the parameters have any ground in physical observable quantities. In such highly approximated FFs the parameters are nothing more than that—a set of constants we input to our model in order to obtain the best possible description of a set of properties we want. Thus, for any

serious MM/MD simulations we want to perform, extensive validation is necessary. We should, however, never expect that a set of parameter will describe as many feature of the system as we could. That is because any FF is highly underparametrised—and that is by design. Consider, for argument's sake, we want to describe the GS of the O₂ molecule. In the HF model with a double-zeta basis set—the minimum we need for a reasonable description—one would need a set of around 200 parameters. A MM description in the CHARMM model would take no more than five parameters (we are excluding the nuclear coordinates from both counts as they are equal in number). Therefore, validations should be carefully targetted and the scope of the simulations must be clearly delimited.

The task of parametrising and validating FF parameters for a given problem from scratch is daunting. In practice, however, one can take advantage of parameter transferability. From our chemical knowledge, both practical and theoretical, we know that molecular motifs will retain many of their properties an behaviour across various molecular environments. The central methylene group in propane is not much different from that on pentane, for example. At the degree of simplification of molecular FFs, various small differences arising from changes in the molecular environment will not actually be captured anyway. Therefore, a set of parameters previously validated in a certain context can be transferred for most other applications, sometimes only needing small additional adjustments. Validation should always follow. Most standard FF implementations will have a general database of validated parameters available to the users. The CHARMM general force field (CGenFF) [211–213] is one such example. Many of them will provide some automated engine to extract these parameters from previously parametrised molecules and apply to other simple organic molecules via *similarity match*. This process is sometimes called *parametrisation by analogy*. This is available for CHARMM via the CGenFF or via the SwissParam engine [214, 215]. This strategy is applied to the problem discussed in Chapter 4.

2.2.1.1 ATOM TYPES, GEOMETRY, AND TOPOLOGY

AS IT HAPPENS WITH QM calculations, in MM/MD we need to specify the initial geometry of the system to be simulated. This is done by specifying the *x*, *y*, and *z* Cartesian coordinates of each particle in the model. Not all carbons are the same, though. In QM calculations, we do not need to specify anything about any atoms based on their chemical environment. All will be taken into account when the wavefunction is determined. Here, since the properties of each atom in their particular environment is determined by specific parameters set by the user, we need some way of differentiating two atoms of the same nature but in different chemical settings. For example, the terminal carbon in a hydrocarbon chain is often different from that in the internal methylene groups. The distinction is possible with the concept of *atom types*. Besides specifying the element (which will then determine the atomic mass) and its coordinates, a sequence of letters is assigned to each unique type of atom. This atom type

will match the definitions in the files holding the FF parameters, so that they can be assigned unequivocally.

In most implementations, the geometry of the system together with atom types, serial numbers, partial charges, and element symbol is stored in a separate text file, often in the protein data bank (PDB) format. This file format allows for many other specifications important in the context of biochemistry, particularly for protein and DNA modelling, that we will not discuss here. More details can be found in [216, 217]. The FF parameters are stored in a separate file with each implementation having their own format. In the CHARMM format, the parameters for each contribution in Equation 2.89 is given in separate sections. For each section, a series of lines starts with a sequence of atom types for which parameters are defined (two for bond stretch, three for bond bend, four for bond torsion and improper dihedrals, and one for the atomic LJ parameters, often in the end) followed by the sequence of values for each pertinent constant in specified units. The values are space-separated.

Still another characteristic of the molecular system needs to be specified, namely, the connectivity between the atoms in a molecule, called the topology of the system. This is setup in yet another, less standard (software-specific) file. For software using the CHARMM FF, the protein structure file (PSF) format, complementary to the PDB file, is used. This file is separated in blocks that closely mirrors the sections in the force field parameters file. There is a section for each of the bond, bend angles, dihedral angles, improper dihedral angles, nonbonded exclusions, donor and acceptor atoms, and cross terms. Each section will hold a block of atom serial number sequences specifying the relationship between the atoms. The serial numbers must match those in the PDB file. Other definitions—some already defined in the PDB file—such as atom types, partial charges, and atomic masses are also included.

With these three types of files, a simulations is ready to be setup and run. Compared to QM calculations, where only the Cartesian coordinates of each nuclei need to be specified alongside the method selection, MM/MD simulations are much more complicated to initialise.

2.2.1.2 REACTIVE FORCE FIELDS

THE TYPES OF FFS DISCUSSED above, in particular the CHARMM FF, are designed to describe properties near the equilibrium geometry of molecular systems. Any significant deviation from a minimum energy structure will come with drastic errors and often unphysical effects. There is, however, one very important nonequilibrium effect we may want to describe in chemical systems: chemical reactions. For that, we need to devise a way to describe dissociation and formation of covalent bonds. With a harmonic potential for bond stretching (Equation 2.94), this is an impossible task. But we already know a better functional form that do allow for bond dissociation, namely, the Morse potential defined in Equation 2.90. Modifying the bond stretch potential in the CHARMM FF to a Morse potential is essentially what is behind

the definition of the reactive (or dissociative) CHARMM (rCHARMM) FF implemented in the MBN EXPLORER package [218].

Moving from an harmonic potential to a Morse potential in the CHARMM force field amounts to the addition of one extra parameter, the dissociation energy D , besides the original $r^{(0)}$ and k . The constant a in the exponent of the Morse potential is related to k and D by Equation 2.93.

As a bond is broken and the stretch potential between the atoms weakens, the torsion and dihedral angles may change to substantially larger values than the reference. Additionally, they must cease to exist between atoms that have been separated. The original harmonic bend potential in Equation 2.96 does not offer a good representation at large angles. rCHARMM substitutes it with the slightly better form

$$E_{ijk} = 2k_{ijk} \left[1 - \cos \left(\theta_{ijk} - \theta_{ijk}^{(0)} \right) \right], \quad (2.113)$$

where k_{ijk} is the same parameter in the original CHARMM set. The comparison of this new potential with the original is shown in Figure 2.3. The form of the dihedral or bond torsion potential is kept unchanged.

To allow the bend and torsion potentials to vanish as a bond is broken, a switching function is defined as

$$f(x_{ij}) = \frac{1}{2} \left\{ 1 - \tanh \left[\beta_{ij} \left(x_{ij} - x_{ij}'^{(0)} \right) \right] \right\}, \quad (2.114)$$

where

$$x_{ij}'^{(0)} = \frac{1}{2} \left(x_{ij}^{(0)} + x_{ij}^{\text{vdW}} \right). \quad (2.115)$$

x_{ij}^{vdW} is the van der Waals contact distance between the two atoms, defined as the sum of the standard atomic van der Waals radii, stored internally by the software. β_{ij} controls how sharply the function decays. The bend or torsion potential multiplied by this function is continuously and smoothly damped to zero as x_{ij} increases (see Figure 2.3). For each potential, there will be one of this function for each bonded atom pair. Thus, two and three switching functions multiply the bend and torsion potentials, respectively.

Besides the changes in functional form described above, a few other chemically relevant information must be supplied: a cutoff bond distance, beyond which the bond is considered broken, and is associated with the Morse bonded parameters for each bond; the valence of each reactive atom type; and the multiplicity of each type of bond that can be formed or broken. The algorithm will use the cutoff values to decide if a bond between two atoms exist or not at every time step of a dynamic simulation (see § 2.2.2). Every time a bond exceeds the cutoff, it is considered broken and the atoms are stored in a special list of active atoms, for which new bonds can be formed in subsequent steps. Bonds are formed every time atoms in this list come within a defined cutoff with another active atom, provided a bonded Morse

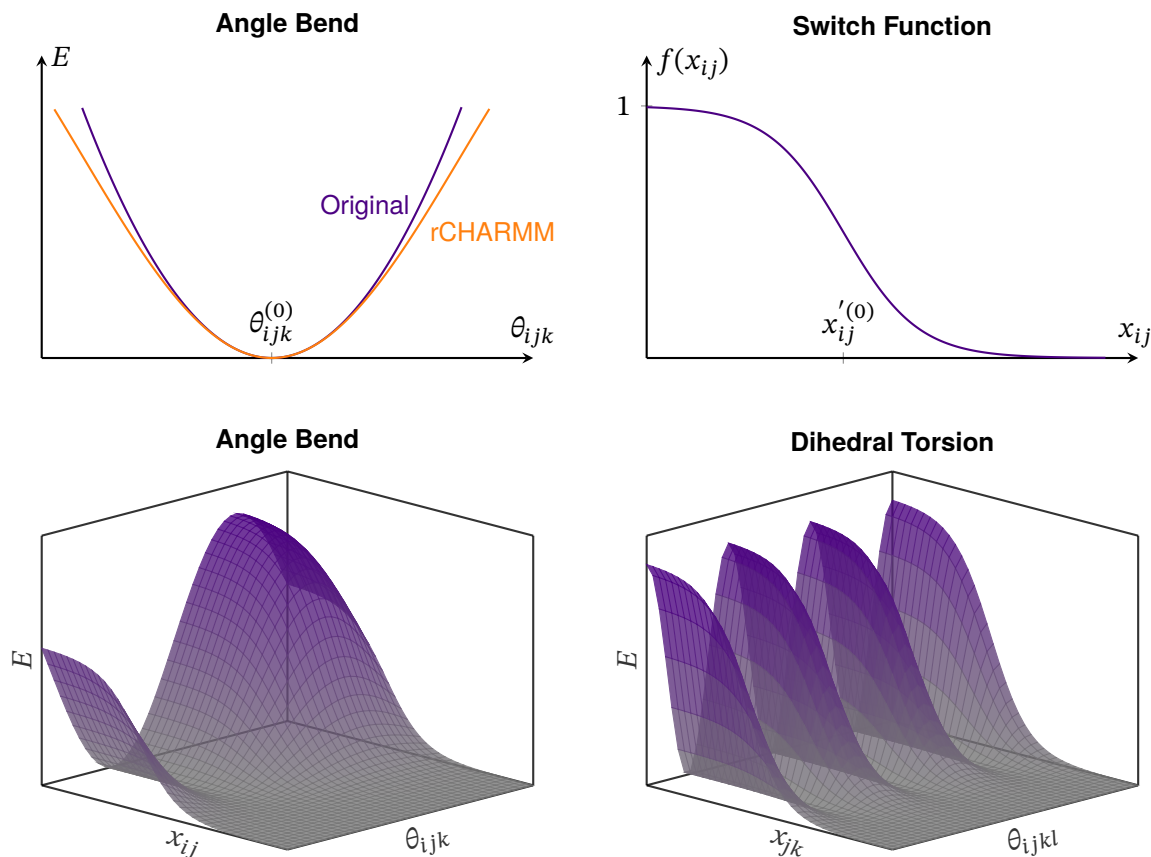


FIGURE 2.3 – Schematic representation of the modified potential energy terms in the rCHARMM force field.

potential for this atom pair is defined. If the full valence of any atom is reached after this process, the atom is removed from the special list of active atoms.

In the event of bond rupture or formation, the topology of the system must be updated accordingly, with changes on bond, bend, and dihedral relationships. The algorithm performs this action as needed at every time step. Additionally, redistribution of partial charges must also be done. The software allows for user-defined charge redistribution for each fragment that can be formed. However, if they are not defined by the user, an automatic algorithm is defined as follows. In the event of bond rupture, the total charge of each of the resulting fragment is rounded to the closest integer and the excess charge is redistributed evenly among all atoms of the fragments. If a new bond is formed, the charge is redistributed inside the newly created molecule in order to lower the values of partial charges. All this redistribution ensure that the total charge is conserved and that each fragment's or molecule's total charge is an integer multiple of the elementary charge.

The approach to reactive FF implemented in MBN EXPLORER is minimalist, in the sense that the fewest possible changes are introduced to a traditional MD setting. This is in line with the simplified form of FFs such as CHARMM. The advantage is that parametrisation of rCHARMM models is relatively simple, as discussed above, particularly when standard CHARMM parameters are available. The tradeoff is that complex chemistry may not be well described with such a minimal model. A counterexample worth mentioning is the highly sophisticated ReaxFF [219, 220]. This is an example of empirical bond-order potential, and is based on the concept of distance-dependent bond order. Although it is designed to describe highly complex chemistry, it also comes with a labour-intensive parametrisation process. The comparison of the rCHARMM to other options such as ReaxFF is desirable, but it has not been done so far. The strategy utilised in this work, nevertheless, has been proved successful for photodissociation processes [61, 221–226]. It is our aim to further put this framework to test with more complex molecules such as those discussed in Chapter 3.

2.2.1.3 BOUNDARY CONDITIONS AND COULOMB METHODS

THE DOMAIN OF SPACE WHERE any MM/MD simulation is defined must be limited. In other word, there should always be boundaries surrounding the system. The enclosing of the domain is called the simulation box. Although various box shapes exist in different packages, the most commonly utilised is a right rectangular prism or rectangular box, for simplicity. That is the only shape available in MBN EXPLORER, so we will limit our discussion to that case.

Once a simulation box is defined, one needs to decide what boundary conditions to apply. There are three possible choices. (1) The simplest is an *absorbing* or *open boundary condition*. If any of a particle's coordinate exceeds one of the boundary limits (the particle crosses one of the faces of the box), the particle is excluded from the simulation or the simulation ends with an error. This type of boundary condition is almost never used because conservation of particle number (conservation of matter) is violated, and it is not allowed in MBN EXPLORER. (2) The other intuitive option is to make the box behave like a proper container by using a *reflective boundary condition*. In this case, once a particle reaches one of the walls, the coordinate of its momentum perpendicular to the wall changes sign, and the particle is elastically reflected. (3) There are many cases in which we do not want the system to suffer the influence of boundaries and we do not want it to have surfaces either (eg, when simulating the bulk of a material or a crystal). In that case, a *periodic boundary condition* (PBC) is available. By setting PBC we are essentially making the system infinite by creating an infinite number of adjacent copies of the boxes and filling those copies with the exact contents of the original box. The copies of the original box and their copied contents are called images of the system (see Figure 2.4). Every time a particle exits the original box through a wall, it enters the adjacent image box while its copy from the diametrically opposite

image box enters the original box with the same momentum. We will focus in more details of PBC as this was utilised in the work discussed in Chapter 4.

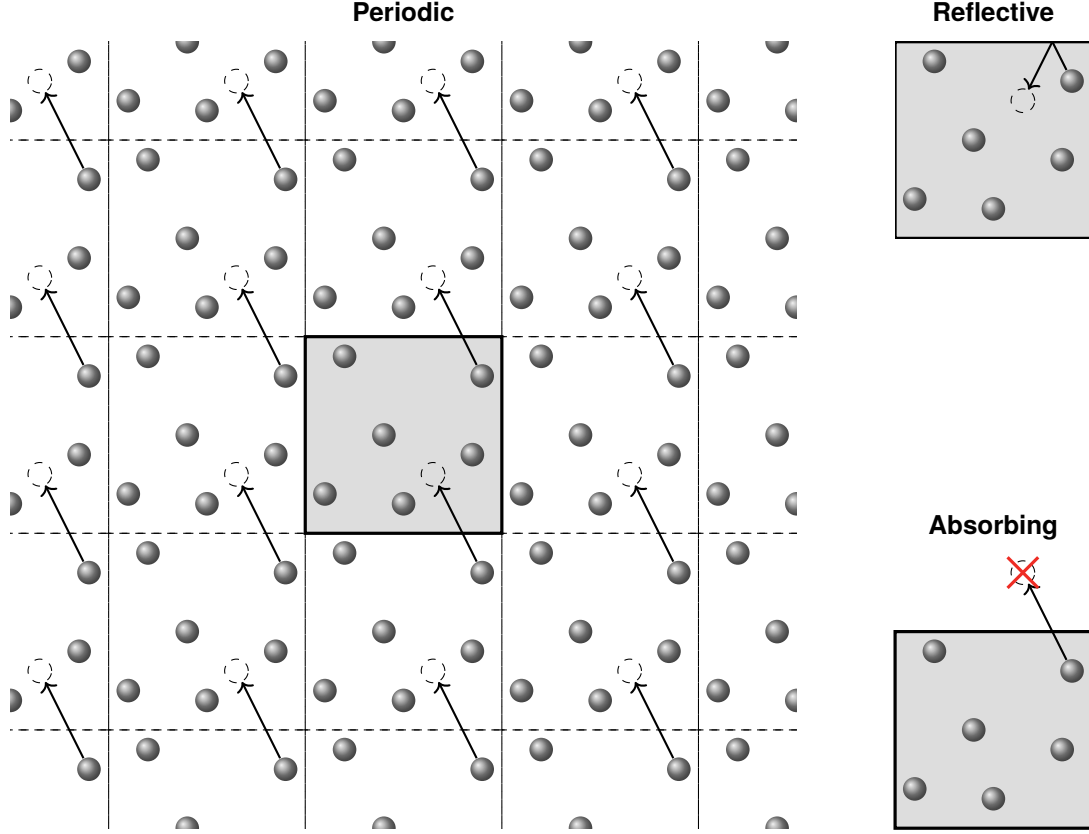


FIGURE 2.4 – Two-dimensional representation of simulation boxes and boundary conditions.

In the case of a rectangular box, the original simulation box is positioned so that each of its edges are parallel to one of the Cartesian axes. The origin of the coordinate system can be set anywhere, but it is conventionally put at the centre of the box. The position of any particle i inside the original box is indicated by the vector $\mathbf{x}_i$. When using PBC, we also define the box or lattice vector

$$\mathbf{n} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 = (n_1, n_2, n_3), \quad (2.116)$$

where $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are the three generic linear independent (but not necessarily orthogonal) lattice vectors defining a cell.¹⁷ In the special case of a rectangular box, $\mathbf{a}_1 = L_x \hat{\mathbf{i}}$, $\mathbf{a}_2 = L_y \hat{\mathbf{j}}$, $\mathbf{a}_3 = L_z \hat{\mathbf{k}}$, and we define

$$\mathbf{n} = n_x L_x \hat{\mathbf{i}} + n_y L_y \hat{\mathbf{j}} + n_z L_z \hat{\mathbf{k}} = (n_x, n_y, n_z), \quad (2.117)$$

¹⁷This general notation comes from the crystallography field, where the lattice vectors are defined for a crystal unit cell that can assume various different shapes depending on the particular translational symmetry of a crystal and its dimensions.

where $\hat{\mathbf{i}}$, $\hat{\mathbf{j}}$, and $\hat{\mathbf{k}}$ are the unit Cartesian vectors along the x , y , and z directions, respectively; L_x , L_y , and L_z are the length of the box edges along each of the Cartesian directions; and n_x , n_y , and n_z are integers. With this definition, we can locate any image box by using integer coordinates. For instance, the second image box along the positive x -axis from the primitive box is $(2, 0, 0)$. The coordinate of the image of a particle i in a box designated by a vector $\mathbf{n}$ is simply $\mathbf{x}_i + \mathbf{n}$.

It is convenient to define the *reciprocal space vector* $\mathbf{m} = m_1 \mathbf{a}_1^* + m_2 \mathbf{a}_2^* + m_3 \mathbf{a}_3^*$ such that

$$\mathbf{a}_1^* = \frac{\mathbf{a}_2 \times \mathbf{a}_3}{V}, \quad (2.118)$$

$$\mathbf{a}_2^* = \frac{\mathbf{a}_3 \times \mathbf{a}_1}{V}, \quad (2.119)$$

$$\mathbf{a}_3^* = \frac{\mathbf{a}_1 \times \mathbf{a}_2}{V}, \quad (2.120)$$

where V is the volume of the lattice cell. In a rectangular box cell, these relationships become

$$\mathbf{a}_1^* = \frac{(L_y \hat{\mathbf{j}}) \times (L_z \hat{\mathbf{k}})}{L_x L_y L_z} = \frac{1}{L_x} \hat{\mathbf{i}}, \quad (2.121)$$

$$\mathbf{a}_2^* = \frac{(L_z \hat{\mathbf{k}}) \times (L_x \hat{\mathbf{i}})}{L_x L_y L_z} = \frac{1}{L_y} \hat{\mathbf{j}}, \quad (2.122)$$

$$\mathbf{a}_3^* = \frac{(L_x \hat{\mathbf{i}}) \times (L_y \hat{\mathbf{j}})}{L_x L_y L_z} = \frac{1}{L_z} \hat{\mathbf{k}}, \quad (2.123)$$

and we can write

$$\mathbf{m} = m_x \frac{1}{L_x} \hat{\mathbf{i}} + m_y \frac{1}{L_y} \hat{\mathbf{j}} + m_z \frac{1}{L_z} \hat{\mathbf{k}} = (m_x, m_y, m_z). \quad (2.124)$$

With this definition, it should be clear why we call them reciprocal space vectors. In the rectangular case, each of these vectors is aligned with a corresponding real space vector and scaled by the reciprocal of its size. Another important property is that, for any pair of real and reciprocal vectors, $\mathbf{a}_i \cdot \mathbf{a}_j^* = \delta_{ij}$.¹⁸ These vectors will be of central importance because any function periodic on the real-space lattice can be expanded in a Fourier series indexed by the reciprocal lattice vectors. In this sense, reciprocal space is the Fourier dual of real space.

THE MOST COSTLY COMPUTATION in a MM/MD simulation is the calculation of the long-range nonbonded interactions. In the case of the CHARMM or other simple FFs, these are simply the Coulomb interactions since the LJ potential is short-range and can be limited by the use of a

¹⁸ In physics texts, it is usual to include a factor of 2π in the definition of these vectors, in which case the relation would be $\mathbf{a}_i \cdot \mathbf{a}_j^* = 2\pi \delta_{ij}$. This is done to simplify subsequent algebra when using the Fourier transform (see n 21 and the discussion below when we derive the Ewald summation method).

cutoff distance with negligible error if properly set. The Coulomb interactions, on the other hand, decreases as $1/x$ and, therefore, will be substantial even at distances larger than the dimensions of typical simulation boxes. When using PBC, the Coulomb interactions should in principle span the infinite number of image boxes. In this setting, the total interaction energy can be written as

$$E^{\text{Coulomb}} = \frac{1}{2} \sum'_{\mathbf{n}} \sum_{i=1}^N \sum_{j=1}^N \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{|\mathbf{x}_{ij} + \mathbf{n}|}, \quad (2.125)$$

where the prime in the first summation indicates that the interaction should not be computed when $i = j$ in the original box ($\mathbf{n} = 0$).¹⁹

The expression in Equation 2.125 is complicated for two main reasons: its convergence is very slow because of the form of the potential and, because of the arrangement of periodic boxes, its convergence is conditional, meaning that it only steadily approaches a constant values if the summation is carried out in a particular order (see [227] for a full demonstration of this fact). Therefore, it is not clear where the sum should be truncated.

Using PBC with any system containing a charge distribution interacting via a Coulomb potential would be impossible if the Ewald summation method, devised by Paul Peter Ewald around the 1920s in the context of X-ray crystallography, did not exist [228]. The method is quite involved mathematically. Nevertheless, we will provide a sketch of it below, accompanied by references to sources that offer a rigorous treatment for the interested reader.

For this method, we model the system of point charges as an infinite spherical array of periodic images (Figure 2.5). The spherical choice is made because of the radial symmetry of the potential. This means that the boundary of the system is the surface of an infinite sphere. There are two key ideas in the Ewald method. The most powerful one is the interplay between Gaussian functions in the real and in the reciprocal space or, equivalently, a Gaussian and its Fourier transform. Figure 2.5 shows the shape of a Gaussian function and its corresponding Fourier transform. The important fact is that the Fourier transform of a Gaussian is another, narrower Gaussian. More precisely, if we have a Gaussian

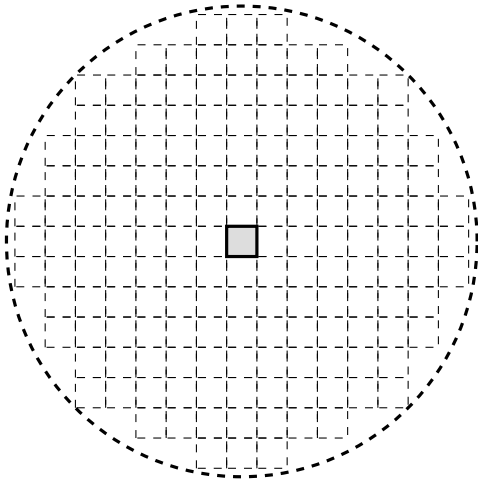
$$g(r) = e^{\frac{-x^2}{2\sigma^2}} \quad (2.126)$$

with the standard deviation (which defines its width) σ , its Fourier transform

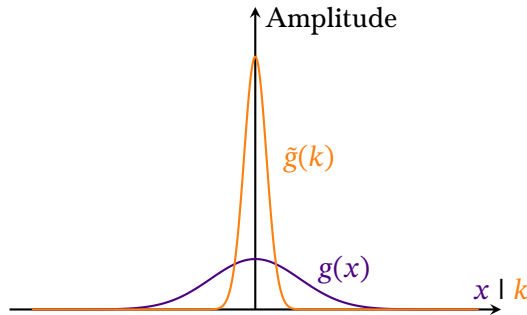
$$\tilde{g}(k) = \int_{-\infty}^{\infty} e^{\frac{-x^2}{2\sigma^2}} e^{-ikx} dx = \sqrt{2\pi\sigma} e^{\frac{-\sigma^2 k^2}{2}} \quad (2.127)$$

¹⁹Note that here we used a slightly different notation than in Equation 2.107 to exclude the double count that summing over all i, j pairs causes. There, the case $i = j$ is naturally excluded. The current notation halves the total interaction instead.

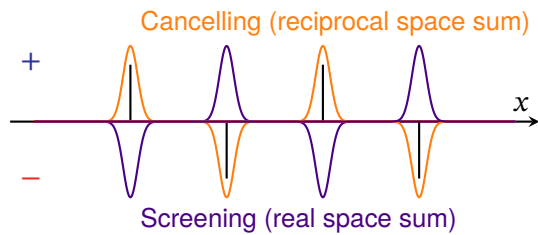
Infinite Spherical Array of Periodic Cells



A Gaussian and its Fourier Transform



Ewald Charge Distribution



Error and Complementary Error Functions

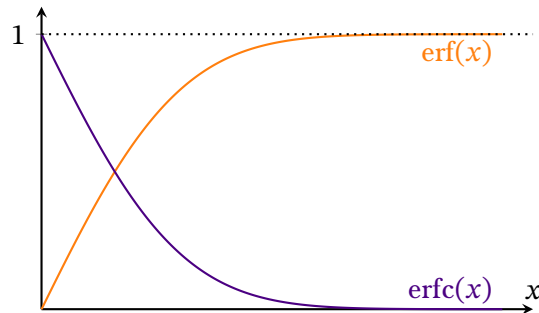


FIGURE 2.5 – Illustrations of various elements in the Ewald summation method. Vertical bars in the charge distribution represent the original point charges. Axes cross at (0,0).

will be a Gaussian with standard deviation $1/\sigma$. That means that the broader the original Gaussian, the smaller the interval $-a \leq k \leq a$ inside which $\tilde{g}(k) > \varepsilon$ for a given cutoff ε . This holds for Gaussians of any dimensions. The significance of this will become clearer soon.

The second key idea of the Ewald method is that we can use a Gaussian charge distribution of opposite sign centred at the position of each point charge in our system to screen it. Each pair point charge–Gaussian charge is then neutral, and therefore the electric field beyond a certain distance of this combination is essentially zero. The more compact the Gaussian, the closer to the point charge the field will become negligible. The result is that the potential of this combination is close-ranged. Now let us put these ideas together.

We know now that we can use the device of Gaussian charge distributions of opposite sign to screen the charges in our system and therefore make the effective field short-ranged. But adding these charges change our system, and we need to compensate this addition with another distribution that exactly cancels it out if we want to have the correct result for the original system. Therefore, for each screening Gaussian we add another one at exactly the same position with opposite sign. This construction is illustrated for the one-dimensional

case in Figure 2.5. We define the Gaussian charge distribution surrounding a charge q_i at the origin²⁰ as

$$\rho_i^G(\mathbf{x}) = -q_i \frac{\alpha^3}{\pi^{3/2}} e^{-\alpha^2 x^2}, \quad (2.128)$$

where α is the screening factor, and is related to the standard deviation as defined in Equation 2.126 by $\alpha = 1/\sqrt{2}\sigma$. The Gaussian above is three-dimensional.

The electrostatic potential generated by a screening charge distribution $\rho_i^G(x)$ as defined in Equation 2.128 is obtained by solving the Poisson equation (Equation 2.101). The solution is (see [227] for a rigorous derivation)

$$\Phi_i^G(x) = -\frac{q_i}{x} \text{erf}(\alpha x). \quad (2.129)$$

$\text{erf}(x)$ is the error function, given by the partial integration of the three-dimensional Gaussian charge distribution from 0 to x in spherical coordinates, in which the angular contributions are integrated out to a constant factor. Now, the resulting potential caused by the screening Gaussian and its corresponding point charge is given by

$$\Phi_i^{Gq}(x) = \frac{q_i}{x} - \frac{q_i}{x} \text{erf}(\alpha x) = \frac{q_i}{x} [1 - \text{erf}(\alpha x)] = \frac{q_i}{x} \text{erfc}(\alpha x), \quad (2.130)$$

where $\text{erfc}(x) = 1 - \text{erf}(x)$ is the complementary error function. Here a very important property must be noticed. The narrower the screening Gaussian (larger α), the faster $\text{erf}(\alpha x)$ integrates to unity (since the original Gaussian is normalised to unity). Therefore, the faster $\text{erfc}(\alpha x)$, and thus $\Phi_i^{Gq}(x)$, approach zero (see the plots of the $\text{erfc}(x)$ and $\text{erf}(x)$ functions in Figure 2.5). By controlling the width of the screening Gaussian, we control how close-ranged the potential is.

Once we have the potential of the combination above, we can compute the full potential energy of our system of charges (as in Equation 2.125) by summing over all pairwise interactions over the original box and the infinite set of all periodic images. The result is

$$E^{\text{real}} = \frac{1}{2} \sum_{\mathbf{n}}' \sum_{i=1}^N \sum_{j=1}^N \frac{q_i q_j}{|\mathbf{x}_{ij} + \mathbf{n}|} \frac{1}{4\pi\epsilon_0} \text{erf}(\alpha |\mathbf{x}_{ij} + \mathbf{n}|). \quad (2.131)$$

For the same reason discussed above, interactions between particles beyond a certain distance from each other, ie, for large values of $|\mathbf{x}_{ij} + \mathbf{n}|$, the magnitude of the terms in the sum above becomes negligible. The series converge steadily and absolutely as a consequence of this homogenous and fast decay. How fast the series will converge depends on the value of α —the larger it is (the narrower the Gaussian), the faster.

²⁰If the charge is not at the origin, $\mathbf{x}$ must be substituted by $\mathbf{x} - \mathbf{x}_i$.

Now we need the second part of the system, ie, the potential generated by the compensating Gaussian distribution that cancels out our artificial screening addition. If we calculate the potential generated by them from Equation 2.129 as we did for the combination of Gaussian and point charge from Equation 2.130, the result is

$$\bar{E}^{\text{real}} = \frac{1}{2} \sum'_{\mathbf{n}} \sum_{i=1}^N \sum_{j=1}^N \frac{q_i q_j}{|\mathbf{x}_{ij} + \mathbf{n}|} \frac{1}{4\pi\epsilon_0} \text{erf}(\alpha|\mathbf{x}_{ij} + \mathbf{n}|), \quad (2.132)$$

where we used a bar over E to denote the complementary charge distribution. Notice the symmetry: Equation 2.132 is the same as Equation 2.131 with $\text{erf}(\alpha|\mathbf{x}_{ij} + \mathbf{n}|)$ in place of $\text{erfc}(\alpha|\mathbf{x}_{ij} + \mathbf{n}|)$. But now that is a problem because $\text{erf}(x)$ has the opposite behaviour of $\text{erfc}(x)$, ie, it grows to 1 as x increases (see Figure 2.5) and therefore $\bar{E}^{\text{real}}$ decays as $1/x_{ij}$ as soon as E^{real} becomes negligible. What we achieved was essentially a separation of the short- and long-range parts of the Coulomb interaction into two terms. Thus, it seems like we are only pushing the original problem elsewhere.

Well, not quite. The final solution comes from performing the sum in Equation 2.132 in reciprocal space. To do so, we can either apply the Poisson summation formula to obtain the Fourier transform coefficients or Fourier transform the original charge density in Equation 2.129 and solve the Poisson equation (Equation 2.101) in reciprocal space (see [227]). Either way, we arrive at²¹

$$E^{\text{reciprocal}} = \frac{1}{2} \sum_{\mathbf{m} \neq 0} \sum_{i=1}^N \sum_{j=1}^N \frac{1}{2\pi V} \frac{q_i q_j}{4\pi\epsilon_0} \frac{4\pi^2}{m^2} e^{-\frac{\pi^2 m^2}{\alpha^2}} \cos(2\pi \mathbf{m} \cdot \mathbf{x}_{ij}), \quad (2.133)$$

where V is the volume of the simulation box (or lattice cell) and $\mathbf{m}$ is the reciprocal vector as defined in Equation 2.124. Each factor in the summation now decreases exponentially with m^2 since the Gaussian term $e^{-\frac{\pi^2 m^2}{\alpha^2}}$ dominates, and the terms become negligible beyond a certain value of m . Similarly to Equation 2.131, this reciprocal-space series also converges absolutely and fast.

Now recall the property of the Fourier transform of the Gaussian distribution discussed above. The original distribution with screening factor α in the numerator of the exponent was translated into another Gaussian with α in the denominator. The broader the real-space Gaussian, the narrower the reciprocal space counterpart. The convergence of Equation 2.133 is faster the smaller the value of α , which is the opposite of what happens to the convergence of Equation 2.131. Therefore, one must chose the value of α so that a balance between the computational expense in real space and in reciprocal space is reached.²² Real and reciprocal

²¹ Notice the appearance of 2π factors. When defining the reciprocal lattice vectors above, we noted (see n 18) that this factor is added to the definition of the vector itself in the physics notation. This makes for visually cleaner equations in electrostatics but is a weird introduction when defining $\mathbf{m}$ without the physics context.

²² That is why one could not have simply computed the Coulomb summation in Equation 2.125 in reciprocal space as a solution to the convergence problem. Looking at how we solved the problem of Equation 2.132 still

cutoff values for x_{ij} and m , respectively, are also chosen to define where the summations in Equation 2.131 and Equation 2.133 are truncated.

The total potential energy of our construction still needs small corrections. In the reciprocal-space sum in Equation 2.133 there is a self-interaction term between the Gaussians that must be removed by subtracting

$$E^{\text{self}} = -\frac{\alpha}{\sqrt{\pi}} \sum_{i=1}^N \frac{q_i^2}{4\pi\epsilon_0}. \quad (2.134)$$

We recall that the system's boundary is the surface of an infinite sphere, which must be considered explicitly. This is the $\mathbf{m} = \mathbf{0}$ term excluded from Equation 2.133. The consequence is yet another correction of the form

$$E^{\text{boundary}} = -\frac{2\pi}{V} \frac{1}{2\epsilon_b + 1} \left| \sum_{i=1}^N q_i \mathbf{x}_i \right|^2, \quad (2.135)$$

where ϵ_b is the permittivity of the external medium. The term above computes the effect of the total dipole moment of the charge distribution. If the system is surrounded by a perfect conductor (a medium of infinite permittivity), we are at the thin foil boundary condition, and the correction term vanishes. This term is only well defined for a neutral system because for charged systems the dipole moment depends on the choice of origin. Therefore, Ewald summations are almost always restricted to neutral systems. The final potential energy is given by

$$\begin{aligned} E^{\text{Ewald}} = & \frac{1}{2} \sum_{\mathbf{n}}' \sum_{i=1}^N \sum_{j=1}^N \frac{q_i q_j}{|\mathbf{x}_{ij} + \mathbf{n}|} \frac{1}{4\pi\epsilon_0} \text{erfc}(\alpha|\mathbf{x}_{ij} + \mathbf{n}|) \\ & + \frac{1}{2} \sum_{\mathbf{m} \neq \mathbf{0}} \sum_{i=1}^N \sum_{j=1}^N \frac{1}{2\pi V} \frac{q_i q_j}{4\pi\epsilon_0} \frac{4\pi^2}{m^2} e^{-\frac{\pi^2 m^2}{\alpha^2}} \cos(2\pi \mathbf{m} \cdot \mathbf{x}_{ij}) \\ & - \frac{\alpha}{\sqrt{\pi}} \sum_{i=1}^N \frac{q_i^2}{4\pi\epsilon_0} \\ & + \frac{2\pi}{V} \frac{1}{2\epsilon_b + 1} \left| \sum_{i=1}^N q_i \mathbf{x}_i \right|^2. \end{aligned} \quad (2.136)$$

THE EWALD SUMMATION METHOD makes an impossible task possible, but it is still very costly. The real-space summation scales as $O(N)$ but the reciprocal-space part, usually the largest, scales with $O(N^{3/2})$. Fortunately, there are improved numerical algorithms that allow the latter to be evaluated at a better scaling. They are called particle-mesh methods, and

being slowly and conditionally convergent by Fourier transforming it, some could wonder why not do it from the beginning. But a point charge is like an infinitely narrow Gaussian function (in fact, a Dirac delta distribution), ie, $\alpha \rightarrow \infty$. This results in the exponential part of Equation 2.133 becoming unit and the series diverging.

leverage on the $O(N \log N)$ scaling of the fast Fourier transform (FFT) algorithm. This is a powerful and ubiquitous numerical implementation to efficiently calculate Fourier coefficients for the expansion of a set of discrete data points in Fourier components, a procedure called discrete Fourier transform.²³ To apply such technique, however, the charge distributions in the system must be discretised in a regular grid of data points. In a nutshell, the strategy consists in (1) interpolating each point charge in the system onto a predefined regular grid, (2) computing the FFT of this discrete data to obtain the Fourier transform of the charge density, (3) calculating the potential generated by this density in reciprocal space, (4) computing the FFT transform of the potential back to real space, and (5) interpolating back the forces to the positions of the original point charges. The dominating step in terms of computational cost is the FFT evaluations and, therefore, the whole procedure scales as $O(N \log N)$, which for large N is approximately linear.

There are three main implementations of particle-mesh methods. The oldest and original method is the particle-particle particle-mesh Ewald (P₃ME), originally derived for the analogous case of gravitational interactions [229, 230]. This method retains some of the close-range point-charge interactions to be calculated as in the original Ewald method (the particle-particle part), which improves the accuracy at close range. Another method does the full calculation of the so called structural factor (the $q_i q_j \cos(2\pi \mathbf{m} \cdot \mathbf{x}_{ij})$ part in Equation 2.133) on the interpolated grid while the $\mathbf{m}$ vector summations is done directly. This is the particle-mesh Ewald (PME) method [231]. An improvement on that, the smooth PME (SPME), uses special functions called cardinal B-splines to perform the grid interpolation (step (1) above) instead of the Lagrange interpolations used in the PME method [232]. This allows for smooth, continuous and analytical derivatives in the calculation of the forces (step 5 above). This is the method implemented in MBN EXPLORER and in the majority of modern codes. Comparisons between these methods can be found in [233, 234]. The best reference to understand them is [230].

2.2.2 MOLECULAR DYNAMICS ALGORITHMS

SO FAR WE HAVE ONLY discussed strategies to model the potentials in a molecular system and how to define it in terms of geometry, topology, and boundaries. Now we want to allow the system to evolve in time subject to these potentials, ie, we need to make our model dynamical. Since we are in a purely classical theory of point-like objects, the suitable dynamic theory is the classical Newtonian mechanics. The equation of motion describing the time

²³There are two unfortunate things in this name. The first is that there is a contradiction in terms since a transform is a generalisation of a discrete series expansion to the continuous case, and therefore discretising it is simply going back to the series expansion case. The second is that the acronym for the technique is DFT, which can be confused with density functional theory (§ 2.1.2). Fortunately, we will not have to define this acronym here as we will not be discussing this Fourier technique any further.

evolution of each particle i in our model is Newton's second law

$$\mathbf{F}_i = \frac{d\mathbf{p}_i}{dt} = m_i \frac{d^2\mathbf{x}_i}{dt^2}, \quad (2.137)$$

where $\mathbf{F}_i$ is the net force acting on particle i , and $\mathbf{p}_i$ and m_i are the particle's linear momentum and mass, respectively.

For a many-body systems of particles with long range interactions, the solution of all coupled equations of motion cannot be solved analytically. Therefore, “numerical integration” methods must be used. In MD this is routinely done by *finite difference methods*. The core idea is to discretise the particle's trajectory in small intervals of time Δt which will sum up to the total simulation time τ . Δt is the simulation time-step. At any time t , the net force acting on each particle is determined through the gradient of each FF potential acting on them. From the position of the particle and the force at time t , Equation 2.137 is used to calculate its new position and velocity at time $t + \Delta t$. The forces are constant during each interval (a linear approximation). The new configuration of the system is then used to start the next propagation of the trajectory.

A series of algorithms for time-step integration is available. Good introductory discussions on many of them can be found in [235, 236]. The modern general framework to develop numerical integrators for classical dynamics is to employ the classical Liouville operator—similar to the quantum version discussed briefly in § 2.1.4.3 (Equation 2.87)—from which a factorisation of an exponential time propagator (Trotter-Suzuki factorisation) is built. This approach is well covered in [237]. A particular application of this procedure that yields modern robust methods is the reference system propagator algorithms by Tuckerman, Berne & Martyna [238]. The class of algorithms available in MBN EXPLORER are variations of the pioneering *Störmer–Verlet integrator* [239, 240]: the *velocity Verlet* [241] and the *leapfrog* [230] methods. They can all be derived by the Liouville operator strategy and can be shown to yield equivalent trajectories. We briefly discuss them.

It is usual to start the derivation of the Verlet equations by expanding the position of a particle at one backward and one forward time-step in a discretised Taylor series around t ,

$$\mathbf{x}_i(t + \Delta t) = \mathbf{x}_i(t) + \dot{\mathbf{x}}_i(t)\Delta t + \frac{1}{2!}\ddot{\mathbf{x}}_i(t)\Delta t^2 + \frac{1}{3!}\ddot{\mathbf{x}}_i(t)\Delta t^3 + O(\Delta t^4) \quad (2.138)$$

and

$$\mathbf{x}_i(t - \Delta t) = \mathbf{x}_i(t) - \dot{\mathbf{x}}_i(t)\Delta t + \frac{1}{2!}\ddot{\mathbf{x}}_i(t)\Delta t^2 - \frac{1}{3!}\ddot{\mathbf{x}}_i(t)\Delta t^3 + O(\Delta t^4). \quad (2.139)$$

Here we use the dot notation for time derivatives to simplify the equations and Bachmann–Landau big O notation to indicate the order of approximation error in truncating the series.

Summing the two equations above and using Equation 2.137 we obtain

$$\mathbf{x}_i(t + \Delta t) = 2\mathbf{x}_i(t) - \mathbf{x}_i(t - \Delta t) + \frac{\mathbf{F}_i(t)}{m_i} \Delta t^2 + O(\Delta t^4). \quad (2.140)$$

The velocity $\dot{\mathbf{x}}(t)$ is not explicitly included in the equation of motion, but can be estimated by interpolation using

$$\dot{\mathbf{x}}(t) = \frac{\mathbf{x}_i(t + \Delta t) - \mathbf{x}_i(t - \Delta t)}{2\Delta t} + O(\Delta t^2). \quad (2.141)$$

For the trajectory propagation using the Verlet algorithm, the positions of the particle must be stored at two time-steps $t - \Delta t$ and t . At each step, the newly obtained positions at $t - \Delta t$ become those at t for the next step. The positions at $t - \Delta t$ are discarded and replaced by those previously at t . Estimated velocities can be recorded if needed, but the exactness is $O(\Delta t^2)$, lower than that for the positions. Another problem of the Verlet algorithm is that information of positions at $t - \Delta t$ is not available at the beginning of a simulation and must be obtained by extrapolation. A variation on the original Verlet is the leapfrog algorithm that explicitly utilises the velocities in the propagation. The idea is to obtain the velocities at half time-steps by

$$\dot{\mathbf{x}}_i\left(t + \frac{1}{2}\Delta t\right) = \dot{\mathbf{x}}_i\left(t - \frac{1}{2}\Delta t\right) + \frac{\mathbf{F}_i(t)}{m_i} \Delta t \quad (2.142)$$

and the positions at integer time-steps by

$$\mathbf{x}_i(t + \Delta t) = \mathbf{x}_i(t) + \dot{\mathbf{x}}_i\left(t + \frac{1}{2}\Delta t\right) \Delta t. \quad (2.143)$$

Therefore, calculation of velocities leapfrogs over positions. If the initial velocity is calculated as $\dot{\mathbf{x}}_i\left(t - \frac{1}{2}\Delta t\right) = [\mathbf{x}_i(t) - \mathbf{x}_i(t - \Delta t)]/\Delta t$, the leapfrog algorithm yields the exact same trajectories as the Verlet, with the same $O(\Delta t^4)$ precision on the positions. As the Verlet algorithm, leapfrog needs to store two arrays of data for each step: one set of velocities and one set of positions. The slight advantage of this method is the explicit calculation of velocities during the propagation, instead of an estimation from positions in retrospect. Besides that, there is no need to extrapolate the position at a previous point at the beginning of the simulation. Only a direct calculation of velocities half a step backwards is needed, and can be obtained by

$$\dot{\mathbf{x}}_i\left(t - \frac{1}{2}\Delta t\right) = \dot{\mathbf{x}}_i(0) - \frac{\mathbf{F}_i(0)}{m_i} \Delta t. \quad (2.144)$$

The problem with the leapfrog approach is the asynchronous calculation of position and velocity. Although one can resort to interpolation (as in Equation 2.141), this is an extra calculation with only $O(\Delta t^2)$ precision. This can be a problem if one needs to calculate velocity-dependent properties accurately and at the same point in time as the positions. This

is the case when thermostats are used (see below), for instance. The velocity Verlet algorithm overcomes this problem. Since in this work the use of a thermostat is essential, this is the integration algorithm of choice. At time t , velocities at the next step are calculated by

$$\dot{\mathbf{x}}_i(t + \Delta t) = \dot{\mathbf{x}}_i(t) + \frac{1}{2m_i} [\mathbf{F}_i(t) + \mathbf{F}_i(t + \Delta t)] \Delta t + O(\Delta t^4) \quad (2.145)$$

and positions by

$$\mathbf{x}_i(t + \Delta t) = \mathbf{x}_i(t) + \dot{\mathbf{x}}_i(t) \Delta t + \frac{1}{2} \frac{\mathbf{F}_i(t)}{m_i} \Delta t^2 + O(\Delta t^3). \quad (2.146)$$

In the initial step ($t = 0$), the positions at $t + \Delta t$ are calculated according to Equation 2.146 using the initial velocities and forces. Then, velocities at half-time step are calculated by

$$\dot{\mathbf{x}}_i\left(t + \frac{1}{2}\Delta t\right) = \dot{\mathbf{x}}_i(t) + \frac{1}{2} \frac{\mathbf{F}_i(t)}{m_i} \Delta t \quad (2.147)$$

and new forces are then calculated from the current position at $t + \Delta t$ to yield accelerations at $t + \Delta t$. In the final step, velocities at $t + \Delta t$ are obtained by

$$\dot{\mathbf{x}}_i\left(t + \frac{1}{2}\Delta t\right) = \dot{\mathbf{x}}_i(t + \Delta t) + \frac{1}{2} \frac{\mathbf{F}_i(t + \Delta t)}{m_i} \Delta t \quad (2.148)$$

This algorithm needs to store one set each of positions, velocities and forces at any time-step evaluation.²⁴ Globally, all these methods have $O(\Delta t^2)$ precision in both positions and velocities. The global precision is of more importance than the higher, local precision for most of the quantitative analyses one would wish to perform.

2.2.2.1 GEOMETRY OPTIMISATION METHODS

WE HAVE ALREADY DISCUSSED the importance of geometry optimisation procedures in molecular simulations in the context of QM methods (see p 17). Here it is not different, and with such simplified FF as CHARMM that lean heavily on the assumption of near-equilibrium geometry, this is even more critical. To restate the problem, we are interested in minimising the total potential energy of the system of particles (governed by the FF potentials) as a function of the $3N$ Cartesian coordinates. There is no general method that guarantees that such procedure will lead to the global minimum, but often we are interested in the nearest local minimum from a given initial configuration. For that task, there is a plethora of algorithms. MBN EXPLORER offers two possibilities: *velocity quenching* and *conjugate gradients*.

²⁴The description of the velocity Verlet algorithm implemented in MBN EXPLORER and given in [82] states the initial steps where velocities are computed at $t + \frac{1}{2}\Delta t$ (Equation 2.147) and then another computation that yields $\dot{\mathbf{x}}_i(t + \Delta t)$ (Equations 30 and 33 in the paper). This procedure is then said to be repeated for every time-step propagation. The two equations amounts to Equation 2.145. If the algorithm actually performs this calculation in two steps every time is unclear, but the final result is equivalent to the original implementation.

The simplest of these is velocity quenching [242]. The geometry optimisation procedure, being usually a nondynamic process, pertains to the realm of MM methods (see n 14). However, this method in particular rely on the velocity Verlet algorithm to find local minima and therefore is a dynamic type of optimisation algorithm. The idea is remarkably simple. By conservation of energy, at any moment in time, the sum of potential and kinetic energies of the system is a constant. Therefore, the variation of these quantities during an interval Δt is related by

$$\Delta E(\mathbf{x}, t) = E(\mathbf{x}, t + \Delta t) - E(\mathbf{x}, t) = -K(\mathbf{x}, t + \Delta t) + K(\mathbf{x}, t) = -\Delta K(\mathbf{x}, t), \quad (2.149)$$

where $\mathbf{x}$ is the collective Cartesian vector positions of the particles and K is the total kinetic energy of the system. Since we want to reach a minimum energy, we want the force to be reduced. By Equation 2.149, $\Delta F < 0 \iff \Delta K > 0$. The algorithm thus consists on running a regular MD simulation and monitoring the particles' velocities at each time-step. If $\dot{\mathbf{x}}_i(t) \leq \dot{\mathbf{x}}_i(t - \Delta t)$, $\dot{\mathbf{x}}_i$ is set to 0. This will stop the particles near or at the point of velocity inversion which is a minimum of potential energy. The forces to which the particles are subject to will pull them towards this minimum in the next step. The procedure is stopped once the desired thresholds are reached within a single simulation time step. In MBN EXPLORER, the thresholds available are maximal force and maximal displacement of each particle.

The velocity quenching algorithm is simple and fast to calculate, but does not converge as fast as other algorithms available, particularly when the potential energy surface has shallow minima. The conjugate gradient algorithm converges much faster and is more robust. The original idea comes from the Hestenes–Stiefel method for analytical minimisation of quadratic functions [243]. The particular numerical implementations in many MD packages, including MBN EXPLORER, is based on the Polak–Ribière–Polyak method [244, 245] which deals better with the nonquadratic form of the MM potential. Each step k in the algorithm consists in moving each particle i in a direction $\mathbf{d}_{i,k}$ defined by

$$\mathbf{d}_{i,k} = \mathbf{F}_{i,k} + \beta_k \mathbf{d}_{i,k-1}, \quad (2.150)$$

where

$$\beta_k = \frac{\sum_{i=1}^N (\mathbf{F}_{i,k} - \mathbf{F}_{i,k-1}) \cdot \mathbf{F}_{i,k}}{\sum_{i=1}^N \mathbf{F}_{i,k} \cdot \mathbf{F}_{i,k}}. \quad (2.151)$$

The forces $\mathbf{F}_{i,k} = -\nabla E_{i,k}$ are the gradients of the potential we want to minimise. Since the initial direction cannot be calculated by Equation 2.150, it is defined as the negative direction of the $3N$ -dimensional gradient as in a steepest-descent algorithm. At each step, particle i is displaced according to

$$\mathbf{x}_{i,k+1} = \mathbf{x}_{i,k} + \alpha_k \mathbf{d}_{i,k}, \quad (2.152)$$

where α_k is the shift rate obtained by a one-dimensional line search in the direction $\mathbf{d}_{i,k}$.

This line search method is what makes the algorithm work properly in nonquadratic potentials. It consists on the one dimensional optimisation problem of finding the displacement α_k that minimises the potential along the direction $\mathbf{d}_{i,k}$. This is an iterative process that consists of finding an interval $[\alpha_{k,\min}, \alpha_{k,\max}]$ that contains the minimum, fitting a polynomial of the energy on α_k to this interval and computing the minimum, and checking if certain convergence criteria were met. If they were, the value of α_k was found. Otherwise, this values is used to construct a new interval and the procedure is repeated. The convergence criteria used in MBN EXPLORER is defined by the change in force

$$D_{k+1} = \sum_{i=1}^N \mathbf{d}_{i,k} \cdot \mathbf{F}_{i,k+1}. \quad (2.153)$$

If this values is within the maximal allowed force tolerance, as defined by the user (see above), the algorithm leaves the linear search and calculates a new direction $\mathbf{d}_{i,k}$. In the case where there is a change in signal of D_{k+1} from D_k , a binary search is used to reduce the interval $[\alpha_{k,\min}, \alpha_{k,\max}]$ in half and select the half-interval that contains the minimum.

In the context of the original formulation of the conjugate gradient method, the following relations would hold:

$$\mathbf{g}_k \cdot \mathbf{g}_l = 0, \quad (2.154)$$

$$\mathbf{d}_k \cdot \mathbf{H} \cdot \mathbf{d}_l = 0, \quad (2.155)$$

$$\mathbf{g}_k \cdot \mathbf{d}_l = 0 \quad (2.156)$$

for all steps $k < l$, where $\mathbf{g}_k$ is the gradient of the function under minimisation and $\mathbf{H}$ is its Hessian matrix. The relation in Equation 2.155 means the directions are conjugate under the metric defined by the Hessian.²⁵ In the actual implementation none of the conditions hold because of numerical error and the fact that away from equilibrium the Hessian is not well defined. The Polak–Ribière–Polyak implementation remedies the problem of nonorthogonality of gradients automatically by the definition in Equation 2.151 which essentially falls back to a steepest descent direction whenever the difference between two consecutive $\mathbf{g}_k$ is small. The mathematical foundation of the conjugate gradient method is well covered in Lecture 38 of [246] and various numerical implementations are discussed in Chapter 5 of [247].

2.2.2.2 TEMPERATURE AND THERMOSTATS

FOR ANY OF THE INTEGRATION algorithms above, initial velocities are required. Verlet utilises it to calculate the positions one time-step backward and leapfrog to calculate the

²⁵Thus, the correct name of the method would be conjugate directions. It looks like the field of numerical methods is particularly plagued by misnomers.

velocities half a time-step backward. The user can supply the initial velocities in the input files for the simulations. They can be obtained from experimental data, previous simulations, or some other way. However, most packages will have a way of generating random initial velocities to match a user-defined initial temperature $T(t = 0)$. The majority of available packages will sample each particle's velocity from a Maxwell–Boltzmann distribution

$$p(\dot{\mathbf{x}}_i) = \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{1}{2}} e^{-\frac{1}{2} \frac{m_i \dot{\mathbf{x}}_i^2}{k_B T}}, \quad (2.157)$$

where k_B is the Boltzmann constant. However, MBN EXPLORER uses a simpler method. The temperature of the system at any given time is related to the ensemble averaged kinetic energy by the equipartition theorem, according to which each degree of freedom of the system will contribute $\frac{1}{2}k_B T$ to the temperature at equilibrium. Therefore, the speed of a particle in a system at temperature T is

$$\dot{x}_i(t) = \sqrt{\frac{3k_B T}{m_i}}. \quad (2.158)$$

MBN EXPLORER, thus, generates a unit vector $\hat{\mathbf{v}}$ with a random direction for each particle and scales it as

$$\dot{\mathbf{x}}_i(0) = \sqrt{\frac{3k_B T(0)}{m_i}} \hat{\mathbf{v}}. \quad (2.159)$$

The result is a system with the desired initial temperature but with a Dirac delta distribution of velocities instead of the Gaussian distribution of Equation 2.157. The initial system will reach the Maxwell–Boltzmann distribution of velocities in a few simulation time-steps by random collisions. That means that reliable properties must be calculated after some equilibration steps to be accurate.

MD simulations are performed in different thermodynamic ensembles. If we simply propagate the equation of motion for the system as described above, keeping periodic or reflective boundary conditions, the number of particles N , the volume V , and the energy E of the system are held constant. This is the microcanonical (NVE) ensemble. Temperature and pressure fluctuate as consequences of the dynamics. This is the most natural ensemble for MD, since energy conservation is built into the integrator.

However, it is often the case that we want to hold the system near a given temperature, as if it were in contact with a thermal bath. In that case, N , V , and the temperature T are fixed, giving rise to the canonical (NVT) ensemble. This is the ensemble of choice when a property depends on temperature but the volume should not change. Temperature control is achieved by a thermostat, that rescales or weakly couples the particle's velocities so that the system samples configurations at the target temperature, while the total energy fluctuates. There are different algorithms that perform this task [101, 236]. Only two such methods are available in MBN EXPLORER, namely, the *Berendsen* and the *Langevin* thermostats, which we now discuss.

The Berendsen thermostat is the simplest of them [248]. It is a simple homogenous rescaling of the velocities applied periodically to the whole system, as if it were in contact with a bath of constant temperature. The NVT ensemble average kinetic energy of a system is given by

$$\langle K \rangle = \frac{3}{2} N k_B T. \quad (2.160)$$

If the velocities of the particles in a system with temperature $T(t)$ are multiplied by a factor λ , the change in temperature is

$$\Delta T = T_\lambda - T(t) = \frac{1}{2} \sum_{i=1}^N \frac{2}{3} \frac{m_i (\lambda \dot{\mathbf{x}}_i(t))^2}{N k_B} - \frac{1}{2} \sum_{i=1}^N \frac{2}{3} \frac{m_i \dot{\mathbf{x}}_i(t)^2}{N k_B} = (\lambda^2 - 1) T(t). \quad (2.161)$$

The Berendsen strategy is to rescale the velocities by a factor λ in such a way that the system's temperature $T(t)$ will decay with a first-order process to the desired bath temperature T_0 in proportion to the temperature difference. The differential equation describing such a process is

$$\frac{dT}{dt} = \frac{1}{\tau} (T_0 - T(t)). \quad (2.162)$$

This gives an exponential decay of temperature to T_0 with a time constant τ . The discrete change in temperature from Equation 2.162 is

$$\Delta T = \frac{\Delta t}{\tau} (T_0 - T(t)) \quad (2.163)$$

and using Equation 2.161, the scaling factor is

$$\lambda^2 = 1 + \frac{\Delta t}{\tau} \left(\frac{T_0}{T(t)} - 1 \right). \quad (2.164)$$

Thus, at each time-step Δt , velocities are rescaled by this factor. The coupling of the system to the bath is controlled by the parameter τ . A large value of τ correspond to a weak coupling and the system's temperature will decay slowly. It is desirable to keep τ large (say, $\tau = 0.4$ ps for $\Delta t = 1$ fs) [101]. This allows the temperature to fluctuate around the desired value, as it would in a real system. This thermostat is classified as a *weak coupling* type.

The Berendsen thermostat is simple, but do not generate a true NVT ensemble average, among other problems [82, 101]. The Langevin thermostat is more robust, producing the correct distribution very closely. The idea is borrowed from the Langevin stochastic dynamics originally developed by Paul Langevin to simulate the Brownian motion of a pollen particle [249, 250]. In this dynamics, a heavy particle is considered immersed in a body of lighter (implicit) particles that collides randomly with it, causing a random redistribution of momentum. In the MD thermostat implementation, originally demonstrated by Schneider

& Stoll [251], the body of light particles is the thermal bath to which the system is coupled. This implementation is therefore classified as a *stochastic thermostat*.

The original equation of motion for the system, in our case, Equation 2.137, is supplemented by two forces coming for the light particles. One is a frictional force $-\gamma\dot{\mathbf{x}}$ that decreases the velocity of the system and the other is a random force $\mathbf{R}(t)$ resulting from random momentum transfer from the light particles in the bath. The new equation of motion is thus

$$m_i\ddot{\mathbf{x}} = \mathbf{F}_i(\mathbf{x}, t) - \gamma\dot{\mathbf{x}} + \mathbf{R}(t). \quad (2.165)$$

The stochastic nature of the thermostat comes from $\mathbf{R}(t)$. Two assumptions are made about its statistic properties. The first is that it follows a zero-mean distribution, ie, $\langle \mathbf{R}(t) \rangle = 0 \quad \forall t$. The second is that the process is uncorrelated in time, which can be stated as $\langle \mathbf{R}(t)\mathbf{R}(t') \rangle = 2m_i\gamma k_B T \delta(t - t')$, where the factor $2m_i\gamma k_B T$ comes from the fluctuation-dissipation theorem (FDT) and ensures that this random force is balanced with the friction, thus making the temperature constant. The probability density function for the random force, $p(\mathbf{R}(t))$, is sampled from a zero-mean Gaussian distribution with a variance $2\gamma k_B T m_i \delta(t - t')$ from the FDT. The friction coefficient γ is related to the thermostat damping time parameter τ by $\gamma = 1/\tau$. Here τ controls the coupling of the system to the bath in a similar way to what happens in the Berendsen thermostat discussed above. Its value must be carefully selected since the Langevin dynamics competes with the desired Newtonian dynamics under the influence of the FF potential. If the coupling is too strong (τ too small), a Brownian dynamics will dominate over the Newtonian.

Different implementations exist for discrete integration of Equation 2.165, including a strategy similar to the velocity Verlet integrator. The particular implementation in MBN EXPLORER is unknown, but likely takes advantage of velocity Verlet. A mathematically rigorous treatment of this approach, including numerical implementations, can be found in [237].

2.3 IRRADIATION-DRIVEN MOLECULAR DYNAMICS AND THE MBN EXPLORER PACKAGE

ONE OF THE UNIQUE FEATURES of MBN EXPLORER, and one that motivated its choice for this work, is the implementation of the irradiation-driven molecular dynamics module [221, 252]. In IDMD, events arising from light-matter interactions are abstracted as stochastic process that modifies the system's state, followed by a regular reactive MD evolution (as we have discussed extensively above) that describes the system's relaxation after the stimuli.

The particular focus, in this work and in the original implementation, is on irradiation events that modifies the electronic structure of the system. This can be effected by irradiation with photons having energy in and above the visible region and with charged particles. We only

consider the photon irradiation case here. Various effects can happen in a molecular system as a consequence of interaction with such radiation, eg, electronic excitation, photodissociation, and ionisation, among others. The IDMD approach is to consider these effects as fast (subfemtosecond), local processes. Since process at the scale of single molecular vibrations are in the femtosecond scale—the usual time-step size of MD simulations—the irradiation processes are virtually instantaneous.

In physics, it is usual to define a phenomenological cross-section value for an irradiation-driven process. We have encountered the absorption cross-section (Equation 2.71) already. The probability of the full photoprocess is given by the product of the process' cross section with the flux density of incident particles. The former can be obtained experimentally or calculated by various means. The discussion in Chapter 3 concerns such endeavour. The latter is defined by the particular process being simulated.

In a reactive MD picture, the effect of irradiation on the system can be (1) the deposition of kinetic energy in a set of atoms, simulating a local vibrational excitation (heating); (2) the change of atom types which will then be governed by a different set of FF potentials, corresponding to an electronic excitation; (3) the change in partial charges of a set of atoms, corresponding to ionisation; (4) the dissociation of a chemical bond, usually accompanied by a deposition of kinetic energy in the atoms involved in the bond. For each such process, a cross section can be defined and given as inputs to the software. In MBN EXPLORER, cases (1) and (4) are implemented and validated [252]. We consider cases (2) and (4) in Chapter 6.

MBN EXPLORER allows for two modes of irradiation. The flooding of the whole simulation box with a homogenous irradiation flux, or the definition of a distribution of intensities over a two-dimensional grid covering the area of one of the box's face, representing the cross section (in the geometrical sense) of an irradiating beam. In either case, the user defines the flux from the particular process. The combination of this flux at each point with the processes' cross sections results in the total probabilities governing the stochastic IDMD process.

Besides the probabilities, a series of parameters controlling the chemistry of the system need to be defined by the user. Those are (1) the valences of the chemically active atoms, defining the maximum number of bonds they can make; (2) the multiplicity of each bond that can be modified in the process; (3) the possible dissociations and bond formations as well as redistribution of charges and atom-type changes that can happen in the process. These will inform the algorithm of all events that must be monitored during any phase of the MD simulation and can be used to output statistical analyses of the chemistry in course.

The algorithm is as follows. (1) The process starts with regular molecular dynamics simulation. (2) During the irradiation phase, it is assumed that random processes (defined by the user as discussed above), eg, the dissociation of certain chemical bonds, occur. The result can be the emergence of reactive molecular fragments with dangling bonds. (3) The irradiation phase is followed by the relaxation phase during which no irradiation driven

transformations are happening and the molecular system relaxes in the course of the dynamical simulation. During this phase, reactive MD is in course, and bond dissociation and formation can happen according to the procedure defined in § 2.2.1.2 [253].

CHAPTER 3

QUANTUM CHEMICAL METHODS APPLIED TO THE PHOTOCHEMISTRY OF PACVD PRECURSORS

FEATURED WORK

C P Souza, A V Verkhovtsev, A V Walker, N J Mason, A V Solov'yov, L McElwee-White, M Zlatar and F Fantuzzi, "Excited-state dissociation of (η^4 -diene)Ru(CO)₃ precursors for photo-assisted chemical vapour deposition", *Phys Chem Chem Phys*, 2026, **28**, 17804–17817, DOI: 10.1039/d6cp00843g. 

CONTENTS

3.1	INTRODUCTION	82
3.2	METHODS	84
3.3	RESULTS AND DISCUSSIONS	86
3.3.1	EQUILIBRIUM GEOMETRIES OF PRISTINE PRECURSORS AND THEIR FRAGMENTS	87
3.3.2	THE RU–DIENE BONDING	91
3.3.3	ABSORPTION SPECTRA OF THE PRISTINE PRECURSORS	94
3.3.4	LOSS OF DIENE FROM PRISTINE PRECURSORS AND FRAGMENTS	97
3.3.5	LOSS OF CO FROM DIENE-CONTAINING FRAGMENTS	103
3.3.6	TOTAL FRAGMENTATION OF Ru(CO) ₃	105
3.3.7	A PROPOSAL OF EXHAUSTIVE DISSOCIATION PATHWAYS	105
3.4	CONCLUSIONS	107

3.1 INTRODUCTION

METAL–CARBONYL COMPLEXES are among the earliest and most widely studied precursors for nanofabrication via CVD [73, 254] and, more recently, focused electron beam–induced deposition (FEBID) [255–257]. Their successful use in these established techniques has also been extended to PACVD. Understanding the excited-state pathways responsible for precursor activation is essential to understand and control these technologies. Among the various metals of interest for nanofabrication, ruthenium has received much attention in recent decades. It has high thermal resistance (melting point 2273 °C), a high work function (4.7 eV), low bulk resistivity (7.16 $\mu\Omega$ cm), and its only stable solid oxide, RuO₂, is also a metallic conductor (with a resistivity of 35.2 $\mu\Omega$ cm) [254, 258]. This makes Ru a promising metal for thin film technologies [259], next-generation capacitors [260], and dynamic random access memory devices [261]. It is also an attractive choice for replacing or enhancing current copper interconnects in nanoelectronic devices [262, 263]. Previous techniques for the preparation of ruthenium films, such as pulsed laser deposition, molecular beam epitaxy, lift-off methods, and electrodeposition, have shown various limitations. CVD and its variations are promising alternatives to overcome these issues [69, 254, 264].

A suitable precursor for PACVD must meet key requirements: (1) be highly volatile, (2) be stable at vaporisation temperatures, (3) possess high photodissociation quantum yields, and (4) have facile thermal reactions on the substrate surface for completion of ligand loss. Although many homoleptic metal–carbonyl compounds meet all these criteria while also being simple and commercially available, Ru(CO)₅ decomposes above –18 °C [254]. The introduction of hydrocarbon polyhapto ligands in place of one or more CO ligands is one strategy to stabilise the complex while maintaining the remaining desirable properties. Ru–carbonyl compounds containing both η^3 and η^4 ligands have recently shown promising performance in PACVD [69, 71, 265, 266]. However, the detailed excited-state landscape, the competition between CO and diene loss, and the ligand-dependent accessibility of these channels remain unresolved.

Although the photochemistry of first-row transition metal–carbonyl complexes has been extensively studied, investigations become markedly scarcer for heavier congeners. To the best of our knowledge, the only study to date on the photochemistry of (η^4 -diene)Ru(CO)₃ complexes (diene = butadiene (BuD), isoprene or 2-methyl-1,3-butadiene (MBuD), cyclooctatetraene (COT),¹ 1,3-cyclohexadiene (CHD), cyclobutadiene (CBuD); Figure 3.1) was reported in [266]. In that work, **3COT** was excluded from the photolysis experiments because it showed evidence of dissociation products in the dark. The solution-phase investigation revealed loss of both CO and diene upon UV irradiation with a Hg(Xe) arc lamp, identifying these complexes as promising precursors for PACVD of ruthenium. Primary CO loss was observed

¹Although COT is technically a tetraene, we will refer to it as a diene for simplicity.

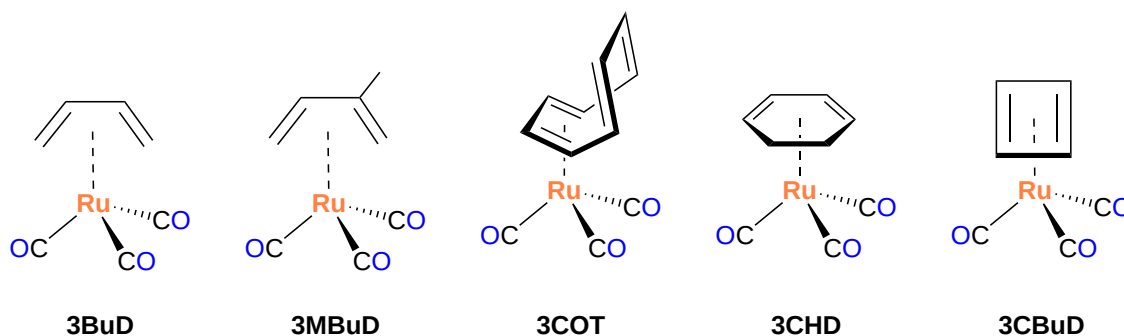


FIGURE 3.1 – $(\eta^4\text{-diene})\text{Ru}(\text{CO})_3$ compounds investigated in this work and previously in [266].

for all compounds, whereas primary diene loss occurred only for **3BuD** and **3MBuD**. The quantum yields for CO loss were wavelength dependent for all compounds except **3BuD**, and diene loss showed a similar wavelength dependence for **3BuD** and **3MBuD**. Extended photolysis produced species consistent with loss of one CO, loss of diene, loss of two CO, and combined CO/diene loss for all complexes except **3BuD**, for which only one- and two-CO loss products were detected. With the exception of **3BuD**, exhaustive photolysis yielded colloidal Ru. DFT calculations indicated that these photodissociation processes originate from localised metal-ligand (ML) excited states, and **3BuD** and **3MBuD** emerged as the most promising candidate precursors.

It is clear that photochemical studies of Ru–carbonyl complexes remain scarce, and even the prototypical $\text{Ru}(\text{CO})_5$ has not been extensively investigated. In contrast, related iron systems are much better characterised, and we briefly summarise the most relevant findings for $(\eta^4\text{-diene})\text{Fe}(\text{CO})_3$ complexes and $\text{M}(\text{CO})_5$ ($\text{M} = \text{Fe}, \text{Ru}$). Jaenicke *et al* [267] examined the solution-phase photolysis of several $(\eta^4\text{-diene})\text{Fe}(\text{CO})_3$ and $(\eta^4\text{-diene})_2\text{Fe}(\text{CO})$ complexes, finding wavelength-dependent CO loss that exceeds diene loss by roughly an order of magnitude and increases at shorter wavelengths; transient $(\eta^2\text{-diene})$ species were also detected. Bachler *et al* [268] observed similar $\eta^4 \rightarrow \eta^2$ photoisomerisation and *cis-trans* isomerisation in $(\text{BuD})\text{Fe}(\text{CO})_3$, while Chang & Zink [269] reported wavelength-dependent CO and diene loss from $(\text{COT})\text{Fe}(\text{CO})_5$ with smaller differences between the respective quantum yields. The homoleptic carbonyls $\text{M}(\text{CO})_5$ provide additional context: $\text{Fe}(\text{CO})_5$ undergoes rapid loss of up to two CO ligands after single-photon absorption, with further dissociation depending on photon energy [270–272]. Complete CO loss can occur in the gas phase or inert matrices [270], and the process is strongly wavelength dependent [273]. Dissociation generally proceeds stepwise, though concerted multi-CO loss via multiphoton absorption has been reported [270, 273]. Vibrational quenching in solution reduces overall dissociation [270, 272, 274], and both experiment and theory indicate that the first CO losses occur primarily on the singlet manifold [272, 275], with possible triplet involvement in later

steps [276]. Reactive fragments such as $\text{Fe}(\text{CO})_2$ and $\text{Fe}(\text{CO})$ can further react with the parent complex to form polynuclear species [270].

In contrast, photolysis of $\text{Ru}(\text{CO})_5$ produces $\text{Ru}(\text{CO})_4$, which readily recombines with CO to regenerate the parent complex [277]. The compound is thermally unstable [254] and can also form $\text{Ru}_3(\text{CO})_{12}$ photochemically [277, 278]. A further distinction is that unsaturated $\text{Fe}(\text{CO})_n$ fragments ($n = 4-1$) have triplet GS [270, 272, 275], whereas the Ru analogues ($\text{Ru}(\text{CO})$ excepted) are singlets [277–279]. The heavier Ru centre is also expected to exhibit stronger spin-orbit coupling, although quantitative data remain limited.

In this chapter, we build upon the previous investigation [266] of the photochemistry of $(\eta^4\text{-diene})\text{Ru}(\text{CO})_3$ (Figure 3.1) using static quantum-chemical methods to further elucidate the photodissociation pathways of these precursors, in line with established strategies for modelling excited states in organometallic systems [83, 280]. The published version is available with open access in [281]. A comparison of geometrical parameters, bonding descriptions, excited states, and energetic profiles of the pristine complexes and their fragments, together with selected ground- and excited-state potential energy surface sections, helps clarify the mechanisms of ligand loss and provides guidance for the design of improved PACVD ruthenium precursors. Where appropriate, we also compare the Ru complexes to their iron analogues. An additional objective is to establish a foundation for multiscale modelling of PACVD through MD simulations as discussed in § 1.2. The present results will support parametrisation of rCHARMM FFs (§ 2.2.1.2) and estimation of photodissociation cross-section for the IDMD simulations of the PACVD process (§ 2.3) employing these precursors. How this can be implemented is discussed in Chapter 6. Such approach has already been successfully applied to FEBID processes involving related precursors such as $\text{W}(\text{CO})_6$ [221, 222, 282], $\text{Fe}(\text{CO})_5$ [224, 274], and other organometallic compounds [223, 225, 226].

3.2 METHODS

THE DETAILS OF THE METHODS utilised in this work is set out in § 2.1. Some of the auxiliary methods utilised here have not been covered because of space constraints, but digestible references are given below. For all compounds investigated here, geometry optimisation and TDDFT vertical transition calculations were performed using the range-separated hybrid GGA functional ωB97X [283] with Grimme’s D3 dispersion correction [128]. As discussed in § 2.1.2, this type of XC functional treats short- and long-range electronic interactions differently, combining short-range DFT exchange with long-range HF exchange. This mitigates delocalisation error, making it excel at describing charge-transfer and Rydberg excited states, as well as electron delocalisation during dissociation. The dispersion correction is also essential for the correct description of fragments interaction during dissociation. The Weigend & Ahlrichs def2-TZVP basis set with ECP was used on the Ru atoms, while the smaller

def2-svp basis set was used for all other atoms [132]. The use of ECP is important to correct for relativistic effects caused by the heavy Ru nucleus. This level of theory was applied to all scans. To perform a rigid scan of the Ru–diene bonds, we stretched and contracted the equilibrium distance between the diene and the $\text{Ru}(\text{CO})_n$ moieties along the line joining the metal to the centroid of the four carbon atoms involved in the η^4 (or the six in the case of η^6) coordination. A contraction of 0.5 Å was used in all cases, while stretching was extended as far as needed to reach the dissociation plateau. Steps of 0.1 Å were used in all scans. At each point in the scans, vertical excitations via TDDFT for 30 singlet and 30 triplet states were calculated. These calculations were performed using GAUSSIAN 16 REV A.03 [284].

For the CBUD- and COT-containing complexes, Ru–diene dissociation pathways were also explored using the nudged elastic band (NEB) method [285]. The initial structure corresponded to the equilibrium geometry with the Ru–diene distance shortened by 0.5 Å along the vector connecting Ru to the centroid of the four coordinating carbon atoms. The final structure was generated by elongating the same coordinate by 1.8 Å from equilibrium and replacing the bound diene with the optimised isolated ligand while keeping the centroid coincident. At each image point in the converged path, vertical TDDFT excitations were obtained for 30 singlet and 30 triplet states. All NEB calculations were carried out with ORCA 5.0.3 [286] using ωB97X together with the D3 dispersion correction and Becke–Johnson damping (D3BJ) [287]. The split basis-set scheme described above and the RIJCOSX approximation with def2 auxiliary basis sets were employed [288]. Transition states (TSS) associated with possible changes in COT coordination (see § 3.3.1) were located using the NEB-TS variant [289] at the same level of theory, with reactant and product geometries optimised prior to the NEB-TS calculations.

To aid in the interpretation of the electronic transitions, the NTO analysis [290, 291], executed with the aid of the THEORETICAL DENSITY, ORBITAL RELAXATION AND EXCITON ANALYSIS (THEODORE) package [292] was used on the GAUSSIAN 16-generated orbitals. Simulated absorption spectra were obtained by applying artificial broadening [149] to the TDDFT transitions. A “stick” vertical transition spectrum is obtained from the calculations, where the total oscillator strength for a given transition is located in a single energy or frequency, ie, the spectral line shape is a Dirac delta distribution (Equation 2.74). In reality, the absorption features are broadened by several effects. We chose here to model this broadening by a Gaussian distribution, which is used in place of the Dirac delta. The procedure consists in fitting cross-section-scaled Gaussian curves to each vertical transition peak in the energy domain and summing them up to construct the final envelopes in the wavelength domain according to

$$\sigma(\lambda) = \sum_i \sigma_i^0 \frac{1}{\sigma_E \sqrt{2\pi}} \exp \left[-\frac{\left(\frac{hc}{\lambda} - \frac{hc}{\lambda_i} \right)^2}{2\sigma_E^2} \right], \quad (3.1)$$

where

$$\sigma_i^0 = \frac{e^2 h}{4\epsilon_0 m_e c} f_i. \quad (3.2)$$

In Equation 3.1, $\sigma(\lambda)$ is the wavelength-dependent photoabsorption cross-section. The variables λ and λ_i refer to the wavelength (independent variable) and wavelength of the i -th transition (the maximum of the Gaussian), respectively. The Gaussian standard deviation, σ_E (not to be confused with the cross-sections σ), is expressed in energy units, ensuring that the exponent remains dimensionless. Eq. 3.2 is used to rescale the oscillator strength f_i (dimensionless), obtained from the QM calculations, for each i -th electronic transition, to the respective integrated cross section σ_i^0 . Notice that, since the base Gaussian function for each transition is normalised to unity, each factor in the summation in Equation 3.1 integrates to σ_i^0 . e is the elementary charge, h is Planck's constant, ϵ_0 is the permittivity of free space, m_e is the electron mass, and c is the speed of light. The definition above differs from Equation 2.74 by a factor of h because of the different domains (energy vs angular frequency). The value of $\sigma_E = 0.4$ eV was used in all fittings and selected to better match the experimental resolution of the spectra in [72, 266]. To convert cross-sections (σ) in cm^2 to molar absorptivities (ϵ) in $\text{L mol}^{-1} \text{cm}^{-1}$, we use

$$\epsilon = \frac{N_A}{\ln(10) \times 10^3 \text{ cm}^3 \text{ L}^{-1}} \sigma, \quad (3.3)$$

where N_A is Avogadro's constant.

The energy decomposition analysis with natural orbitals for chemical valence (EDA-NOCV) [293] was performed using the Amsterdam Density Functional (ADF) [294] module of the AMSTERDAM MODELLING SUITE (AMS v 2024.101) [295] to characterise the Ru–diene interactions. The diene and the remaining fragment were treated as separate moieties, and five fragmentation schemes were tested: (1) neutral singlets, (2) neutral triplets, (3) doublet fragments with charges ± 1 , (4) singlet fragments with charges ± 2 , and (5) triplet fragments with charges ± 2 . All calculations employed the PBE0 functional [296] with D4 dispersion [130], TZ2P basis set [297], and scalar relativistic ZORA corrections [135].

3.3 RESULTS AND DISCUSSIONS

THIS SECTION IS ORGANISED as follows. § 3.3.1 presents the equilibrium GS geometries of the precursors and their fragments, followed by an analysis of Ru–diene bonding using EDA-NOCV (§ 3.3.2). Computed UV–vis spectra and assignment of key transitions via NTO analysis conclude the preamble in § 3.3.3.

We then examine the photodissociation pathways through TDDFT PES scans for Ru–ligand bond cleavage, presented in the adiabatic picture with excited states referenced to their ordering at the GS equilibrium geometry. Figure 3.2 summarises all pathways from the pristine precursors to bare Ru and serves as a guide for the discussion. § 3.3.4 addresses diene loss

from pristine precursors and fragments (steps 2, 2.1, 2.3, and 2.5 in Figure 3.2), followed by CO loss from diene-containing species (steps 1, 2.2, and 2.4) in § 3.3.5. § 3.3.6 examines CO loss from the $\text{Ru}(\text{CO})_n$ fragments (steps 1.1–1.3). The section concludes with the proposed exhaustive dissociation pathways for the three most thoroughly analysed systems, **3COT**, **3BuD**, and **3CBuD** as supported by the current method (§ 3.3.7). In the ensuing discussion, the proposed pathways should be regarded as a subset of the channels accessible within the coordinates explored here. Additional geometrical degrees of freedom may open alternative routes that require more detailed dynamical investigations beyond the scope of this work.

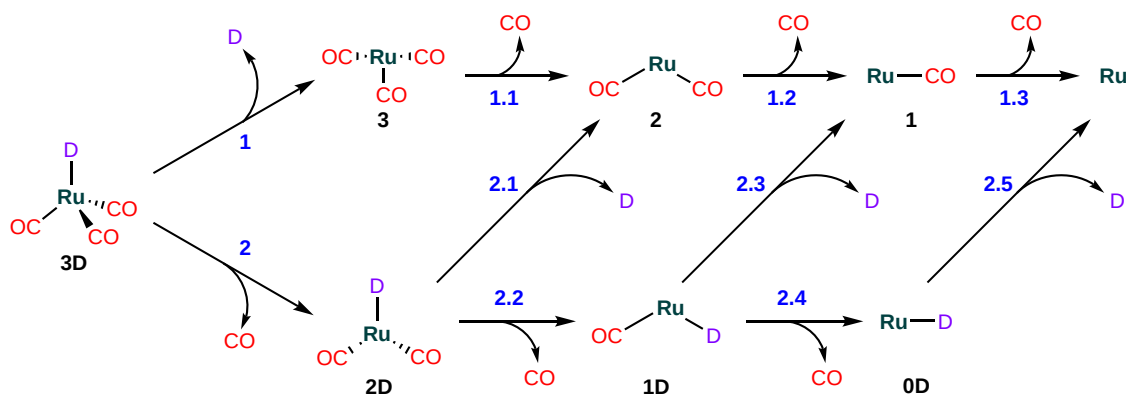


FIGURE 3.2 – General exhaustive dissociation pathways for $(\eta^4\text{-diene})\text{Ru}(\text{CO})_3$ compounds. D = diene. Only **3COT**, **3BuD**, and **3CBuD** were considered for the total dissociations. For **3MBuD** and **3CHD**, only the primary dissociations of diene and CO (ie, steps 1 and 2) were considered.

3.3.1 EQUILIBRIUM GEOMETRIES OF PRISTINE PRECURSORS AND THEIR FRAGMENTS

BEFORE ANALYSING THE photodissociation pathways, we briefly summarise the GS equilibrium geometries of the precursors and their fragments. For **3COT**, **3BuD**, and **3CBuD**, full dissociation sequences to bare Ru were explored through Ru–ligand bond scans, whereas for **3MBuD** and **3CHD**, only the first CO and diene losses were considered. Figure 3.3 shows the optimised geometries of all species. With the exception of $\text{Ru}(\text{CO})$ (**1**), all have singlet GS well below the lowest triplets if they exist. The smallest gap is 3.4 kcal mol^{-1} (0.15 eV) for C_{2v} $\text{Ru}(\text{CO})_2$ (see Table 3.1 and discussion below). All pristine precursors except **3MBuD** adopt C_s symmetry, as do most fragments, with a few notable exceptions discussed below.

Loss of the diene at any stage of the dissociation sequence generates $\text{Ru}(\text{CO})_n$ fragments, common to all precursors. Fragment **1** ($n=1$) adopts the expected linear triplet GS ($\text{C}_{\infty v}$), with the singlet lying $24.7\text{ kcal mol}^{-1}$ (1.07 eV) higher in energy. Fragment **2** ($n=2$) has a singlet C_{2v} GS with a small singlet–triplet gap to the lowest-lying triplet state (C_{2v}) of 3.4 kcal mol^{-1} (0.15 eV). In turn, fragment **3** ($n=3$) adopts a singlet C_s GS with a 7.8 kcal mol^{-1} (0.34 eV) gap to the lowest triplet (C_{2v}). This trend contrasts markedly with the case for Fe analogues:

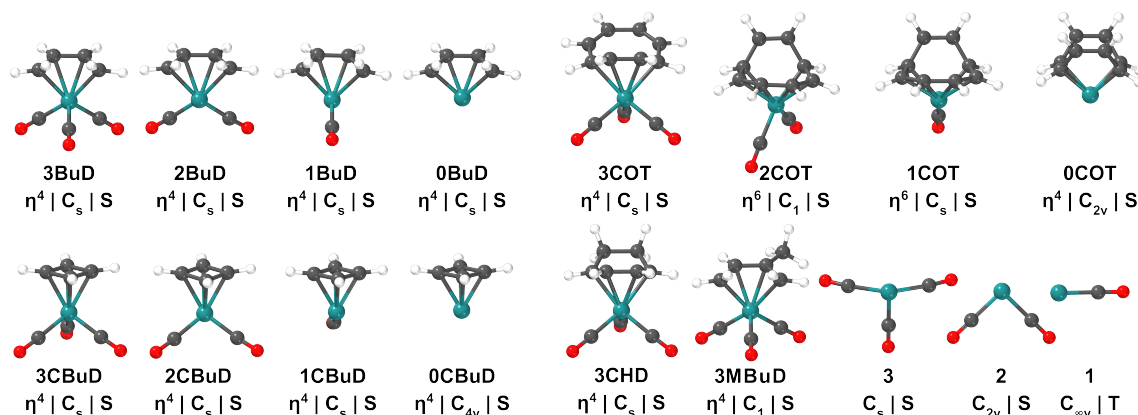


FIGURE 3.3 – Optimised GS geometries of the precursors and fragments at the DFT/ ω B97X-D3/def2-SVP, def2-TZVP(Ru) + ECP level of theory. Labels indicate diene coordination (except for the $\text{Ru}(\text{CO})_n$ fragments), point-group symmetry, and electronic multiplicity (S = singlet, T = triplet).

TABLE 3.1 – Calculated scf singlet–triplet gaps in kcal mol^{-1} (eV) and triplet $\langle S^2 \rangle$, for various diene-containing molecules other than **3cOT** and their fragments (see also Figure 3.4). Molecules whose ligand coordination is not indicated are η^4 -coordinated. Level of theory: DFT/ ω B97X-D3/def2-SVP, def2-TZVP(Ru) + ECP.

	Singlet–Triplet gap	Symmetry		T $\langle S^2 \rangle$
		S	T	
3CHD	45.0 (1.95)	C_s	C_1 (η^2)	2.040
3MBuD	98.3 (4.26)	C_s	C_1 (η^2)	2.044
3BuD	46.6 (2.02)	C_s	C_1 (η^2)	2.044
2BuD	39.4 (1.71)	C_s	C_s	2.008
1BuD	21.9 (0.95)	C_s	C_s	2.019
0BuD	10.0 (0.43)	C_s	C_s	2.021
3CBuD	66.0 (2.86)	C_s	C_s	2.015
2CBuD	19.7 (0.85)	C_s	C_{2v}	2.004
1CBuD	36.9 (1.60)	C_s	C_s	2.012
0CBuD	18.9 (0.82)	C_{4v}	C_{2v}	2.019

all unsaturated $\text{Fe}(\text{CO})_n$ fragments have triplet GS and $\text{Fe}(\text{CO})_2$ is linear ($D_{\infty h}$), as established by experiments and theory [270, 272, 275, 276]. From our calculations, even the triplet state of the Ru analogue **2** has C_{2v} symmetry. These differences are consistent with established trends between first- and second-row transition metals, where the greater spatial extent and polarisability of 4d orbitals, together with relativistic effects, can lead to distinct metal–ligand bonding patterns and structural preferences [298–300].

Fragment **3** and its analogue $\text{Fe}(\text{CO})_3$ are interesting cases. In both instances, the triplet C_{2v} and C_{3v} geometries are nearly degenerate, differing by $0.9 \text{ kcal mol}^{-1}$ (0.04 eV) for $\text{Fe}(\text{CO})_3$ and only $0.3 \text{ kcal mol}^{-1}$ (0.01 eV) for **3**. Our calculations favour the C_{2v} geometry

in both cases, although a triplet C_{3v} GS has previously been assigned for $Fe(CO)_3$ [270, 272]. Given the very small energy separation, such assignments are uncertain. Indeed, Troß *et al* [276] argued that the two structures for $Fe(CO)_3$ interconvert readily and likely coexist in equilibrium, with DFT and CCSD(T) results differing on the preferred geometry. This ambiguity is unlikely to affect the Ru-containing precursors considered here. Table 3.2 summarises the singlet and triplet geometries and relative energies of the $Ru(CO)_n$ fragments and their Fe analogues.

TABLE 3.2 – Calculated relative scf energies, in kcal mol⁻¹ (eV) and $\langle S^2 \rangle$ (for triplets), for the various geometries and electronic multiplicities of $M(CO)_n$ fragments ($M = Ru, Fe$; $n = 3, 2, 1$) at the DFT/ $\omega B97X-D3/def2-SVP, def2-TZVP(M) + ECP$ level of theory.

n	Symmetry	Multiplicity	$Ru(CO)_n$		$Fe(CO)_n$	
			Energy	$\langle S^2 \rangle$	Energy	$\langle S^2 \rangle$
3	C_s	Singlet	0.00 (0.00)		20.66 (0.90)	
	D_{3h}	Singlet	49.92 (2.16)		31.05 (1.35)	
	C_{2v}	Triplet	7.79 (0.34)	2.010	0.00 (0.00)	2.062
	C_{3v}	Triplet	8.13 (0.35)	2.008	0.90 (0.04)	2.107
2	C_{2v}	Singlet	0.00 (0.00)		34.87 (1.51)	
	$D_{\infty h}$	Singlet	31.46 (1.36)		32.01 (1.39)	
	C_{2v}	Triplet	3.41 (0.15)	2.013	20.03 (0.87)	2.378
	$D_{\infty h}$	Triplet	6.70 (0.29)	2.020	0.00 (0.00)	2.097
1	$C_{\infty v}$	Singlet	24.66 (1.07)		35.56 (1.54)	
	$C_{\infty v}$	Triplet	0.00 (0.00)	2.033	0.00 (0.00)	2.531

For the diene-containing fragments, two points are worth noting. First, the **CBuD** ligand is a perfect square in **OCBuD** and **1CBuD**, but becomes slightly deltoid (kite shaped) in **2CBuD** and **3CBuD** owing to the out-of-symmetry-plane carbonyl groups. In **3CBuD**, adjacent C–C bonds measure 1.44 Å and 1.46 Å, while in **2CBuD** they are 1.43 Å and 1.48 Å. Second, η^4 -coordinated dienes may in principle convert to η^2 coordination under UV irradiation, as observed experimentally for $(\eta^4\text{-diene})Fe(CO)_3$. However, rapid reversion to η^4 prevents trapping of such intermediates in solution [267]. For this reason, these structures were not considered here.

The remaining structural nuance concerns the **COT**-containing species, whose ligand offers greater flexibility in metal coordination. Because of the four double bonds, three coordination modes are possible for the singlet GS of $(COT)Ru(CO)_n$ precursors: edge η^4 (1,2,3,4), centre η^4 (1,2,5,6), and η^6 coordination, although not all fragments support all arrangements. We, therefore, identify which of these geometries are relevant for the subsequent analysis of the dissociation pathways. Figure 3.4 shows the complete set of

optimised singlet and triplet structures and their energies relative to the most stable geometry (at the bottom) for each fragment. Fe analogues are included for comparison. The pristine **3COT** precursor admits two C_s η^4 isomers (edge and centre), with the edge form lower in energy by 10.8 kcal mol⁻¹ (0.47 eV), consistent with crystallographic data for (COT)Fe(CO)₃ [269, 301] and with our calculated separation of 12.7 kcal mol⁻¹ (0.55 eV) for the iron analogue. Although COT–Ru complexes can be fluxional [302], only the lowest-energy structures were retained for the dissociation analysis. No triplet η^4 minima were located for either metal, though η^2 -coordinated structures (not shown) exist.

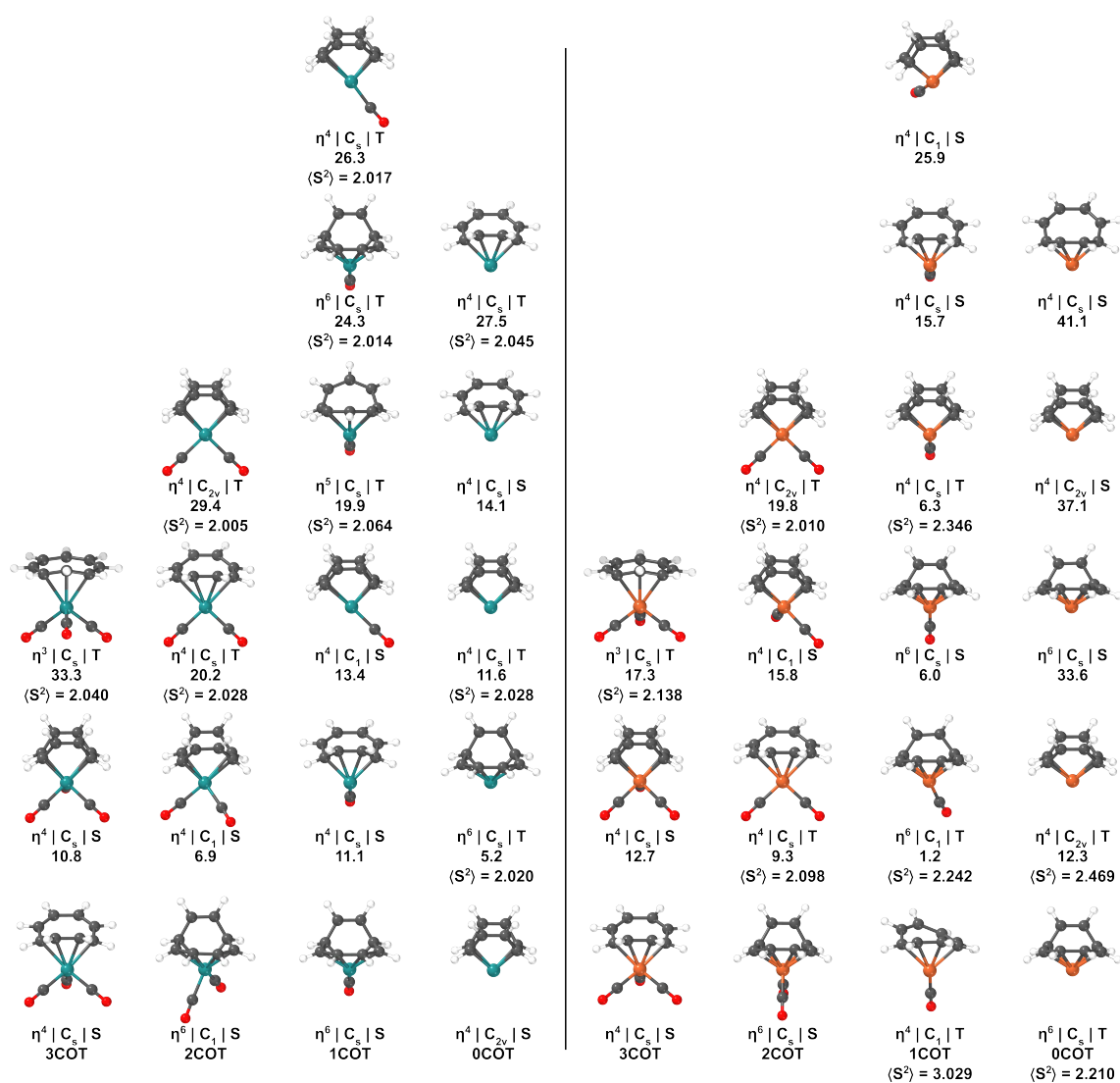


FIGURE 3.4 – Summary of all singlet and triplet equilibrium geometries for COT-containing Ru (left-side panel) and Fe (right-side panel) complexes obtained at the DFT/ ω B97X-D3/def2-svp, def2-tzvp(Ru) + ECP level of theory. Labels indicate COT coordination, point-group symmetry, and electronic multiplicity (S = singlet, T = triplet). For triplets, $\langle S^2 \rangle$ is shown. Energies below each molecule are relative to the respective minima at the bottom and expressed in kcal mol⁻¹.

After loss of one CO from **3COT** to form **2COT**, the initially unstable η^4 -coordinated fragment relaxes to an η^6 C_s structure. NEB calculations indicate this conversion is barrierless (Figure 3.5). The alternative centre-coordinated minimum lies 6.9 kcal mol⁻¹ (0.30 eV) higher in energy and is distorted (C_1 symmetry). The Fe analogue (COT)Fe(CO)₂ also has a singlet η^6 C_s GS, but in contrast to the Ru system, the next-lowest energy structure is a triplet η^4 edge-coordinated species, reflecting the greater energetic competitiveness of triplet states in the Fe series.

Further CO loss from **2COT** yields **1COT**, which retains an η^6 C_s GS; a centre-coordinated η^4 minimum lies 11.1 kcal mol⁻¹ (0.48 eV) above. The Fe analogue instead adopts a distorted triplet η^4 edge-coordinated GS (C_1 symmetry), with a triplet η^6 structure only 1.2 kcal mol⁻¹ (0.05 eV) above. Final CO loss gives **0COT**, which undergoes a further rearrangement: the unstable η^6 structure converts to a centre-coordinated η^4 C_{2v} minimum via a small barrier of 2.9 kcal mol⁻¹ (0.13 eV) as evidenced by NEB TS calculation (Figure 3.5). Although this energy is close to the accuracy limit of the method, a TS structure was found. The closest higher-energy structure to the **0COT** minimum is the triplet η^6 (5.2 kcal mol⁻¹, 0.23 eV above). The Fe analogue remains a triplet η^6 C_s species, with a triplet centre-coordinated η^4 structure 12.3 kcal mol⁻¹ (0.53 eV) higher.

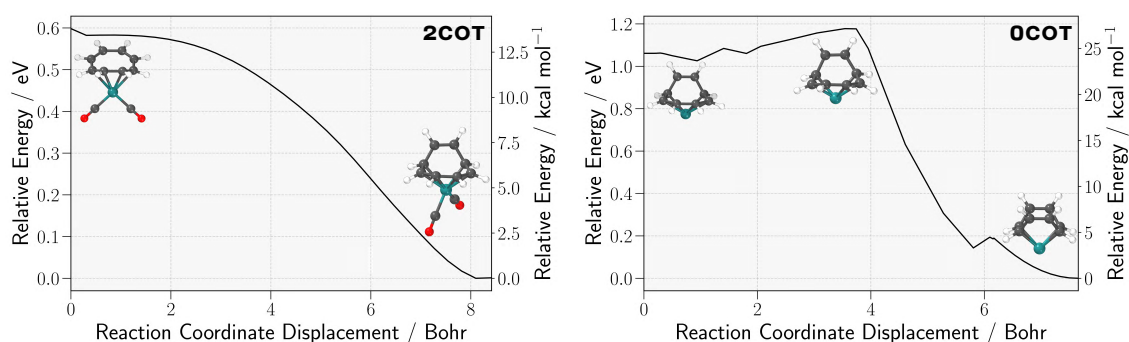


FIGURE 3.5 – NEB MEPS for the conversion of (left) singlet **2COT** from the η^4 edge-coordinated structure to the GS η^6 -coordinated structure in a barrierless rearrangement and (right) singlet **0COT** from the η^6 -coordinated structure to the GS η^4 centre-coordinated structure passing through an early TS with a 2.9 kcal mol⁻¹ barrier. Level of theory: DFT/ ω B97X-D3/def2-SVP, def2-TZVP(Ru) + ECP. All endpoints pre-optimised except the **2COT** “reactant”.

3.3.2 THE RU-DIENE BONDING

THE COMPLEXES CONSIDERED in this study (Figure 3.1) are formed from Ru(0) with the electronic distribution [Kr] 4d⁷ 5s¹. Coordination of one η^4 and three CO ligands produce a compound with 18 valence electrons at the metal center. This is a classical example of an 18-electron transition metal complex. As for the ligands, we have two acyclic (BuD and MBuD) and three cyclic (COT, CHD, and CBuD) alkenes. Among the latter, COT and CBuD

have eight and four electrons in the π space, respectively, matching Breslow’s $4n$ -electron rule for antiaromaticity. While isolated CBuD is indeed antiaromatic, COT assumes a nonplanar structure and is nonaromatic.

While M–CO bonding has been extensively investigated in transition-metal chemistry [303, 304], the nature of the Ru–diene interaction is less well established. To characterise this interaction, we performed EDA-NOCV fragment analyses in which each complex was partitioned into the diene ligand and the remaining Ru(CO)₃ unit. Several coupling schemes were explored (see § 3.2), but in all cases the bonding is best described in terms of neutral fragments combined either as singlets or as triplets. Within the EDA-NOCV framework, the fragment partitioning scheme that best describes the bonding yields the smallest absolute total orbital interaction energy [305, 306]. This indicates that the selected scheme provides a description of the fragments that is closest to the electronic structure in the bonded system, as it requires the smallest orbital reorganisation upon bond formation. This criterion assigns **3COT** and **3CBuD** to a triplet-fragment description, whereas the remaining complexes are better described by singlet fragments. The orbital interaction energies are summarised in Table 3.3.

TABLE 3.3 – EDA-NOCV orbital interaction energies in kcal mol^{−1} for the pristine precursors decomposed in the diene and Ru(CO)₃ moieties with different charge and multiplicity combinations. Smallest values in bold indicate the most suitable description. Level of theory: SR-ZORA-DFT/PBE0-D4/TZ2P.

Charge	Multiplicity	3COT	3CHD	3BuD	3MBuD	3CBuD
0	Triplet	−191	−202	−205	−205	−196
0	Singlet	−205	−200	−198	−200	−259
±1	Doublet	−213	−225	−217	−221	−238
±2	Triplet	−476	−492	−469	−476	−500
±2	Singlet	−338	−395	−371	−374	−364

The difference in bond description can be rationalised in terms of the ligand’s HOMO–LUMO gaps (Table 3.4). COT and CBuD are the ligands with the smallest HOMO–LUMO gaps when isolated, both in their relaxed and in their bonded geometries, making their triplets closer in energy to their singlets in comparison with the others.

The deformation densities in Figure 3.6 show that, in all complexes, the Ru–diene interaction is dominated by the frontier orbitals of the two fragments. On the ligand side, these correspond to π orbitals formed from the sp² carbon p orbitals, while on the metal fragment they are Ru d orbitals with some contribution from the CO ligands. In the systems best described by triplet fragments (**3COT** and **3CBuD**), the interaction follows an electron-sharing pattern, with complementary transfer of electron density between singly occupied orbitals on the diene and metal fragments. For the remaining complexes, described by singlet fragments, the interaction instead follows a donor–acceptor pattern, involving donation from

TABLE 3.4 – HOMO–LUMO gaps (kcal mol^{-1}) for the isolated diene ligands in their bonded geometries (Bonded) and in their relaxed equilibrium geometries (Relaxed), and the gap for their pristine complexes (Complex). The first values (Bonded) are calculated at the level SR-ZORA-DFT/PBE0-D4/TZ2P while the others were obtained at the level DFT/ ω B97X-D3/def2-SVP, def2-TZVP(Ru) + ECP.

	Bonded	Relaxed	Complex
COT	32	193	173
CBuD	40	179	222
CHD	74	210	217
MBuD	81	226	217
BuD	83	216	218

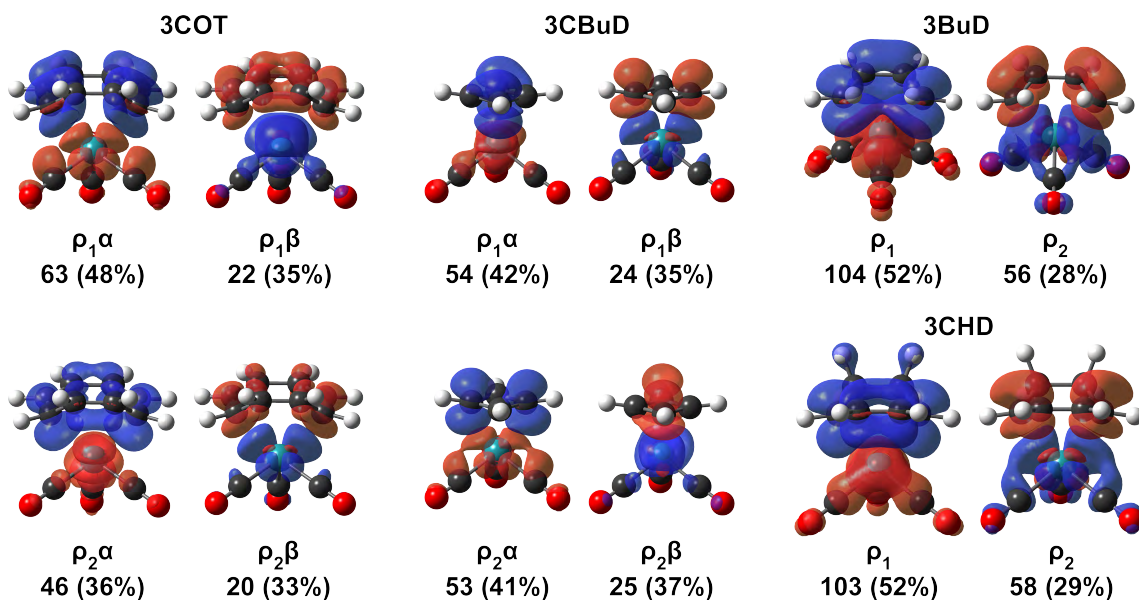


FIGURE 3.6 – EDA-NOCV deformation densities (ρ) describing the interaction between diene and $\text{Ru}(\text{CO})_3$ fragments. Contributions to the total orbital interaction energy (kcal mol^{-1} and percentage) are given below each density. For triplet-fragment cases (**3COT** and **3CBuD**), percentages refer to each spin component. **3MBuD** is similar to **3BuD** and is omitted. Charge flows from red to blue. Isovalues: 0.002 au. Level of theory: SR-ZORA-DFT/PBE0-D4/TZ2P.

the diene HOMO to a metal-centred orbital and backdonation from a metal-centred orbital into the diene LUMO. In both cases, the dominant contributions arise from frontier and low-lying orbitals, so electronic excitation from these orbitals is expected to weaken or disrupt the Ru–diene interaction.

The preference for a triplet-fragment description in **3CBuD** is consistent with the electronic structure commonly attributed to cyclobutadiene in transition-metal complexes, where coordination stabilises a near-square geometry that is often rationalised in terms of triplet (Baird-type) aromaticity [307–309]. The corresponding result for **3COT** is less straightforward

to rationalise. For present purposes, it suffices to note that, irrespective of whether the interaction is best described in donor–acceptor or electron-sharing terms, the Ru–diene bonding in all cases involves frontier orbitals that are susceptible to electronic excitation, supporting the expectation that photoexcitation will facilitate diene dissociation. Table 3.5 summarises the energy decomposition for the most favourable descriptions of each precursor.

TABLE 3.5 – EDA-NOCV results in kcal mol^{−1} for the pristine precursors decomposed in the diene and Ru(CO)₃ moieties in their most favourable description (see Table 3.3). Level of theory: SR-ZORA-DFT/PBE0-D4/TZ2P.

	3COT	3CHD	3BuD	3MBuD	3CBuD
Pauli Repulsion	249.84	238.03	223.08	230.43	243.74
Electrostatic Interaction	−168.24	−176.63	−161.19	−168.94	−168.02
Orbital Interaction	−191.23	−199.71	−198.29	−199.53	−196.38
Dispersion Energy	−5.64	−4.94	−3.88	−4.54	−3.37
Total Bonding Energy	−115.27	−143.26	−140.28	−142.58	−124.03

3.3.3 ABSORPTION SPECTRA OF THE PRISTINE PRECURSORS

IT IS ALSO USEFUL TO consider the absorption spectra of the pristine precursors and the character of their main transitions when discussing dissociation pathways. Figure 3.7 shows the calculated gas-phase spectra. Experimental spectra in heptane have been reported previously [72, 266]. Although no solvent effects were included in the calculations, qualitative comparisons with solution spectra remain possible given the close match between experimental and calculated spectra. We expect solvent effects to minimally shift transition energies and, given the PACVD context, gas-phase spectra are more realistic tools. The most striking feature is the distinct spectrum of **3COT**, which displays substantially higher absorptivity across the whole wavelength range and is the only complex with absorption extending into the visible region. This enhanced absorptivity can be attributed to the extended π -conjugation of the COT ligand, which increases electronic delocalisation and leads to a larger number of allowed transitions with higher oscillator strengths (see Equation 2.72). The remaining precursors show similar spectral profiles among themselves, with **3BuD** having the most compact absorption range, consistent with experiment.

The main transitions are summarised in Table 3.6 and assigned from NTO analysis (full set in § A.1). Transitions with oscillator strength below 0.01 were treated as forbidden. Because the PACVD experiments employed a 500 W Hg(Xe) arc lamp [72, 266], only transitions above 225 nm were considered relevant and are highlighted in bold. With the exception of **3COT**, the active transitions are predominantly ML in character, involving Ru d orbitals together with CO and diene π/σ orbitals. The relative ligand contributions vary: in **3CHD** and **3CBuD**, CO orbitals dominate at lower energy and diene contributions increase at higher energy,

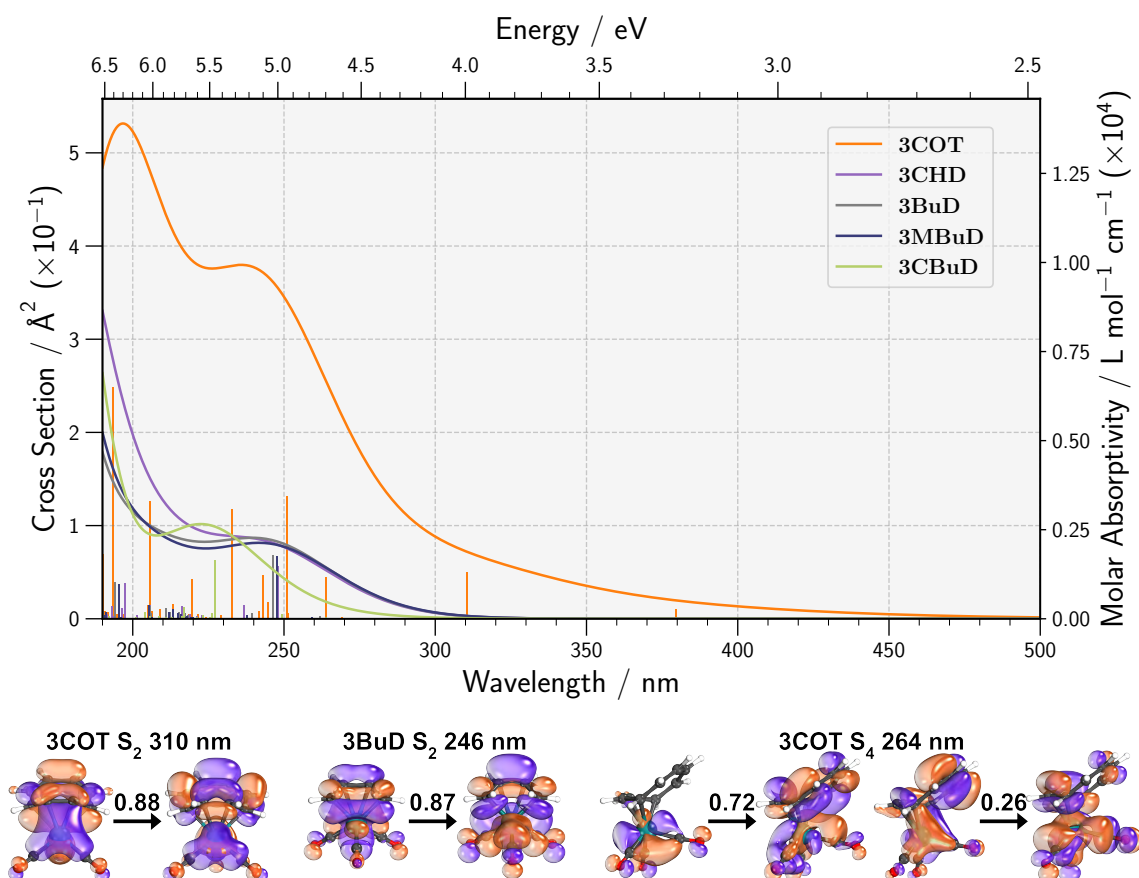


FIGURE 3.7 – (Top) calculated spectra for the pristine precursors considered in this work. The spectral envelopes are Gaussians with $\sigma = 0.4$ eV. (Bottom) NTOs for selected electronic transitions representing distinct characters (see Table 3.6). Values over the arrows are the occupation transfer of each orbital pair in the transitions. NTOs are represented as 80% of the density. Level of theory: TDDFT/ ω B97X-D3/def2-SVP, def2-TZVP(Ru) + ECP.

whereas the opposite trend is found for **3BuD** and **3MBuD**. For this latter pair, an additional charge-transfer transition appears near 210 nm–215 nm. In **3BuD**, this transition has ligand-to-ligand charge-transfer (LLCT) character between diene and CO orbitals, whereas in **3MBuD** it combines LLCT with ML contributions. No clear metal-to-ligand charge-transfer (MLCT) transition is found for **3BuD**, in contrast to suggestions for the analogous iron complex [267].

Precursor **3COT** differs markedly. Its lower-energy transitions are mainly ML but involve strong diene contributions with little CO participation. The S₂ transition (Figure 3.7, bottom panel) promotes electron density from an orbital bonding all ligands to one antibonding for the Ru–diene interaction. A further transition at 264 nm (S₄) shows mixed MLCT (to COT) and LLCT character, comparable to the MLCT feature reported for (COT)Fe(CO)₃ [269]. At higher energy, LLCT contributions become more prominent. **3COT** also exhibits a larger number of allowed transitions above 225 nm (six versus one or two for the other precursors).

TABLE 3.6 – Summary of relevant excitations for the pristine precursors considered in this work. Only transitions with oscillator strength above 0.01 (cross sections $> 10^{-18} \text{ cm}^2$; molar absorptivities $> 286 \text{ L mol}^{-1} \text{ cm}^{-1}$) are included. Transitions in bold lie above the 225 nm wavelength cut-off of the Hg(Xe) arc lamp. In the Character column, ligands in italics have the major contributions. ML = metal-ligand; MLCT = metal-to-ligand charge transfer; LLCT = ligand-to-ligand charge transfer.

	Wavelength / nm	f	State	Character
3COT	310	0.0453	S₂	ML (COT)
	264	0.0403	S₄	MLCT (COT), LLCT (COT to COs)
	251	0.1197	S₆	ML (COT)
	245	0.0163	S₇	ML (COT)
	243	0.0424	S₈	ML (COT)
	233	0.1078	S₁₁	ML (COT)
	220	0.0388	S ₁₆	LLCT (COT to COs), ML (COs)
	206	0.1150	S ₂₄	ML (<i>COT</i> and <i>COs</i>), LLCT (COTto COs)
	194	0.2274	S ₃₀	ML (<i>COT</i> and <i>COs</i>)
3CHD	248	0.0516	S₂	ML (CHD and COs)
	237	0.0132	S₃	ML (CHD and COs)
	216	0.0124	S ₁₁	ML (<i>CHD</i> and <i>COs</i>)
	206	0.0134	S ₁₅	ML (<i>CHD</i> and <i>COs</i>)
3BuD	246	0.0627	S₂	ML (BuD and COs)
	211	0.0100	S ₁₃	LLCT (BuD to COs; COs to BuD)
	206	0.0123	S ₁₅	ML (BuD and COs)
3MBuD	248	0.0616	S₂	ML (MBuD and COs)
	205	0.0133	S ₁₅	ML (MBuD and COs)
3CBuD	227	0.0571	S₅	ML (CBuD and COs)
	217	0.0109	S ₁₀	ML (<i>CBuD</i> and <i>COs</i>)

Overall, these assignments are consistent with previous analyses [72, 266]. Calculated spectra for all fragments considered in this work is presented in § A.1.

The relevance of these transitions to photodissociation becomes apparent when compared with the EDA-NOCV description of the bonding. Most ML excitations promote electron density from orbitals contributing to metal–ligand bonding into antibonding combinations, thereby weakening the Ru–ligand interactions. As a result, excitation can lower dissociation barriers and, in some cases, access nonbonded or directly dissociative states, as discussed in the following sections.

3.3.4 LOSS OF DIENE FROM PRISTINE PRECURSORS AND FRAGMENTS

HAVING ESTABLISHED THE equilibrium geometries and absorption features of the precursors, we now examine diene-loss pathways (steps 2, 2.1, 2.3 and 2.5 in Figure 3.2). The discussion is restricted to singlet excited states, as scans on the triplet surfaces rarely reveal accessible dissociative channels and generally involve barriers too high to compete under the present conditions. For related iron carbonyl systems, the involvement of triplet manifolds in ligand dissociation is also minor [276]. In addition, no phosphorescence was observed in solution-phase photochemical experiments for the present precursors [266], indicating limited population of long-lived triplet states. These observations suggest that, even if accessed via SOC, triplet states are unlikely to provide competitive dissociation pathways due to the associated barriers. Accordingly, the dominant photodissociation pathways are expected to proceed on the singlet manifold under conditions relevant to PACVD. A complete assessment of the role of triplet states, however, would require explicit treatment of spin-orbit coupling and nonadiabatic dynamics, which lies beyond the scope of the present work.

Substitution chemistry has been reported for **3COT** in the dark in the presence of phosphites [266], motivating consideration of thermal diene loss. In the intact complex, the COT ligand adopts a chair conformation, whereas the free ligand relaxes to a boat structure; dissociation therefore involves substantial conformational reorganisation. Rigid Ru-COT scans reflect this distortion showing GS instabilities at larger separations, consistent with near-degeneracies with low-lying singlet excited states. NEB calculations connecting the equilibrium structure to a geometry with an elongated Ru-COT distance and a relaxed boat COT ligand yield excited-state curves with lower dissociation energies compared to the rigid scans (see Figure A.8), highlighting the importance of ligand relaxation during dissociation. When it is possible to safely infer on D_0 values from NEB MEP, this has been included in Table 3.7.

Besides the low BDE for Ru-diene from **3COT**'s S_2 state, the Ru-diene and Ru-CO GS BDEs in **3COT** are among the smallest in the series (Table 3.7), which may explain its observed reactivity in the dark. While photodissociation of **3COT** has not been explored experimentally in solution owing to this instability [266], the precursor performs exceptionally well in PACVD [72], plausibly reflecting its markedly larger absorption cross section across the relevant spectral range (Figure 3.7). Among the secondary channels, loss of COT from **2COT** (step 2.1) is also predicted to be a favourable route from the bright S_7 state (Table 3.7).

Precursors **3BUD** and **3MBUD** show the best PACVD performance alongside **3COT** [72], while **3CHD** displays very similar photochemistry in solution studies [266] but somewhat poorer PACVD performance. The computed primary dissociation pathways for these three precursors are likewise closely related and are therefore discussed together. In contrast to the **3COT** (and **3CBUD**) cases, no substantial ligand relaxation is expected during Ru-diene

TABLE 3.7 – Selected bond dissociation energies (BDE)s for all fragmentation pathways investigated in this work. The numbers below each species indicate the dissociation step as defined in Figure 3.2. GS = ground state, GS BDE obtained from the optimised geometries of reactants and products; ZPE = zero-point energy; BS = bright state; D_0 = dissociation energy from the bottom of potential energy curve to dissociation plateau; NA = not available, meaning no alternative lower energy pathway including internal conversion exists. All values are SCF energies in kcal mol⁻¹. Except when indicated otherwise, D_0 values were obtained from rigid scans.

	GS	GS (+ZPE)	GS D_0	Lowest BS D_0	Lowest Effective D_0		GS	GS (+ZPE)	GS D_0	Lowest BS D_0	Lowest Effective D_0
3COT						3CBuD					
1	63	60	212	10 (S ₂)*	NA	1	107	104	234	54 (S ₅)*	NA
2	39	36	44	9 (S ₂)	0 (S ₆ -S ₃)	2	49	46	50	23 (S ₅)	0 (S ₅ -S ₃)
2.1	65	63	102	36 (S ₇)*	NA	2.1	99	97	154	49 (S ₈)*	NA
2.2	37	34	44	26 (S ₅)	0 (S ₇ -S ₄)	2.2	50	47	49	9 (S ₆)	0 (S ₈ -S ₄)
2.3	76	74	137	80 (S ₃)	NA	2.3	97	94	227	73 (S ₁)*	NA
2.4	54	51	74	44 (S ₃)	NA	2.4	54	52	53	36 (S ₁₀)	0 (S ₁₀ -S ₈)
2.5	88	88	161	95 (S ₈)	NA	2.5	109	107	187	82 (S ₆)*	NA
3BuD						3CHD					
1	71	68	138	64 (S ₂)	46 (S ₂ -GS)	1	67	65	141	68 (S ₂)	47 (S ₂ -GS)
2	48	45	47	0 (S ₂)	0 (S ₂)	2	48	45	47	0 (S ₁)	0 (S ₂ -S ₁)
2.1	64	62	94	46 (S ₈)	22 (S ₄ -S ₁)	Ru(CO)₃					
2.2	43	40	50	23 (S ₈)	0 (S ₈ -S ₇)						
2.3	68	66	149	97 (S ₄)	71 (S ₄ -GS)						
2.4	57	55	60	25 (S ₈)	0 (S ₈ -S ₅)						
2.5	77	76	169	100 (S ₁₆)	NA						
3MBuD						1.1	41	39	44	20 (S ₄)	12 (S ₁₂ -S ₉)
1	72	69	141	67 (S ₂)	45 (S ₂ -GS)	1.2	47	44	70	31 (S ₁₂)	NA
2	47	45	40	0 (S ₂)	NA	1.3	67	65	72	23 (T ₉)	0 (T ₉ -GS)

* Values estimated from NEB MEP (see Appendix A).

elongation, and rigid scans show no instability of the GS wavefunction. The Ru–diene scans for **3BuD** and **3CHD** (Figure 3.8 and Figure 3.9) are nearly identical, consistent with their η^4 -1,3-diene coordination, similar frontier-orbital descriptions (§ 3.3.2), and common C_s symmetry (Figure 3.3). The additional ring closure in **CHD** and the methyl substituent in **MBuD** introduce only minor perturbations, as confirmed by scans and structures.

The GS Ru–diene BDEs for these three precursors (Table 3.7) are all close to 70 kcal mol⁻¹ (3.0 eV). No diene loss in the dark was observed in solution photochemistry experiments, although **3MBuD** showed minimal deposition in the dark under PACVD conditions [72]. This is more plausibly attributed to thermal CO loss, as **3MBuD** also has the lowest Ru–CO BDE among the three, close to that of **3COT**.

Considering now the singlet excited states, only one relevant diene-loss pathway (step 2 in Figure 3.2) emerges from the pristine precursors. For both **3BuD** and **3CHD**, the vertical excitation from the S_0 minimum (purple lines in Figure 3.8 and Figure 3.9) populates the bright S_2 state, which is the only allowed transition in the accessible spectral range. The Franck–Condon region lies at a slightly contracted Ru–diene distance from equilibrium, leading to excess vibrational energy. Near this region, S_1 , S_2 , and S_3 approach and cross (see insets). NTO analyses (below each plot) confirm these crossings, showing clear inversion of states, except for the S_1 – S_2 crossing in **3CHD**, which shows slight distortion of the excited states’ orbital densities and phase inversion instead. This latter effect may indicate a crossing is nearby, but not exactly at the calculated geometry for **3CHD**. Conical intersection optimisation is necessary to confirm if that is indeed the case, but this is beyond the scope of the present investigation. In any case, the results support the hypothesis that rapid internal conversion can populate the S_1 state. This state, in turn, becomes nearly degenerate with the GS near the dissociation plateau. The NTOs do not evidence clear state inversion and the energy difference between S_1 and the GS is at least 0.03 eV for **3CHD** (see insets). The geometry may lie close to a crossing, and with sufficient vibrational energy the system is expected to proceed toward dissociation rather than deactivation. The effective pathway—photoexcitation to S_2 , internal conversion to S_1 , further Ru–diene elongation, and crossing to the GS surface—yields an effective dissociation barrier of ca 45 kcal mol⁻¹ (2 eV) (Table 3.7).

The main distinction between these precursors is in the position of the S_1 – S_2 crossing relative to the S_0 equilibrium geometry: for **3BuD** (and **3MBuD**) the crossing occurs ca 0.1 Å shorter than the equilibrium Ru–diene distance, whereas for **3CHD** it appears further away (ca 0.2 Å). This difference results in a somewhat higher-energy crossing from the Franck–Condon region for **3CHD**, though whether this significantly alters relative reactivity remains unclear. Further insight into the dissociation dynamics and relevant timescales will require nonadiabatic dynamics and time-resolved spectroscopy studies.

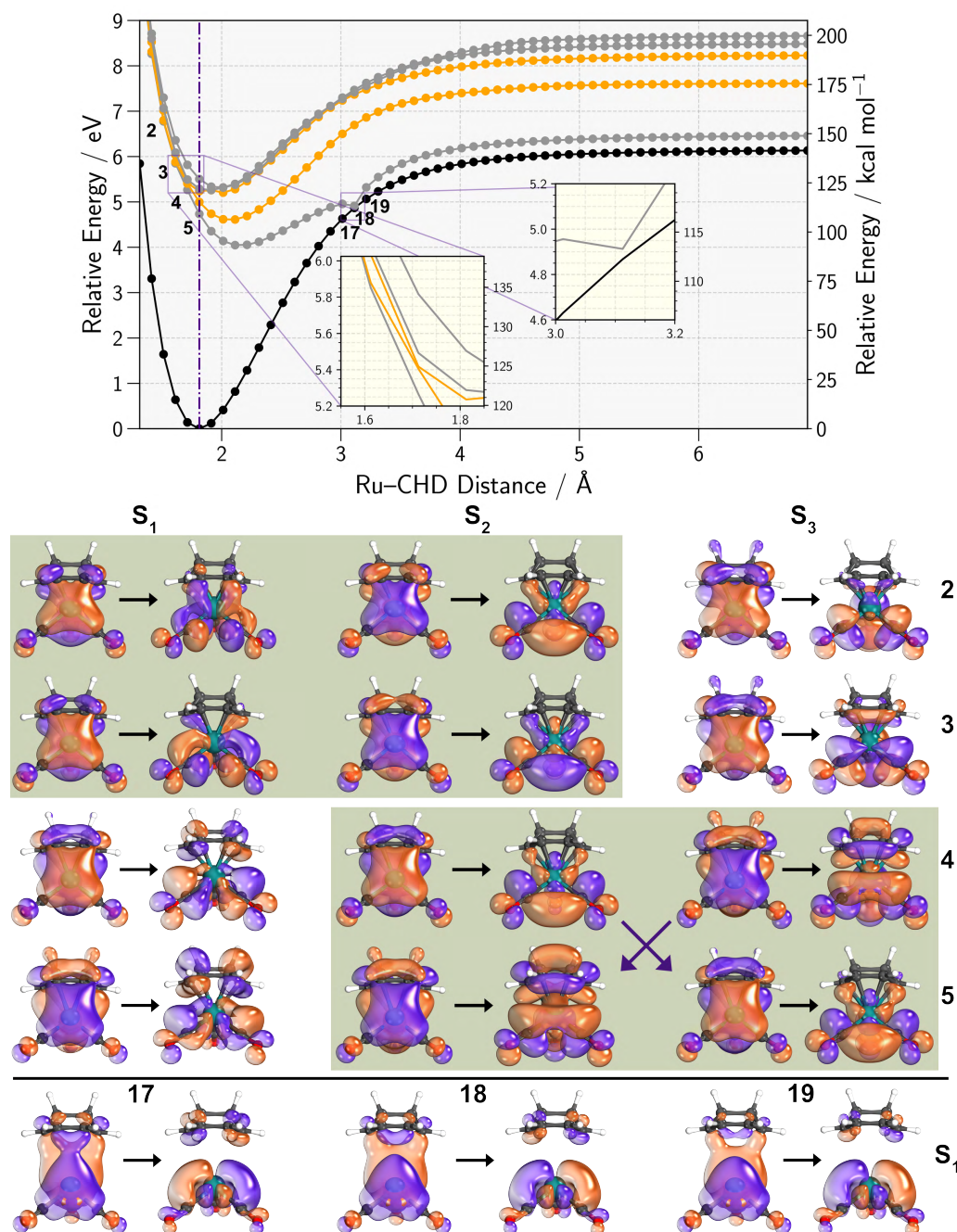


FIGURE 3.8 – Rigid scans for Ru-CHD dissociation in **3CHD** accompanied by the main NTO components for electronic transitions near PEC crossings or near-degeneracies. The purple vertical line indicates vertical excitation from the GS equilibrium geometry. The black curve is the GS PEC. Orange curves denote bright excited states, and grey curves denote dark excited states. Points numbered in bold in the plots correlates to the numbers on the NTO pairs. Electronic states are indicated by their usual order from lowest to highest energy at the GS geometry. Crossed arrows indicate state character inversion. NTO plots represent 80% of the density. Level of theory: TDDFT/ ω B97X-D3/def2-SVP, def2-TZVP(Ru) + ECP.

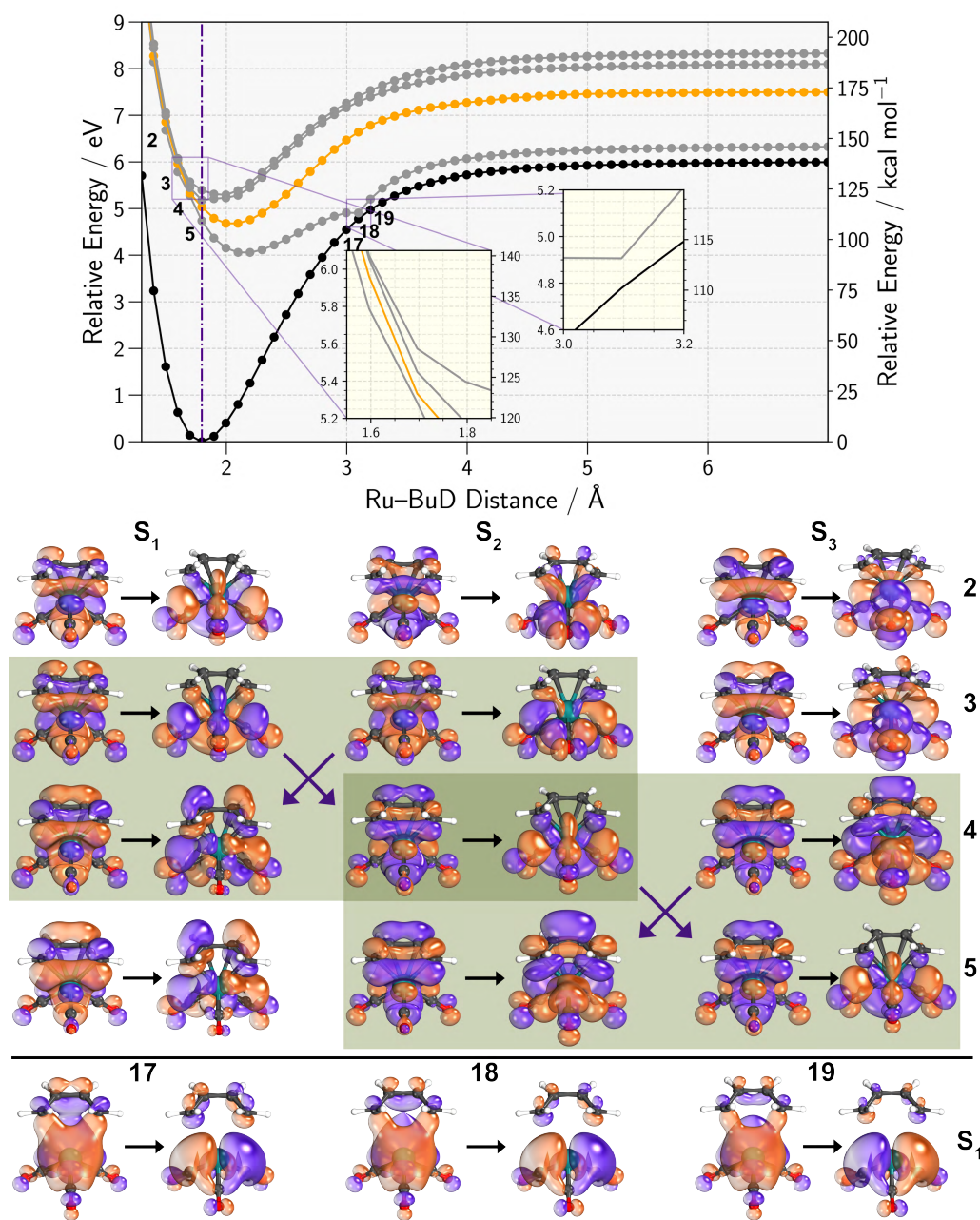


FIGURE 3.9 – Rigid scans for Ru-BuD dissociation in **3BuD** accompanied by the main NTO components for electronic transitions near PEC crossings or near-degeneracies. The purple vertical line indicates vertical excitation from the GS equilibrium geometry. The black curve is the GS PEC. Orange curves denote bright excited states, and grey curves denote dark excited states. Points numbered in bold in the plots correlates to the numbers on the NTO pairs. Electronic states are indicated by their usual order from lowest to highest energy at the GS geometry. Crossed arrows indicate state character inversion. NTO plots represent 80% of the density. Level of theory: TDDFT/ ω B97X-D3/def2-SVP, def2-TZVP(Ru) + ECP.

Subsequent diene-loss steps in the exhaustive dissociation of **3BUD** were also examined. After CO loss (step 2.1 in Figure 3.2), rigid Ru–BuD scans reveal multiple crossings among S_1 – S_5 and the GS near the dissociation plateau (Figure 3.10). NTO analysis (below plot) confirms that the state labelled S_5 at the equilibrium geometry evolves into the lowest excited state at large Ru–diene distances. Although S_5 is dark, S_2 – S_4 are bright and can lead to low-barrier dissociation through these crossings; the lowest effective barrier (from the S_4 minimum) is ca 22 kcal mol⁻¹ (1 eV). Diene loss from more CO-depleted fragments (steps 2.3 and 2.5) is unlikely owing to significantly higher barriers (Table 3.7; Figure A.11).

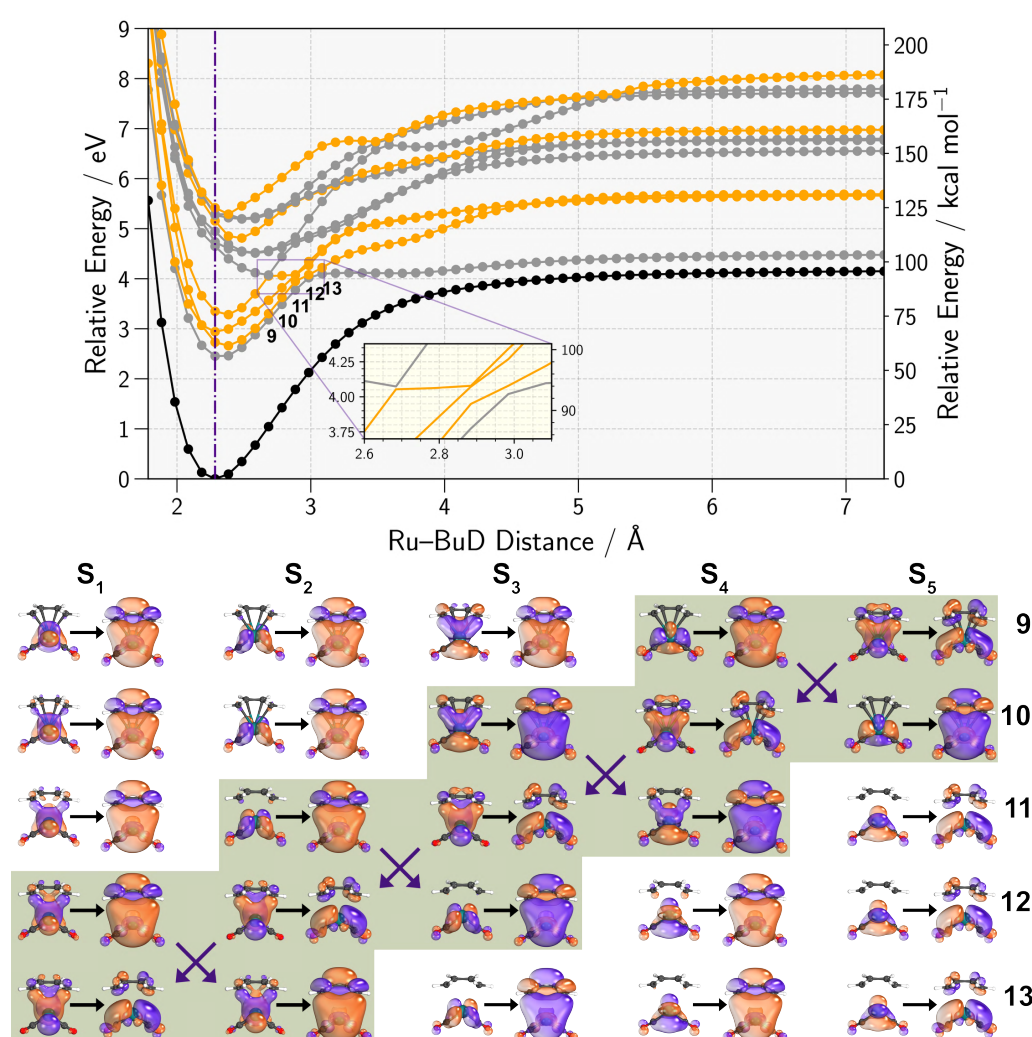


FIGURE 3.10 – Rigid scans for Ru–BuD dissociation in **2BUD** accompanied by the main NTO components for electronic transitions near PEC crossings. The purple vertical line indicates vertical excitation from the GS equilibrium geometry. The black curve is the GS PEC. Orange curves denote bright excited states, and grey curves denote dark excited states. Points numbered in bold in the plots correlates to the numbers on the NTO pairs. Electronic states are indicated by their usual order from lowest to highest energy at the GS geometry. Crossed arrows indicate state character inversion. NTO plots represent 80% of the density. Level of theory: TDDFT/ ω B97X-D3/def2-SVP, def2-TZVP(Ru) + ECP.

Finally, regarding **3CBuD**, this precursor shows no detectable diene loss in either extended photochemical experiments [266] or PACVD studies [72]. As discussed in § 3.3.1, the coordinated ligand adopts a deltoid geometry in **3CBuD** and **2CBuD** but becomes square in **1CBuD** and **OCBuD**, while the free ligand is rectangular (D_{2h}). Elongation of the Ru–CBuD coordinate therefore leads to instabilities in rigid scans, with dark S_1 and S_2 states falling below the GS at larger distance (Figure A.14). This occurs not only for the intact precursor but also for fragments formed after CO loss (steps 2.1, 2.3 and 2.5). NEB calculations connecting the intact structures to geometries with elongated Ru–CBuD bonds and relaxed D_{2h} ligands do not remove these instabilities but yield lower D_0 values than rigid scans overall. Given the rigidity of the CBuD ligand, alternative low-energy pathways appear unlikely, consistent with the absence of diene loss under both thermal and photochemical conditions.

3.3.5 LOSS OF CO FROM DIENE-CONTAINING FRAGMENTS

THE PATHWAYS FOR CO LOSS from pristine precursors and their diene-containing fragments (steps 1, 2.2, and 2.4 in Figure 3.2) are influenced by the inequivalence of the CO ligands imposed by molecular symmetry. In the C_s precursors, one CO lies on the σ_h plane while the remaining two are out of plane and equivalent to each other. These small geometric differences lead to distinct PEC profiles and reactivities.

Three general scenarios emerge: (1) dissociation via a bright state that is dissociative or has a negligible barrier; (2) dissociation through an effective pathway involving internal conversion (IC) between excited states; and (3) absence of accessible excited-state channels, in which case thermal dissociation from the GS may compete. These situations are discussed below.

Direct CO loss through dissociative bright states (case 1) is found only for **3COT** and **3BuD**. In **3BuD**, any CO can dissociate through the low-lying S_2 state reached by an ML transition (Table 3.6). Figure 3.11 shows a representative scan for an out-of-plane CO. The associated NTOS (Figure 3.7) indicate a redistribution of density away from the Ru–CO bonding region, weakening the bond despite the absence of a strongly antibonding acceptor orbital. In **3COT**, only the CO lying in the σ_h plane dissociates via a bright state (S_4), populated by a mixed MLCT/LLCT transition (Table 3.6). The remaining two CO ligands lack dissociative bright states and therefore follow case 2 (see Figure A.7 for scans). The NTOS (Figure 3.7) reflect this asymmetry: the dominant excitation weakens the in-plane Ru–CO bond while maintaining or even reinforcing bonding for the out-of-plane CO ligands.

For **2COT** and **1COT**, CO loss does not proceed via dissociative excited states. In particular, dissociation of the CO adjacent to the out-of-plane ethylene moiety in **2COT** (step 2.2; Figure 3.11, middle) and CO loss from **1COT** (step 2.4) correspond to case 3. In these systems, only relatively low barriers on the ground or excited state surfaces suggest possible thermal release (Table 3.7).

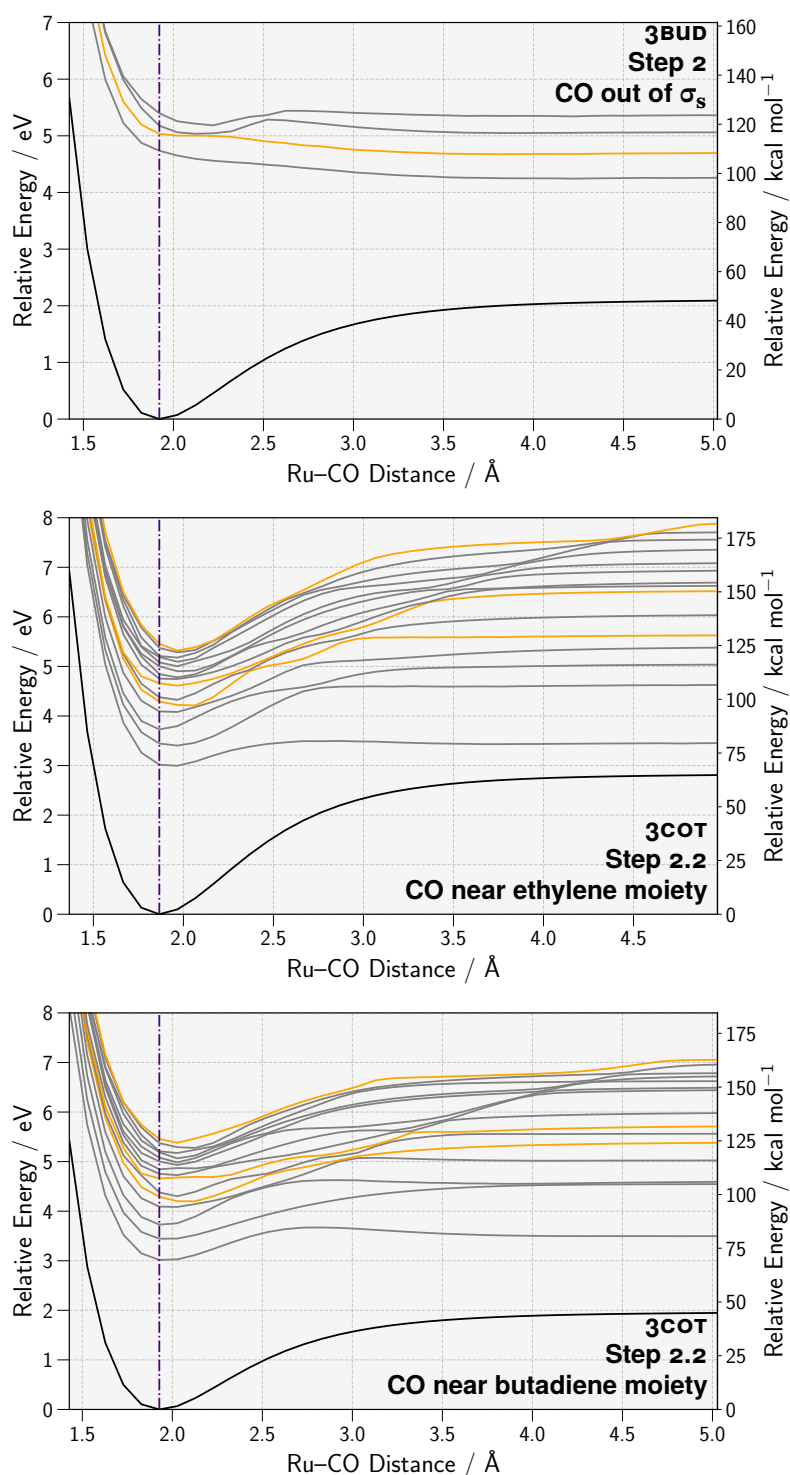


FIGURE 3.11 – Rigid scans of representative Ru–CO bonds in diene-containing molecules. The purple vertical line marks vertical excitation from the GS equilibrium geometry. Black curves denote the GS PEC. Orange curves denote bright excited states, and grey curves denote dark excited states. Level of theory: TDDFT/ ω B97X-D3/def2-SVP, def2-TZVP(Ru) + ECP.

All remaining systems fall into case 2, where effective dissociation occurs through IC between excited states. Some channels require population of higher excited states. For example, removal of the CO opposite the ethylene unit in **2COT** requires excitation to S_7 , followed by a cascade of IC steps leading to S_4 , from which dissociation becomes accessible (Figure 3.11, bottom). This contrasts with the lower-energy channel for the other CO in the same molecule discussed above (Figure 3.11, middle).

Overall, CO loss from diene-containing species is generally accessible under photoexcitation, although its efficiency depends on the accessibility of bright states and IC pathways. Definitive answer regarding such details and the definition of the main dissociation channels will only be obtained with further computational and experimental investigations of the systems' dynamics. Nevertheless, the results are consistent with solution-phase photochemistry, where higher CO yields are observed at shorter irradiation wavelengths [72, 266].

3.3.6 TOTAL FRAGMENTATION OF $\text{Ru}(\text{CO})_3$

WE END OUR SURVEY DISCUSSING the loss of CO from $\text{Ru}(\text{CO})_n$ ($n = 1, 2, 3$). For **3** (step 1.1; Figure 3.2), dissociation is facilitated by several low-lying excited states, with S_4 providing the lowest direct barrier. An additional effective pathway originates from S_{12} and proceeds through S_9 via multiple internal conversions, yielding an overall barrier of only 12 kcal mol^{-1} (0.52 eV ; Table 3.7). Subsequent CO loss from **2** (step 1.2) is less favourable. The lowest barrier from a bright state is 31 kcal mol^{-1} (1.34 eV), accessed from S_{12} , and no lower-barrier effective pathway involving internal conversion was identified. Although this barrier remains accessible at elevated temperatures, dissociation is expected to be slower than for **3**. For **1** (step 1.3), which has a triplet GS, dissociation proceeds through the lowest bright triplet state, T_9 . This state connects to lower dark states and eventually to the GS near the dissociation plateau, where an unavoidable GS instability appears. The T_9 surface also provides the lowest direct dissociation barrier (23 kcal mol^{-1} , 1 eV). Its oscillator strength is modest ($f = 0.0185$), suggesting limited population and therefore a relatively slow dissociation rate if this channel dominates. Full scans for CO loss from all three fragments are provided in Figure A.15.

3.3.7 A PROPOSAL OF EXHAUSTIVE DISSOCIATION PATHWAYS

THIS STUDY PROVIDES A STATIC analysis of the photodissociation landscape. Processes involving sequential ligand loss from fragments formed within a single photoabsorption event are not considered, as these require an explicit dynamical treatment. Such pathways may nonetheless contribute to the overall fragmentation pattern, as shown for iron carbonyl systems [270, 271, 273, 276], particularly for CO loss where several high-energy bright states with low barriers are available. Diene loss generally becomes less favourable at higher excitation energies, making cascading dissociation less likely. As some of the pathways involve internal conversion, their realisation depends on the probability of nonadiabatic transitions at crossing

regions, which cannot be quantified within the present framework. While this may affect the relative probabilities of competing channels, the overall trends identified here, including the accessibility of low-barrier pathways, are expected to remain qualitatively valid. A more complete assessment would require explicit treatment of nonadiabatic couplings and quantum dynamical simulations, which lies beyond the scope of the present work and will be addressed in future studies.

Nevertheless, even in the scope of static, adiabatic processes, some critical appraisal of the method employed here is necessary, as it comes with limitations. The core electronic structure method, DFT, strikes a balance between accuracy and computational cost. As discussed in § 2.1, it includes electronic correlation by design, putting it ahead of many HF-based methods, particularly when computational efficiency is considered. However, the accuracy of approximate functionals will vary greatly and sometimes unpredictably for different systems, with no systematic way for improvement. In the KS model, correlation is included to some extent, but multireference states cannot be adequately described with the single KS determinant structure, although some effects can be covered by the approximate XC part. Both of these effects are important when describing organometallic systems. Range-separated functionals like the ω B97X-D employed here are among the best-performing for such contexts, including the demanding task of describing dissociation—often leading to multireference states at large bond distances—and charge-transfer and Rydberg excited states, although no functional performs with excellence in all fronts [310–314]. Because of their multireference character, MC and MLCT states are expected to have the worst descriptions. However, since most of the states of interest here are ML in character (Table 3.6), this should not be a problem. GS instabilities, with eventual “negative-energy transitions”, can also happen during dissociation (see Figure A.14, for instance). The fact that the calculated spectra for the pristine precursors agree well, at least qualitatively, with experimental measurements and that the state-assignment is consistent with previous studies, is reassuring.

The most concerning methodological point that should be taken with care is the use of LRT. As we have discussed in § 2.1.4, LRT TDDFT in the form of Equation 2.78, can only account for singly-excited states [315, 316]. Indeed, this equation for a HF wavefunction and in the TDA is exactly the CIS method. Although multiply-excited states are not that frequent, they can be important dark states mediating photochemical process, even in main-group molecules and at low energy [317–319]. The blindness of the method to such states means some dissociation channels may be missing from our description. While this possibility does not invalidate our results so far, it deserves further investigation with higher-level methods such as EOM-CCSD(T) or CASSCF. Besides that, LRT TDDFT uses the adiabatic approximation, with the consequence that state-mixing is not well-described. This is one of the reasons state inversions are not always shown near possible IC regions, even though the energy profile suggests a crossing is nearby (see Figure 3.8, for instance). More problematic are conical

intersections with the GS, that cannot have the correct dimensionality [320, 321]. This means that, although regions near an IC can be found with TDDFT, any further assessment must be done with better methods. The summary below therefore reflects only the pathways within the scope of the selected method.

3COT	3BuD	3CBuD
1* $\longrightarrow$ 1.1 $\longrightarrow$ 1.2 $\longrightarrow$ 1.3	1 $\longrightarrow$ 1.1 $\longrightarrow$ 1.2 $\longrightarrow$ 1.3	2 $\longrightarrow$ 2.2 $\longrightarrow$ 2.4 Ends in 0CBuD
2 $\longrightarrow$ 2.1 $\longrightarrow$ 1.2 $\longrightarrow$ 1.3	2 $\longrightarrow$ 2.1 $\longrightarrow$ 1.2 $\longrightarrow$ 1.3	
Most favourable (partial):	Most favourable (partial):	
2 $\longrightarrow$ 2.2 $\longrightarrow$ 2.4 Ends in 0COT	2 $\longrightarrow$ 2.2 $\longrightarrow$ 2.4 Ends in 0BuD	

FIGURE 3.12 – Proposed dissociation channels for PACVD precursors. For **3COT** and **3BuD**, complete fragmentation to bare Ru proceeds through sequences involving initial CO loss (step 1 or 2), followed by successive CO loss (steps 1.1–1.3 or 2.1–1.3). The most favourable partial pathways instead follow step 2 $\rightarrow$ 2.2 $\rightarrow$ 2.4, terminating in (diene)Ru fragments (**0COT** and **0BuD**, respectively). In contrast, for **3CBuD**, only the sequence 2 $\rightarrow$ 2.2 $\rightarrow$ 2.4 is accessible, leading to (CBuD)Ru with no viable route to complete metal stripping. See text for details. Numerical labels follow the definition in Figure 3.2. * indicates channel also accessible via thermal dissociation from the ground state, consistent with experiment.

Figure 3.12 collects the accessible channels leading to bare Ru or partially stripped fragments for **3COT**, **3BuD**, and **3CBuD**. In all cases, formation of (diene)Ru is the most accessible endpoint. For **3CBuD**, this is the only viable termination. Complete fragmentation to bare Ru is predicted for **3COT** and **3BuD** through similar sequences. For **3COT**, the pathway starting with step 1 may also proceed thermally as suggested by the lowest GS BDE and experimental observations. Along the alternative route, step 2.4 is more favourable for **3BuD** than for **3COT**, in line with the barriers in Table 3.7. Loss of diene from fragments containing one or no carbonyl is unlikely in all cases.

3.4 CONCLUSIONS

IN THIS WORK, GROUND STATE DFT scans and TDDFT excited-state analyses were combined to examine the photodissociation pathways of $(\eta^4\text{-diene})\text{Ru}(\text{CO})_3$ precursors relevant to PACVD. For three representatives (**3COT**, **3BuD**, and **3CBuD**), complete fragmentation sequences towards bare Ru were mapped, enabling direct comparison of Ru–CO and Ru–diene cleavage channels within a consistent framework. The joint use of EDA–NOCV and NTO analyses connects the frontier-orbital character of the Ru–diene interaction with the accessibility of dissociative excited states and clarifies why certain ligands are preferentially lost under irradiation whereas others are retained. The calculated UV–vis spectra reproduce the overall position and intensity of the bands observed in solution-phase measurements. The

transition assignments are consistent with previous analyses and provide a coherent basis for interpreting the photochemical trends across the series.

The results indicate that **3COT** and **3BuD** can access pathways leading to bare Ru under photoactivation, with closely related routes likely for **3CHD** and **3MBuD**, whereas **3CBuD** is expected to terminate at a stable (CBuD)Ru fragment. These differences can be traced to the topology of the low-lying excited states and to the degree of structural relaxation along the Ru–diene coordinate, which together control access to internal conversion regions and effective dissociative pathways, in line with photochemical and PACVD observations. The general conclusions are consistent with current experimental evidence and indicate that the participation of triplet states is likely to be minor, if any. In a strict sense, however, the results apply to the singlet manifold. A complete assessment of the role of triplet states would require explicit treatment of spin–orbit coupling and nonadiabatic effects.

Although the present treatment is static and does not address the full excited-state dynamics, the mapped potential energy surfaces delineate the regions where bond weakening and cleavage become accessible. The use of NEB calculations accounts for the principal structural relaxation of the COT and CBuD ligands beyond rigid bond stretching, although additional nuclear degrees of freedom are not explicitly explored. The dissociation profiles obtained here therefore provide an initial map and quantitative basis for future dynamical simulations for parametrising multiscale models of PACVD growth, helping bridge molecular-level photochemistry with predictive descriptions of photo-assisted nanofabrication processes that can be directly compared with deposition experiments.

CHAPTER 4

A REFINED ATOMISTIC MODEL OF ALKANETHIOL SELF-ASSEMBLED MONOLAYERS

FEATURED WORK

C P Souza, A V Verkhovtsev, N J Mason, A V Solov'yov and F Fantuzzi, "A refined atomistic model of functionalized self-assembled monolayers on gold: Assessment of force field parameters", *J Chem Phys*, 2025, **163**, 094704, DOI: 10.1063/5.0274290. 

CONTENTS

4.1	INTRODUCTION	110
4.2	METHODS	113
4.2.1	EVALUATING FF PERFORMANCE VIA LIGAND TILT ANGLE	115
4.2.2	THE CHOICE OF OPTIMISATION STEPS FOR THE LIGAND TILT ANGLE ANALYSIS	116
4.2.3	ANGLE ANALYSIS ALGORITHM	117
4.2.4	FULL GEOMETRICAL DESCRIPTION	119
4.3	RESULTS AND DISCUSSIONS	119
4.3.1	INITIAL FORCE FIELD ASSESSMENT WITH ISOLATED LIGANDS	120
4.3.2	EVALUATING THE EFFECT OF NONBONDED PARAMETERS	121
4.3.3	TILT ANGLE ANALYSIS ON Au(111)	122
4.3.4	TILT ANGLE ANALYSIS ON Au(100)	125
4.3.5	INFLUENCE OF SURFACE COVERAGE DENSITY	127
4.3.6	FINAL DEPOSITION GEOMETRY ON Au(111)	127
4.3.7	PRELIMINARY MOLECULAR DYNAMICS SIMULATIONS	128
4.4	CONCLUSIONS	131

4.1 INTRODUCTION

SELF-ASSEMBLED MONOLAYERS ARE key nanoscale architectures with widespread impact on today's scientific and technological landscape. Since the first report of self-assembled chemical systems [322], SAMs have been extensively studied and used in various applications. These range from electronic devices—such as electroanalytical sensors [323, 324], biosensors [325, 326], and organic electronics [327–330]—to the control and enhancement of catalysts [331, 332], crystal nucleation [333], and other nanotechnology applications [334–337]. Among the many types of SAMs, alkanethiols—organic molecules consisting of a hydrocarbon chain with a thiol ($-\text{SH}$) head-group—have been widely used because of their strong chemisorption onto metal surfaces, especially gold and silver. Functionalised alkanethiol SAMs, in which the terminal end of the hydrocarbon chain is modified with specific functional groups, have proven particularly robust and versatile. Since their introduction in the early 1980s [338], these alkanethiol-based SAMs have found increasing utility in the fields mentioned above due to their high degree of structural organisation, tunable chemical functionality, and relative ease of preparation.

Recently, SAMs of alkanethiols on gold have been used as substrates for PACVD [69–71]. The highly organised structure, controllable density, and functional versatility of SAMs make them ideal model systems for achieving selective and patterned deposition. For example, it has been demonstrated that ruthenium- and aluminium-based precursors [71, 339] selectively adsorb on SAMs terminated with $-\text{OH}$ and $-\text{COOH}$ groups, but not on bare hydrocarbon chains, thus enabling a precise, area-selective coating.

Despite their importance, the accurate and predictive computational modelling of alkanethiol SAMs remains a significant challenge. In relation to PACVD, understanding the photochemistry of precursor molecules and optimising them for specific applications also requires reliable computational models of the substrate. Such models must capture key structural features of the SAMs, such as adsorption sites, chain orientation, and intricate superlattice patterns under different conditions. However, developing an atomistic model that reproduces all the experimentally observed properties of SAMs has proven difficult, reflecting the complexity of these systems.

ON MOST METAL SURFACES, thiols lose their terminal hydrogens and chemisorb on the metal through a $\text{M}-\text{S}$ (M = metal) covalent bond [336, 337]. The exact mechanism of hydrogen release and its subsequent reactions still poses some difficulty [340, 341]. For the scope of this work, however, since we are considering the final assembled system, it is only necessary to know how the ligands are connected to the metal surface. Any other unsolved questions are only relevant to the formation processes which is ulterior to our model.

A fundamental structural feature of the alkanethiol ligands is their division into three distinct regions: the sulphur head-group anchoring the chain to the metal, the hydrocarbon spacer chain, and the functional terminal group (Figure 4.1, left-side panel). In fully packed

SAMs, the chains adopt an all-antiperiplanar conformation and form a tilt angle α relative to the surface normal—approximately 30° for Au(111) and 15° for Au(100) at room temperature [336, 337, 342, 343], with other possible tilt angles discussed elsewhere [343]. The α angle varies with the length of the ligand chain [344], the temperature [342, 345], and the nature of the metal surface [336]. The tilt angle maximises interchain interactions and defines the thickness of the SAM, thereby influencing various properties [322, 336, 346–350]. To fully describe the ligand orientation, two additional angles are required (Figure 4.1, left-side panel), the precession angle β , which defines the azimuthal orientation of the chain projection on the surface, and the rotation angle ω , which represents the rotation around the molecular axis m .

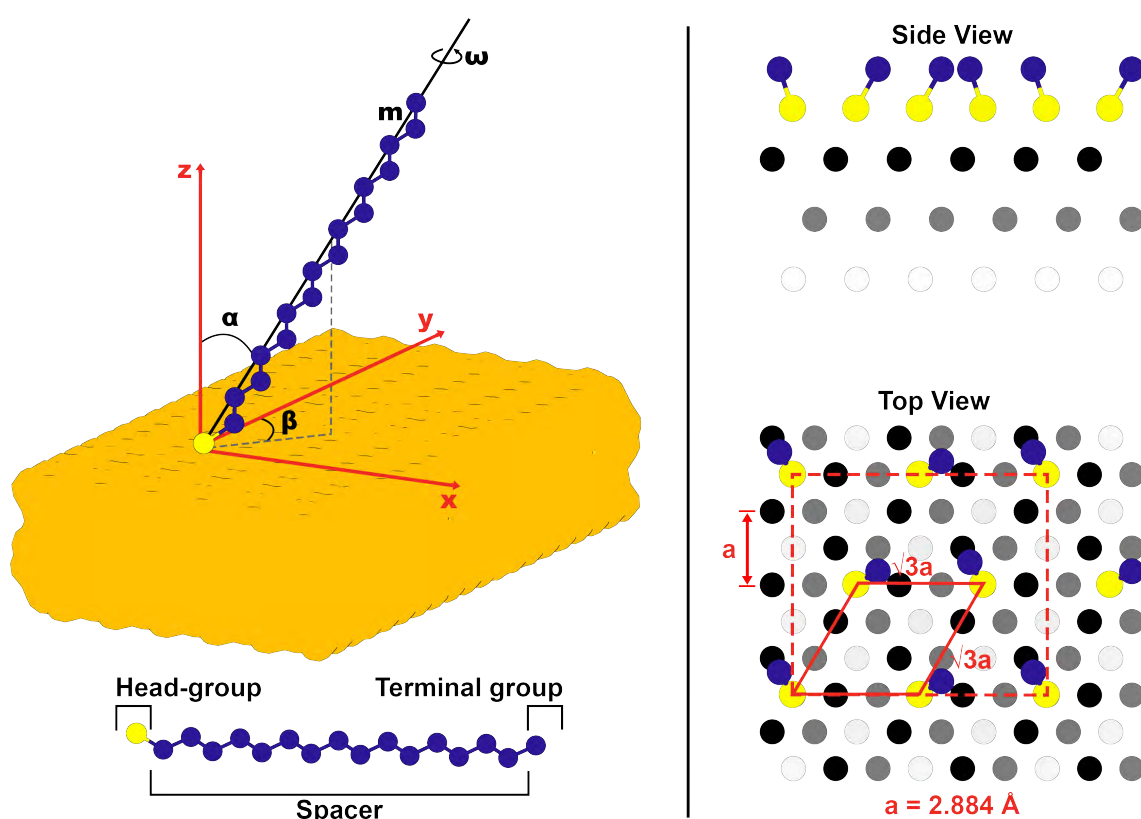


FIGURE 4.1 – Schematic representations of the alkanethiol SAM on Au(111). Yellow circles: Sulphur; blue circles: carbon; black, grey, and white circles: first, second, and third gold layer, respectively, from top to bottom. Hydrogens are omitted for clarity. **Left:** representation of a single alkanethiol molecule adsorbed on the metal surface. Here, m is the molecular principal axis contained in the plane of the carbon chain in the head-group–terminal group direction. α is the ligand tilt angle, β is the precession or azimuthal angle, and ω is the rotation angle. The different regions of the ligand are indicated. **Right:** representation of the hexagonal ($\sqrt{3} \times \sqrt{3}$) R30° pattern (solid rhombus) and of the $c(4 \times 2)$ superlattice (dashed rectangle) formed by alkanethiol molecules on Au(111) at full coverage. The alkanethiol chains have been truncated after the first carbon atoms (attached to the sulphurs) for clarity. Notice the disposition of the angles β within a unit cell. This pattern corresponds to Structure III from [342].

At full coverage, organised SAMs typically exhibit two key patterns [336, 337, 342, 343, 351–353]. First, the sulphur head-groups form a well-defined adsorption lattice. On Au(111), this corresponds to a hexagonal ($\sqrt{3} \times \sqrt{3}$) R30° arrangement (Figure 4.1, right-side panel, solid rhombus) with a coverage of about 21.4 Å² per molecule [351, 354]. Secondly, the relative orientations of the alkanethiol chains produce a $c(4 \times 2)$ superlattice pattern (Figure 4.1, right-side panel, dashed rectangle). Although the detailed origin of the superlattice is still debated, the most compelling evidence points to differences in the ω angles of neighbouring ligands [342]. For Au(100), the patterns are less conclusive; the coverage varies from 17.75 Å² to 20.6 Å² per molecule [355, 356], and the exact adsorption sites of sulphur remain uncertain [336, 357]. DFT studies suggest that the adsorption site on Au(111) is around the threefold fcc position [337, 342, 354, 358, 359], while on Au(100), atop and hollow sites appear to be occupied simultaneously [354].

It is important to recognise that SAMs are not always perfectly ordered. Under certain conditions, including lower-than-full coverage [360, 361], a SAM will be less ordered or even disordered, in which case the characterisation of its structure is unprofitable. The substrate's surface influence the ordering of fully-covered alkanethiol SAMs on gold, for instance, with well-ordered systems happening on Au(111) and Au(211), a mixture of ordered and disordered domains present on Au(311), and completely disordered systems seen on Au(221) [362]. The chain size and temperature can also affect ordering [337].

The structural complexity of SAMs, their singular properties, and even their process of formation are emergent phenomena (see § 1.1), that can only exist at the supramolecular level. An isolated alkanethiol molecule will lie stretched down on the metal surface to maximise interaction, while a small, sparse group of them will form various entangled, globular shapes sometimes described as mushroom conformations. As densification reaches a maximum, cooperative interactions will often give rise to highly complex order such as those discussed above, as a result of the delicate thermodynamic balance in the system [337, 363]. At the molecular level, intermolecular interactions and entropy are at play, giving rise to larger-scale properties assumed by the collection of ligand on the surface. For that reason, a model able to describe reasonably well the molecular properties, should be able to describe the emergent properties as well, since the latter is subordinate to the former, as discussed in § 1.1.

Capturing this structural complexity with computational models is no small feat. Previous simulations have struggled to reproduce the experimental superlattice patterns on Au(111). For example, an earlier work by Sellers *et al* [354] shows the development of an all-atom *ab initio* FF for alkanethiols on gold and silver that reproduced the ligand tilt angles and the hexagonal pattern but not the superlattice. Since then, many authors tackled the same problem, without many improvement on the description of these systems. Djebaili *et al* [364] systematically studied the influence of LJ parameters on the adsorption pattern of alkanethiols on both Au(100) and Au(111). They were able to reproduce the low level pattern

for both surfaces and demonstrated that the choice of Au–S LJ parameters have an important impact on the SAMs’ structure. They point out that, up to that point, no author, including themselves, was able to reproduce the $c(4 \times 2)$ structure observed on Au(111). This problem was subsequently investigated by a couple of other groups, without success [365, 366].

Gerdy & Goddard first reproduced the $c(4 \times 2)$ pattern resorting to disulfide units [367]. However, there is not agreement that such units are important for the description of these systems. Zhang, Goddard & Jiang, to the best of our knowledge, were the only ones to succeed in obtaining an all-atom FF capable of predicting this structure at room temperature [342]. They use a Morse potential to describe the Au–S bond as well as LJ parameters from the UFF. A subsequent development implemented a reactive model using the ReaxFF [359]. Two caveats of their work is that no functionalisation of the alkanethiols was attempted, and the development is restricted to a particular FF form and software package. Therefore, a comprehensive strategy for a model that accurately captures all relevant structural and energetic properties is still lacking.

In this work, we address this challenge using the advanced software package MBN EXPLORER and its dedicated multitasking toolkit MBN STUDIO to systematically investigate how different FF parameters—bonded terms, partial charges (and their scaling), and LJ interactions—impact the stability and structural properties of alkanethiol SAMs on Au(111) and Au(100). Central to our approach is an energy decomposition analysis, performed as a function of the ligand tilt angle, which isolates the contributions of each parameter to the overall characteristics of the SAM. By considering both pristine and functionalised alkanethiol chains—relevant for the selective metallisation of SAMs under PACVD conditions, for instance—we obtain a set of optimised FF parameters that consistently reproduce key structural features such as adsorption patterns, chain conformations, and the experimentally observed superlattice arrangements on Au(111) surfaces. We not only cover the cases of functionalised alkanethiol SAMs, which are particularly scarce in the computational literature, but we also describe a detailed procedure to extend the study of the effect of FF parameters on key properties of these systems for different ligand-surface combinations, making it a general strategy that can be used in various contexts. Ultimately, this study represents an important step toward atomistic modelling of the PACVD process. The SAMs modelled and analysed here will be employed as representative substrates to simulate their metallisation process under PACVD conditions (Chapter 6).

4.2 METHODS

ALL ATOMISTIC SIMULATIONS in this chapter were performed using MBN EXPLORER 5.0 [82], which enables the combination of multiple interaction potentials and flexible FF parametrisation. The aim of this work was to develop parameters for the alkanethiols compatible

with the CHARMM FF by combining directly available parameters from preexistent data bases. Specifically, SwissParam [214, 215] and the CGenFF [211–213] were employed to generate bonded and nonbonded parameters for the ligands (Figure 4.2), namely 1-hexadecanethiol (HDT^{H}), 16-hydroxy-1-hexadecanethiol (HDT^{OH}), and 16-mercaptohexadecanoic acid (HDT^{COOH}). Additional LJ parameters from the UFF [368] were included because of their proven reliability in modelling alkanethiol SAMs on gold surfaces [342]. The criteria for selecting these sources were twofold: (1) the availability of a simple tool for extracting all necessary FF parameters, as well as geometry (PDB) and topology (PSF) files for ligand molecules in a CHARMM-compatible format; and (2) the general applicability of the data set. Our intention was not to conduct an exhaustive survey, but rather to keep the number of FF sets to a minimum while still demonstrating the capabilities of our strategy in identifying a suitable final parameter set. Here, the all-atom optimised potentials for liquid simulations (OPLS-AA) FF deserves mention [369]. While the LigParGen engine [370] allows for the extraction of FF parameters for organic molecules in CHARMM and other formats, it does not provide PSF files. Moreover, OPLS-AA has been shown to perform less reliably than alternative FFs in reproducing characteristic tilt angles of alkanethiol SAMs [371]. For these reasons, and in line with our goal of a streamlined selection, OPLS-AA was not included in the present work.

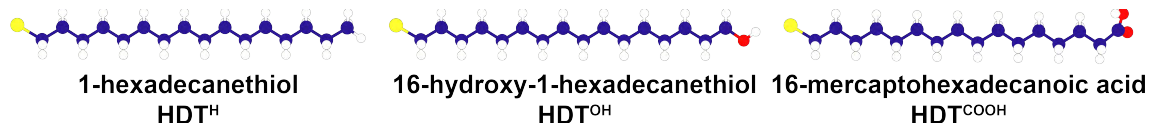


FIGURE 4.2 – Alkanethiyl structures considered in this study. The names are those of the parent thiols. White: hydrogen; blue: carbon; red: oxygen; yellow: sulphur. Their respective abbreviations are utilised throughout this text.

The ligands were modelled as thiyl radicals formed by the abstraction of a hydrogen atom from the thiol ($-\text{SH}$) group. Geometry optimisation of the isolated radicals was performed at the DFT level using the M06-2X functional [372] in combination with Grimme’s D3 dispersion corrections [128] and the Ahlrichs def2-TZVP basis set for all atoms except sulphur, for which the def2-TZVPPD basis set was employed [132]. Vibrational frequency calculations confirmed all optimised structures as energy minima, and natural bond orbital (NBO) analysis [373] provided partial charges for use in the FF parametrisation. All DFT calculations were performed using GAUSSIAN 16 REV A.03 [284].

The gold substrates, consisting of five-layer slabs of Au(111) and Au(100), were constructed using MBN STUDIO 5.0 [374]. The Au(111) substrate had dimensions of $59.856 \text{ \AA} \times 95.172 \text{ \AA}$ (3960 atoms), while the Au(100) substrate had the size of $73.408 \text{ \AA} \times 73.408 \text{ \AA}$ (3240 atoms). Au–Au interactions were described using the Finnis–Sinclair many-body potential [375, 376]. Each gold slab was initially optimised under periodic boundary conditions using the

velocity quenching algorithm with a 0.1 fs time step. All tolerances were set to 10^{-6} , and the optimisations were run until these criteria were met. For all subsequent simulations, the bottom-most layer was frozen to simulate bulk crystal behaviour. Morse [342] and LJ [377] parameters for Au–S interactions were applied to account for the chemisorption of the alkanethiols onto the gold surface.

To evaluate the suitability of different FF parametrisations, we tested eight different sets that varied in their bonded parameters, partial charge values, and LJ parameters (Table 4.1). Each FF set was assessed based on its ability to reproduce key geometrical properties of SAMs, such as the ligand tilt angle, on both the Au(111) and Au(100) surfaces.

TABLE 4.1 – Nomenclature and composition of the different force field sets tested in this work. MMFF was obtained from SwissParam.

Set	Bonded	Charges	Lennard-Jones
1	CGenFF	CGenFF	CGenFF
2	CGenFF	NBO	CGenFF
3	CGenFF	CGenFF	UFF
4	CGenFF	NBO	UFF
5	MMFF	CGenFF	MMFF
6	MMFF	NBO	MMFF
7	MMFF	CGenFF	UFF
8	MMFF	NBO	UFF

4.2.1 EVALUATING FF PERFORMANCE VIA LIGAND TILT ANGLE

FOR THE TILT ANGLE ANALYSIS, ligands were arranged in a rectangular grid with target densities of 4.67 nm^{-2} (as measured experimentally for Au(111) [351]) as well as 90% of this value for both surfaces. The actual densities were 4.67 nm^{-2} and 4.21 nm^{-2} for Au(111), and 4.73 nm^{-2} and 4.17 nm^{-2} for Au(100). In order to scan the α angles, the ligands had to be positioned accordingly. We considered a range from 0° to 40° in steps of 5° . To drive the ligands to the required positions while ensuring the boundary conditions were respected, we ran short MD simulations in which we applied a constant velocity to each ligand atom. No interaction parameters were included in these short simulations. The velocity components were calculated according to

$$v_x(A) = 0, \quad (4.1)$$

$$v_y(A) = -\sqrt{(Y_A - Y_S)^2 + (Z_A - Z_S)^2} \times \frac{\sin 30^\circ}{30 \text{ fs}}, \quad (4.2)$$

$$v_z(A) = -\sqrt{(Y_A - Y_S)^2 + (Z_A - Z_S)^2} \times \frac{1 - \cos 30^\circ}{30 \text{ fs}}, \quad (4.3)$$

where A is the atom for which the velocity is being calculated, with y and z initial coordinates given by Y_A and Z_A respectively; and Y_S and Z_S are the initial y and z coordinates of the S atom, respectively. This allows for an approximate 1° fs^{-1} drive around the S atom on the yz plane. The selected angles were then controlled by the simulation length accordingly. The simulation time step used was 0.1 fs.

A custom-built Python code was utilised to set up and handle all files related to these calculations. Having built all initial geometries for each angle as described above, we performed velocity quenching geometry optimisation for 25 000 steps on each point in order to relax any distortion introduced by the angle-driving procedure. It was important, however, to ensure that the optimisation procedure did not move the chains away from the intended initial angle. Thus, for the subsequent analysis, a particular step from each of the optimisation trajectories was utilised for each different FF parameter set. We provide a description of the strategy for such selection in § 4.2.2. The optimisations were performed using the velocity quenching algorithm with 0.01 fs time step for a total of 25 000 steps. All tolerances were set to 10^{-6} . The interactions were treated under the linked-cell algorithm [82, 378]. The Coulomb interactions were treated using the PME algorithm with $\alpha = 0.169 \text{ \AA}^{-1}$, real cutoff of 12 $\text{\AA}$, and a $64 \times 64 \times 128$ mesh grid. The van der Waals cutoff was set to 10 $\text{\AA}$. Three-dimensional periodic boundary conditions were used. The simulation box had a height of 50 $\text{\AA}$ and widths matching those of the substrate surface. Trajectory and log files were updated every 100th step.

4.2.2 THE CHOICE OF OPTIMISATION STEPS FOR THE LIGAND TILT ANGLE ANALYSIS

THE STRATEGY UTILISED IN the tilt angle analysis described above is practical and fast to generate the high number of input geometries necessary for the simulations. The drawback is that the use of an approximate linear velocity to drive the angles introduces stretch and compression to the bonds. Thus, to minimise the extraneous energy contribution from this artefact, short optimisations were run. The optimisation also contributed to better positioning of the sulphur atoms over the surface. However, since there are preferred angles for the molecules, a too long optimisation would disrupt the initial arrangement. Therefore, for the angle analysis, a particular optimisation step has been chosen. This step should be advanced enough to relax the distortions and sulphur interaction but not too far to deviate too much from the initial intended configuration.

A way of evaluating the optimisation step to be sampled is by following the total energy, the tilt angle, and the sulphur atoms root-mean-squared deviations (RMSD) from the initial positions, as a function of the number of optimisation steps. Two exemplary cases are shown in Figure 4.3. In both cases, the selected systems are SAMs on Au(111) with a density of 4.67 nm^{-2} and with the Set 4 of FF parameters. For both cases, slight alterations of tilt angle happen, but they are not significant in any point along the optimisation. The sulphur

atoms adjust their positions in very similar ways in both cases, with the major displacements happening before 5000 optimisation steps. Ideally, the sampled point should be selected when S atoms had virtually stood still, which happens around 20 000 optimisation steps. This is possible for HDT^{H} , but not for HDT^{COOH} . The reason is that, while for HDT^{H} the potential energy slightly decreases from 10 000 steps on, for HDT^{COOH} there is a stepwise decrease of the potential energy. The plateau after 15 000 steps happens after distortion of the chains' carbon backbone out of the original molecular plane—a scoliosis-like distortion—starting from the head-group. Thus, for HDT^{COOH} , the selected optimisation step was 7000. Not all systems behaved smoothly, so that some data shown in § 4.3 and Appendix B do contain some distortions. As this analysis is only a screening process, not meant to be quantitative, the results are satisfactory for our purposes. Table 4.2 summarises the steps selected for each case.

TABLE 4.2 – Optimisation steps sampled for tilt angle scans analysis. For each gold surface, the values apply to both densities tested in this work.

Set	Au(100)			Au(111)		
	HDT^{COOH}	HDT^{H}	HDT^{OH}	HDT^{COOH}	HDT^{H}	HDT^{OH}
1	3000	3000	3000	10 000	20 000	20 000
2	3000	3000	3000	10 000	20 000	20 000
3	4000	4000	4000	10 000	20 000	20 000
4	4000	4000	4000	7000	20 000	20 000
5	4000	3000	3000	10 000	20 000	20 000
6	3000	3000	3000	10 000	20 000	20 000
7	4000	3000	3000	10 000	20 000	20 000
8	4000	3000	3000	10 000	20 000	20 000

4.2.3 ANGLE ANALYSIS ALGORITHM

TO ANALYSE THE LIGAND angles from the dynamics simulations we considered only the 12 carbon atoms closest to the surface for each chain, as well as the sulphur head-group. The reason for excluding the top part of the chain is that the intermolecular interaction of the terminal groups can disrupt the local order of the chains, particularly in the case of HDT^{COOH} . The vector $\mathbf{m}$ for each molecule is obtained by finding the principal component vector for the collection of the coordinates of the carbon and sulphur atoms. This is the eigenvector of the covariance matrix of their Cartesian coordinates associated with the largest eigenvalue.

The tilt angle α is calculated as the angle between $\mathbf{m}$ and the z axis. This is obtained for each molecule in a given frame of the simulation. The precession angle β is calculated by projecting the vector $\mathbf{m}$ for each molecule in a frame on the xy plane and calculating the angle between the projected vector and the y axis. For both these angles, the ensemble

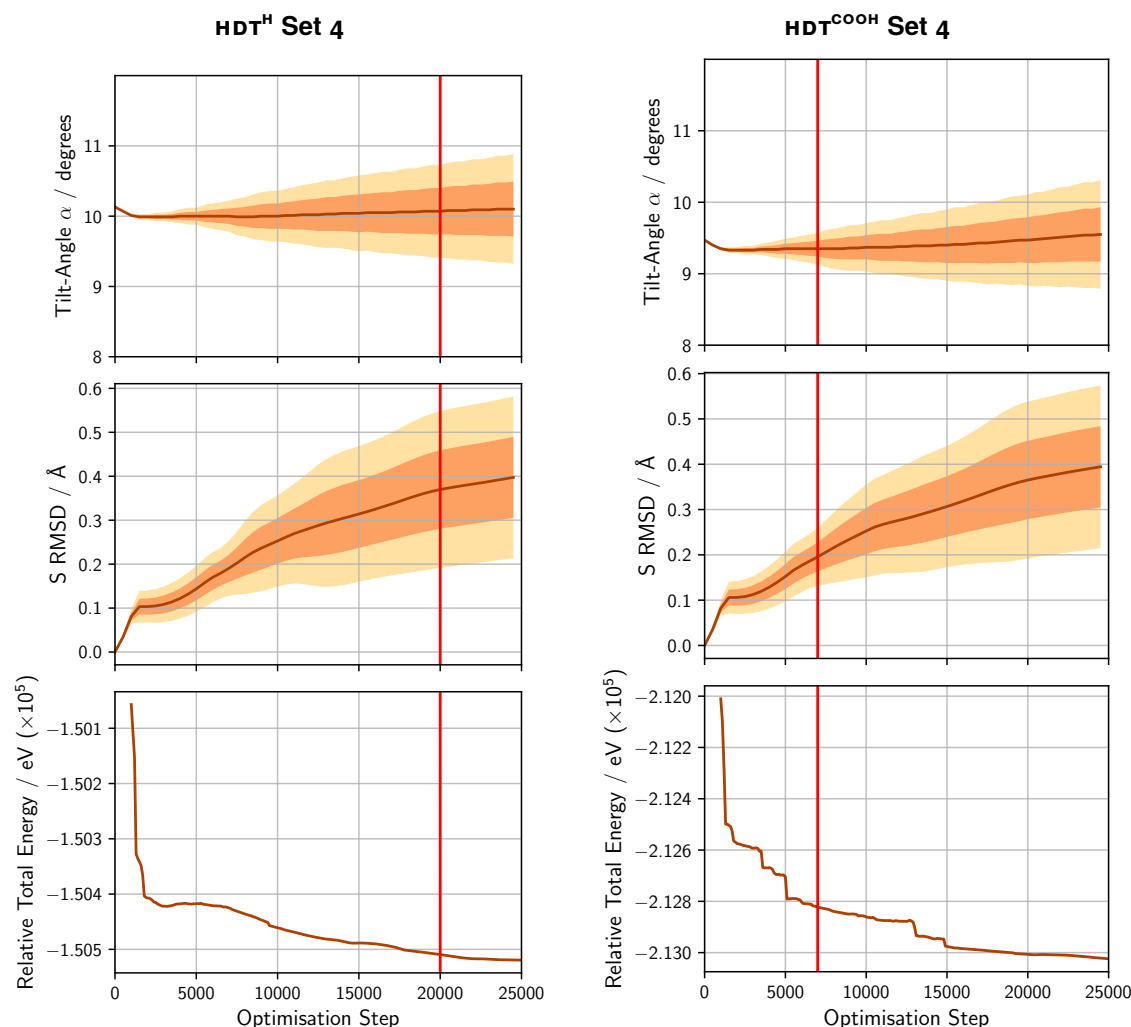


FIGURE 4.3 – Auxiliary plots for optimisation step selection utilised for the tilt angle analysis for two exemplary cases. Plots show the evolution of ligand tilt angle (top), sulphur RMSD (middle), and relative total energy (bottom) along the optimisations. Both cases are of SAMs on Au(111) at a density of 4.67 nm^{-2} . Vertical red line show the selection of optimisation step for the tilt angle analysis.

averages and standard deviations are plotted as a function of the simulation step. Finally, for the twist angle ω , the vector connecting the S atom to the immediate C atom in each chain is obtained. The angle between the projection of this vector and the projection of the vector $\mathbf{m}$ on the xy plane is then calculated as ω . Histograms for ω for any frame in a simulation can be calculated. While α is unsigned, β and ω range from -180° to 180° , with counterclockwise angles being considered positive. This angle analysis was performed by a custom-built Python script using MDtraj [379] and Matplotlib [380].

4.2.4 FULL GEOMETRICAL DESCRIPTION

THE BEST-PERFORMING PARAMETER set (Set **3**, see below) was further validated by constructing SAMs on Au(111) with experimentally observed sulphur-atom arrangements and superlattice patterns for all three ligands [342]. Long velocity quenching optimisation runs (three million steps) confirmed the stability of these structures and the ability of the chosen parameter set to describe correctly the adsorption sites and tilt angles. All convergence tolerances, namely, displacement ($\text{\AA}$), maximum displacement ($\text{\AA}$), and force ($\text{eV \AA}^{-1}$), were set to 10^{-6} . These thresholds were not reached by the end of the optimisation cycles. This is because the velocity quenching algorithm can cycle around shallow minima, as discussed in § 2.2.2.1. Rather than a drawback, this algorithm was selected intentionally for this property. If the FF parameters were not robust, the system's geometry would easily drift from the initial configuration under this optimisation. The remaining optimisation parameters were the same as described above. We analysed the ligand tilt angle α and precession angle β frame by frame in the same way as described above. Because of the larger mobility of the chains, the analysis of ω angles described above was not suitable and had to be attested visually from the trajectory snapshots.

Finally, trial MD simulations were performed starting from the final optimised geometry for the HDT^H SAM on Au(111), using the selected FF parameter set. The system was simulated for 10 ns at 300 K, with a time step of 1 fs using the velocity Verlet integrator. This choice of integration algorithm is important in the NVT ensemble since synchronous calculation of position and velocities are necessary for the thermostat performance, as discussed in § 2.2.2.2. A Langevin thermostat with damping time of 100 fs was applied. charge-damping factors ranging from 0.0 to 1.0 in steps of 0.1 were applied to fine-tune the partial charges, followed by a refinement in steps of 0.025 once an optimum value was identified (see § 4.3.7). All other simulation parameters were the same as those for the optimisations described above.

4.3 RESULTS AND DISCUSSIONS

THIS SECTION IS ORGANISED as follows. In § 4.3.1, we assess different force field sets by comparing the geometries of isolated alkanethiol ligands with DFT references to establish an initial benchmark. § 4.3.2 then explores how nonbonded parameters, particularly the interplay between electrostatic and van der Waals interactions, affect the ligand tilt angle. In § 4.3.3, we focus on tilt angle analysis for SAMs on Au(111) considering different charge-damping factors, while § 4.3.4 extends this investigation to Au(100). § 4.3.5 and § 4.3.6 discuss how coverage density and ligand arrangement influence the geometry and energetics of SAMs. Finally, § 4.3.7 reports on the fine-tuning of partial charges that ensures stability of the system upon 300 K MD simulations, thus yielding the final FF parameter set.

4.3.1 INITIAL FORCE FIELD ASSESSMENT WITH ISOLATED LIGANDS

AS AN INITIAL EVALUATION of the quality of each FF set, we conducted a detailed comparison of the MM-optimised geometries of the three thiol radicals—1-hexadecanethiol (HDT^{H}), 16-hydroxy-1-hexadecanethiol (HDT^{OH}), and 16-mercaptohexadecanoic acid (HDT^{COOH})—with their corresponding geometries obtained by DFT optimisation. The RMSD values for the MM- vs DFT-optimised geometries are listed in Table 4.3. This comparison provides an important basis for evaluating the parametrisation quality of the selected FF combinations and their ability to reproduce reliable molecular geometries.

TABLE 4.3 – Comparison between MM- and DFT-optimised geometries as coordinates RMSD (Å) for each FF set (see Table 4.1) for the three ligands (as thiol radicals) considered in this work. HDT^{H} = 1-hexadecanethiol; HDT^{OH} = 16-hydroxy-1-hexadecanethiol; HDT^{COOH} = 16-mercaptohexadecanoic acid.

Set	HDT^{H}	HDT^{OH}	HDT^{COOH}
1	0.241	0.252	0.359
2	0.237	0.253	0.365
3	0.239	0.251	0.165
4	0.236	0.253	0.203
5	1.487	1.480	0.467
6	1.482	1.489	1.128
7	1.482	1.486	0.361
8	1.479	1.484	0.390

The data show a consistent trend: SwissParam (MMFF, Sets 5–8) generally underperforms compared to CGenFF (Sets 1–4) for all three ligands, with the RMSD values for SwissParam being up to six times higher. This discrepancy is most evident for HDT^{H} and HDT^{OH} , while for HDT^{COOH} , the differences between the two FF sources are somewhat mitigated. This observation suggests that the inherent parametrisation approach used in MMFF may not be as robust as that of CGenFF, especially for complex or functionalised ligands.

As expected, nonbonded interactions play a relatively minor role in determining the optimised geometries of isolated molecules whose structures are mainly governed by bonded parameters. Nevertheless, slight improvements were observed when LJ parameters from UFF were employed (Sets 3, 4, 7, and 8). These improvements are particularly noticeable for HDT^{COOH} , where UFF parameters give slightly better agreement with DFT geometries than those derived from CGenFF or SwissParam. For HDT^{H} and HDT^{OH} , the differences introduced by the choice of LJ parameters are negligible, evidencing the limited influence of these parameters in the absence of intermolecular interactions.

The choice of partial charge assignment—whether from CGenFF or derived using NBO analysis—also influences the geometry optimisation results. Overall, CGenFF charges exhibit superior performance compared to NBO-derived charges, particularly for HDT^{COOH} . This

difference is likely to be due to the greater compatibility of CGenFF charges with the CHARMM FF framework, which ensures better parameter synergy during MM optimisation, and the fact that NBO charges are not devised to describe effective multipolar interactions as discussed in § 2.2.1. For HDT^H, the RMSD values are comparable regardless of the charge source, suggesting a reduced sensitivity to partial charges for simpler alkanethiols.

The performance of the FF combinations tested in this work varies, with Sets **1**–**4** offering reasonable accuracy in reproducing DFT geometries. Among these, Set **3** demonstrates the best overall performance, achieving a consistent balance between the contributions of the bonded and nonbonded parameters. The superiority of Set **3** is particularly evident in its handling of HDT^{COOH}, where the interplay between the carboxyl terminal group and the rest of the molecule requires a more nuanced parametrisation.

4.3.2 EVALUATING THE EFFECT OF NONBONDED PARAMETERS

WHILE THE BONDED PARAMETERS primarily define the molecular geometry of each alkanethiol chain, the nonbonded parameters are expected to play a more significant role in influencing the overall morphology of the SAMs. To evaluate this effect, the behaviour of the ligand tilt angle α (Figure 4.1) was investigated for different FF parameter sets. This assessment was performed by energy scans of α , incorporating a homogeneous partial charge damping factor to investigate the interplay between the Coulomb and van der Waals interactions. For each angle–charge damping combination, we performed short geometry optimisations, selecting specific optimisation steps to plot the resulting energies (see § 4.2.2). The provided scans highlight how the FF parameters influence the stability and preferred configurations of the SAMs.

A comprehensive analysis of the energy components contributing to the total system energy was performed, focusing on their dependence on the ligand tilt angle α . For clarity and brevity, Figure 4.4 shows the results for two representative systems, both corresponding to HDT^H SAMs on Au(100). The first system (left-side panel) was simulated using the FF parameter Set **1**, while the second (right-side panel) was simulated using Set **3**. The total energy for the system is the sum of all (1) bonded (bond, angle, and dihedral) and (2) nonbonded (Coulomb and van der Waals) interactions defined by the CHARMM parameters, as well as (3) the Au–S Morse bonded interaction (included in the “pairwise” contribution along with the van der Waals LJ interactions) and (4) the Finnis–Sinclair many-body potential between the Au atoms (this last contribution, which is nearly constant, is not shown in the plots). The complete data set is presented in § B.1.1.

The total energy profile for Set **1** shows a minimum at a tilt angle below 10°, followed by a sharp increase in energy as α grows. This behaviour is predominantly driven by Coulomb repulsion, indicating that electrostatic interactions are a critical factor for this FF configuration. At first sight, one might infer that the partial charges in Set **1** are poorly parametrised and

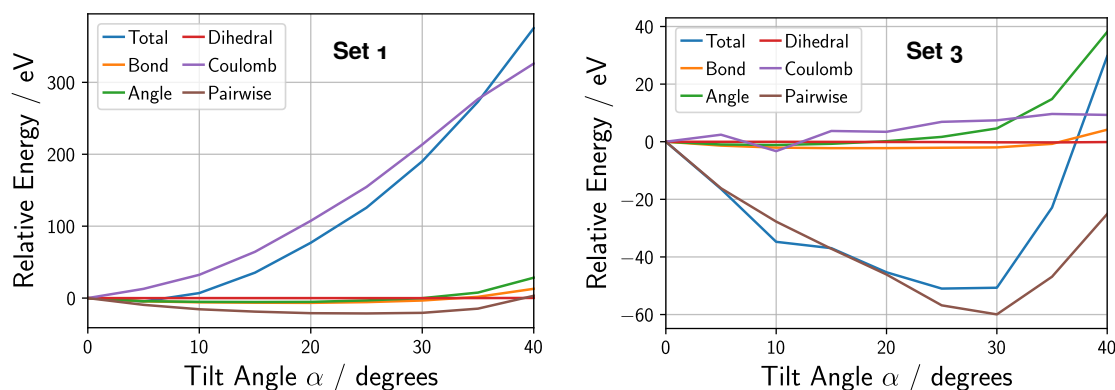


FIGURE 4.4 – Energy decomposition analysis as a function of ligand tilt angle for FF parameter sets **1** and **3** for HDT^{H} on $\text{Au}(100)$ with a density of 4.17 nm^{-2} . For each component, the relative energy is referenced to the respective value at 0° .

cause the system to stabilise at smaller α angles. However, if we compare the energy profile of Set **1** with that of Set **3**, which differ only in the choice of LJ parameters (Table 4.1), the data for Set **3** show that LJ interactions, rather than Coulomb forces, are the primary determinants of the energy dependence. The pairwise interaction component, which included both LJ and the Au–S Morse potential, drives the stabilisation. Since the Au–S bonded interaction remains constant after sufficient optimisation, it is evident that the variation of the LJ interactions determines these differences.

4.3.3 TILT ANGLE ANALYSIS ON $\text{Au}(111)$

HAVING CONFIRMED THAT the LJ components are primarily responsible for determining the tilt angles α , we now examine in more detail the HDT^{H} SAM on $\text{Au}(111)$ at a surface density of 4.67 nm^{-2} , the highest of the two densities considered here. Figure 4.5 presents the energy profiles, showing both the pairwise interaction and the total energy, as functions of the tilt angle α for each of the FF sets listed in Table 4.1. These profiles have been analysed for different charge-damping factors, ranging from 0.0 (fully damped, ie, all atomic partial charges are equal to zero) to 1.0 (undamped).

To allow for a clear comparison between the different FF sets and charge damping, the total energy curves for each set (Figure 4.5, bottom panel) were normalised to their respective values at $\alpha = 0^\circ$. Similarly, the pairwise interaction energy curves for all FF sets (Figure 4.5, top panel) have been calculated with respect to the values at $\alpha = 0^\circ$ with a zero charge damping factor. This normalisation ensures that variations in the energy profiles can be directly attributed to the changes in tilt angle α and the influence of the charge damping factor.

The first notable observation is the dependence of the pairwise interactions on the partial charges, which is evident for Sets **1**, **2**, **5**, and **6**. This is demonstrated by the lack of

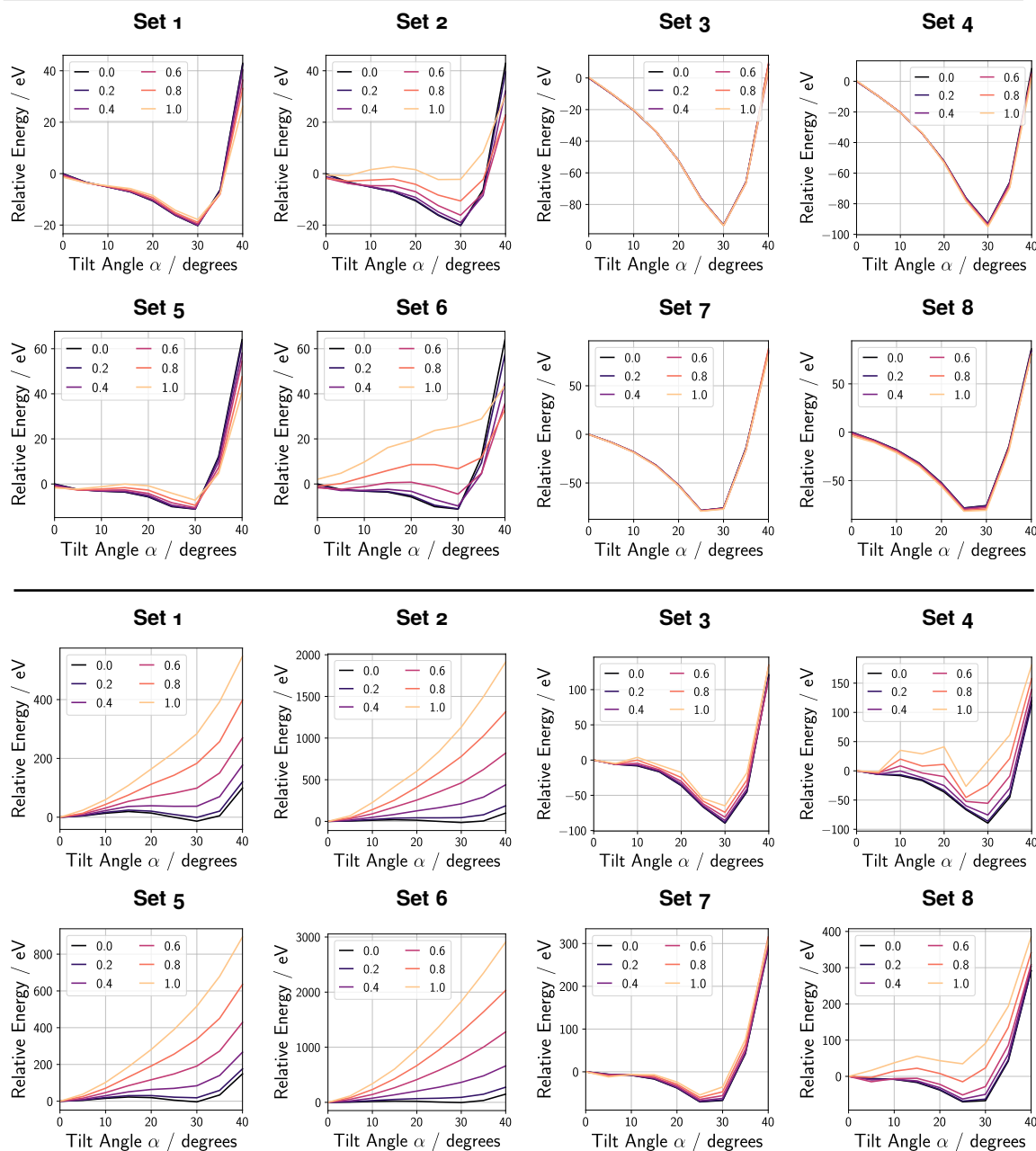


FIGURE 4.5 – Ligand tilt angle analysis for HDT^{H} on $\text{Au}(111)$ at a density of 4.67 nm^{-2} . Pairwise interaction energies (top) and total energies (bottom) against ligand tilt angle α for different charge-damping factors.

superposition in the pairwise interaction energy scans across different charge-damping factors for these sets. This is more pronounced for Sets 2 and 6. In contrast, Sets 3, 4, 7, and 8 exhibit pairwise energy profiles that are nearly identical across different damping factors, indicating a better separation of nonbonded parameter effects.

This dependence suggests an undesirable coupling between the nonbonded parameters, particularly the Coulomb and LJ interactions, which should ideally behave as independently additive in the CHARMM framework. The main source of this artefact appears to be the choice of LJ parameters. The sets employing UFF LJ parameters (ie, Sets **3**, **4**, **7**, and **8**) show minimal or no coupling, effectively mitigating this issue. Conversely, sets without UFF LJ parameters fail to decouple the interactions, resulting in distorted energy profiles.

The strength of this dependence is further influenced by the values of the partial charges used. Sets utilising NBO partial charges show a stronger dependence on the charge damping factor than those using CGenFF charges. Even among sets with UFF LJ parameters, such as Sets **7** and **8**, a slight residual dependence remains when NBO charges are used. These results highlight the critical interplay between the parametrisation of partial charges and LJ potentials and emphasise the superior performance of combinations that minimise this coupling.

Looking now at the total energies (Figure 4.5, bottom panel), Coulomb repulsion dominates the behaviour of Set **1** (Figure 4.4), most likely because at larger tilt angles the chains are oriented so that their charged sites are located closer together. Without appropriately chosen LJ parameters to buffer these interactions, electrostatic forces become the primary factor increasing the total energy. This pattern is similarly observed in Sets **2**, **5**, and **6**, where the energy rises steeply with increasing angle. The effect is even more pronounced in Sets **5** and **6**, which rely on NBO partial charges that are larger in absolute value than those provided by CGenFF for the hydrocarbon chain atoms (see Table B.1). Consequently, the electrostatic repulsion is enhanced, leading to higher total energies. In contrast, Sets **3**, **4**, **7**, and **8**—especially those with UFF LJ parameters—mitigate the dominance of Coulomb repulsion, resulting in more stable energy profiles. Although systems with NBO charges in this group (Sets **4** and **8**) still exhibit greater variation when the charge damping factor is varied, their overall energetic behaviour remains less sensitive to angle changes compared to the sets without UFF parameters.

It is evident at this stage that the sets with UFF LJ parameters consistently outperform the other parameter sets. The non-UFF LJ sets exhibit shallow minima in their pairwise interaction energy curves, sometimes accompanied by slight energy barriers between 0° and 30° . These shallow minima and barriers suggest a lack of adequate stabilisation for the ligand tilt angle, which is critical for accurate modelling of the system. In contrast, the UFF LJ parameter sets (Sets **3**, **4**, **7** and **8**) exhibit well-defined and significantly deeper minima, free of such barriers, providing a much more stable and physically realistic description of the system. This trend is reflected most clearly in the total energy profiles, especially for Sets **3** and **7**, further confirming the superiority of the UFF LJ parameters and the inadequacy of the NBO partial charges.

Among the UFF LJ sets, those with bonded parameters derived from CGenFF (Sets **3** and **4**) exhibit particularly deep and sharp minima around 30° , which closely match the experimental observations [336, 337, 342, 343]. This suggests that the combination of UFF LJ parameters and CGenFF bonded parameters provides a more reliable description of the ligand tilt angle and its associated energy landscape for the considered molecules. The use of NBO partial charges (as in Sets **4** and **8**) introduces some instability and variation, particularly in response to charge damping, and obscures the energy minimum around 30° . Thus, Set **3**, which integrates UFF LJ parameters with CGenFF charges, emerges as the most robust and accurate choice for describing the system.

The conclusions drawn from the analysis of HDT^{H} are largely applicable to the HDT^{OH} and HDT^{COOH} ligands, although some minor differences are observed (see Figure B.19 and Figure B.21). For HDT^{OH} , the interference between Coulomb and LJ potentials is significantly reduced in Sets **5** and **6**. This reduction is evident in the LJ energy profiles and becomes particularly clear in the total energy curves, which show a less steep increase at higher tilt angles than is observed for HDT^{H} . This improvement suggests that the interaction balance in these sets is better suited for hydroxyl-terminated ligands. Set **3** again emerges as the best descriptor among its peers.

Similar energy profiles have been observed for HDT^{COOH} , and a less steep increase in total energy occurs for non-UFF sets, although all of them present a barrier between 0° and 30° , as well as shallow minima at 30° . This effect is most likely due to inter-chain interactions between the carboxyl groups, which introduce additional complexity to the system. Notably, Sets **3**, **4**, and **8** show slight interactions between LJ and Coulomb potentials that were not observed for the other ligands. These anomalies highlight the possible need to refine the parameters associated with the carboxyl group to achieve a more consistent description. Once again Set **3** offers the best performance over all others.

4.3.4 TILT ANGLE ANALYSIS ON Au(100)

A SIMILAR INVESTIGATION WAS carried out for the SAMs on Au(100) at a density of 4.17 nm^{-2} , the lowest of the two densities tested. The results for the HDT^{H} ligand are depicted in Figure 4.6. The general conclusions drawn from the analysis of the SAMs on Au(111) largely apply to this case as well. However, there are two notable differences. Firstly, the energy profiles for Au(100) have generally less pronounced minima, approaching a more parabolic shape. This is in contrast to the sharper, V-shaped curves observed for Au(111). Secondly, the equilibrium tilt angle for the ligands on Au(100) is smaller than that for Au(111). This result is consistent with the experimental characterisations discussed above. The less pronounced minima observed for Au(100) correlate with the lack of experimental consensus on the precise values of α for alkanethiol SAMs on this surface. This ambiguity likely reflects

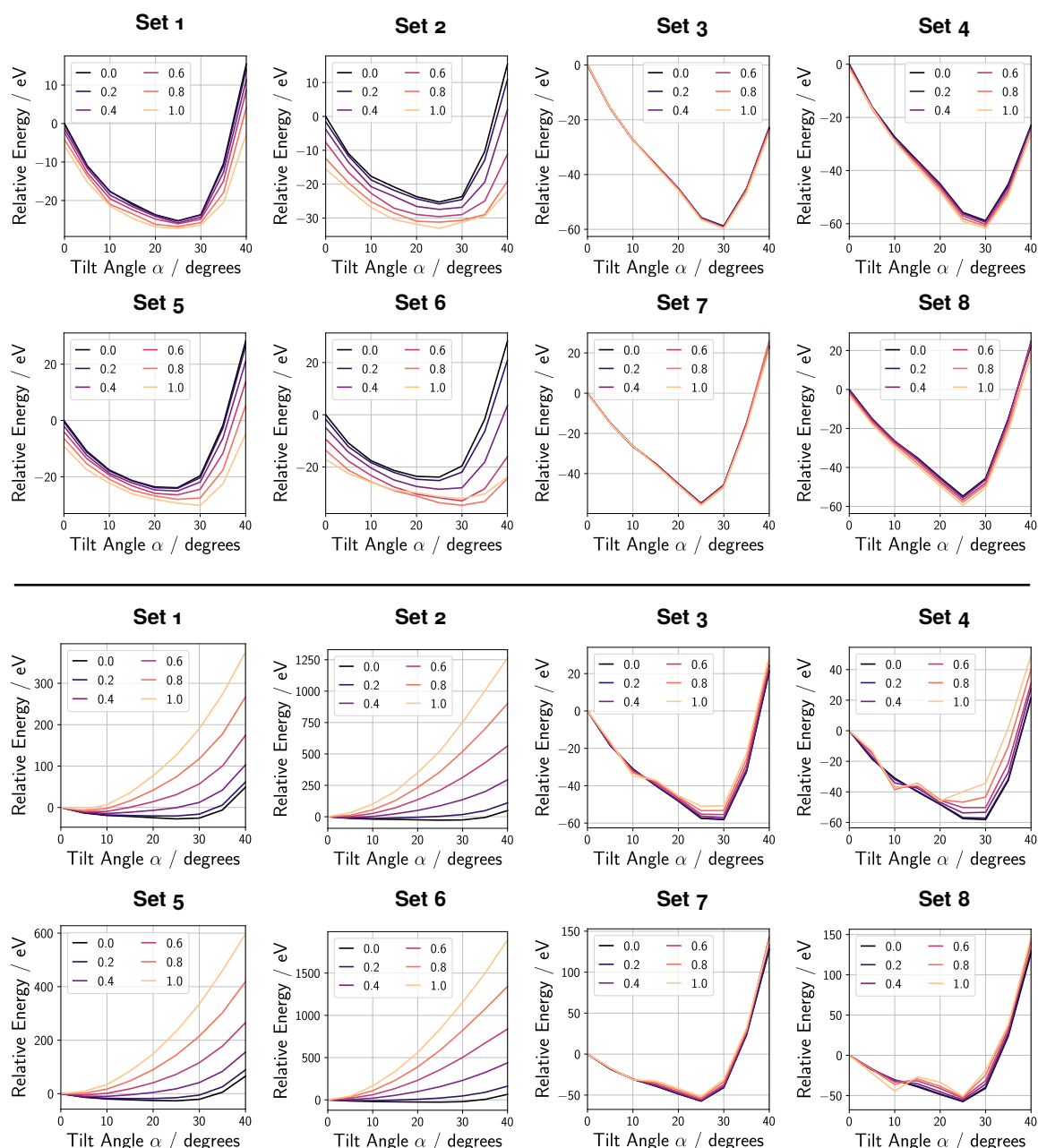


FIGURE 4.6 – Ligand tilt angle analysis for HDT^{H} on $\text{Au}(100)$ at a density of 4.17 nm^{-2} . Pairwise interaction energies (top) and total energies (bottom) against ligand tilt angle α for different charge-damping factors.

the inherent structural flexibility and variability of the SAMs on the $\text{Au}(100)$ surface, in contrast to the more ordered arrangements on $\text{Au}(111)$.

The differences in behaviour between the different ligands for SAMs on $\text{Au}(111)$ discussed previously are similarly observed for SAMs on $\text{Au}(100)$, with significantly more distortion in the energy profiles for sets using NBO partial charges in the case of HDT^{COOH} . These

variations highlight the influence of terminal group interactions and chain organisation on the energy profiles and tilt angle distributions. Further details of these differences are shown in Figure B.16 and Figure B.18.

4.3.5 INFLUENCE OF SURFACE COVERAGE DENSITY

NEXT, WE EVALUATE THE impact of surface coverage on the morphology of SAMs by analysing different coverage densities on Au(100) and Au(111) surfaces. We considered two other cases: a slightly higher density of 4.73 nm^{-2} for Au(100) and a slightly lower density of 4.21 nm^{-2} for Au(111). These densities are compared with the experimentally measured values of 4.67 nm^{-2} for Au(111). For all cases, the total and pairwise interaction energies increase steeply as the ligand tilt angle α deviates from its low equilibrium value (see Figure B.13–Figure B.15, Figure B.22–Figure B.24).

This behaviour suggests that densities deviating from an optimum value, whether *higher* or *lower*, disrupt the intermolecular interactions responsible for maintaining the molecular tilt angle. In both scenarios, Coulomb repulsion prevails, undermining tilt stability. At higher density, this occurs because the ligands are too closely packed, causing repulsion that overrides the stabilisation provided by the LJ interaction. Conversely, at lower density, the increased spacing prevents effective short-range LJ stabilisation.

While the optimal density (ie, the density that correctly reproduces the ligand tilt angle) for Au(111) is close to the experimental value, the optimal density for Au(100) exceeds the experimental benchmark for Au(111) by 0.06 nm^{-2} . Furthermore, despite its simple construction, the regular rectangular deposition does not capture the experimentally observed packing patterns, including the hexagonal sulphur arrangement and the superlattice formation of ligand chains, as shown in Figure 4.1. Therefore, in the next section, we discuss the results of simulations based on initial deposition patterns that explicitly reproduce the experimentally observed features of alkanethiol SAMs on Au(111).

4.3.6 FINAL DEPOSITION GEOMETRY ON Au(111)

FROM THE EVALUATION of the FF parameter sets, Set 3 consistently demonstrated superior performance compared to other configurations. Consequently, all subsequent analyses were carried out using Set 3 to further investigate its ability to reproduce the experimental morphological features of SAMs. To test its predictive ability, an initial geometry was constructed based on experimental observations, incorporating the hexagonal ($\sqrt{3} \times \sqrt{3}$) R30° arrangement of sulphur atoms and the $c(4 \times 2)$ superlattice packing of the ligand chains (see Figure 4.1). These arrangements, corresponding to Structure III from [342], were not spontaneously obtained from the initial rectangular grid arrangement, but have been shown in previous studies to stabilise when explicitly used as the starting geometry.

Pool *et al* [381] provided LJ parameters for sulphur atoms that demonstrated superior performance in a previous comparative study on the effect of sulphur LJ parameters on alkanethiol adsorption site on gold [364]. Substitution of these parameters into Set 3 resulted in improvement in structural predictions, leading us to substitute the original sulphur UFF parameters for these. The results of the MM optimisation are summarised in Figure 4.7. The optimised geometry achieves an average tilt angle $\alpha \approx 35^\circ$ (Figure 4.7A) and an azimuthal angle $\beta \approx 60^\circ$ (Figure 4.7B). The dispersion of these angles, shown by the shaded areas in the plots, is very small. The bimodal distribution of ω angles is centred at the values of $\omega \approx -25^\circ$ and -55° , corresponding to the nearest-neighbour and third nearest-neighbour Au directions, respectively (Figure 4.7C). These results are in good agreement with experimental data and the results obtained from Zhang, Goddard, & Jiang [342], underlining the effectiveness of the parameter set. The side and perspective views of the final geometry in Figure 4.7D clearly show the characteristic chain tilt angle, as well as the relative twist angle ω between the chains. The top view also shows the uniformity of the precession angle across the surface, as evidenced in Figure 4.7B. The inset provides a focused view of the sulphur head-group arrangement by isolating the first carbon atoms directly connected to the sulphurs. This representation confirms the stability of the $(\sqrt{3} \times \sqrt{3})$ R30° hexagonal arrangement and the formation of the $c(4 \times 2)$ superlattice shown in Figure 4.1, both of which are consistent with experimentally observed patterns.

4.3.7 PRELIMINARY MOLECULAR DYNAMICS SIMULATIONS

THIS WORK FOCUSES PRIMARILY on the impact of force field parameters on the energetic and structural properties of alkanethiol SAMs. A detailed analysis of the dynamical behaviour of these systems is planned as future investigations. However, omitting the dynamical results would leave this study incomplete, since the final parameter set must produce not only a stable, optimised geometry, but also structural integrity and stability at finite temperatures. As shown in the optimisation analysis above, partial charges significantly influence the total energy landscape, occasionally counteracting the van der Waals interactions and altering the depth and shape of the energy minima (see Figure 4.5). Although these effects were mitigated in the selected parameter set, the inclusion of thermal energy could still destabilise the system depending on the energy profile, potentially necessitating further fine-tuning of the partial charges.

To assess this aspect, we conducted a preliminary 10 ns MD simulation at 300 K for the HDT^H SAM, starting from the optimised geometry presented in § 4.3.6. As anticipated, we observed an additional impact of the partial charges on structural features at finite temperatures. We, therefore, conducted additional simulations with uniformly scaled charges, using a damping increment of 0.1. A uniform scaling factor of 0.7 (ie, 30% damping of the original values) was the minimal adjustment required to maintain the tilt angle near

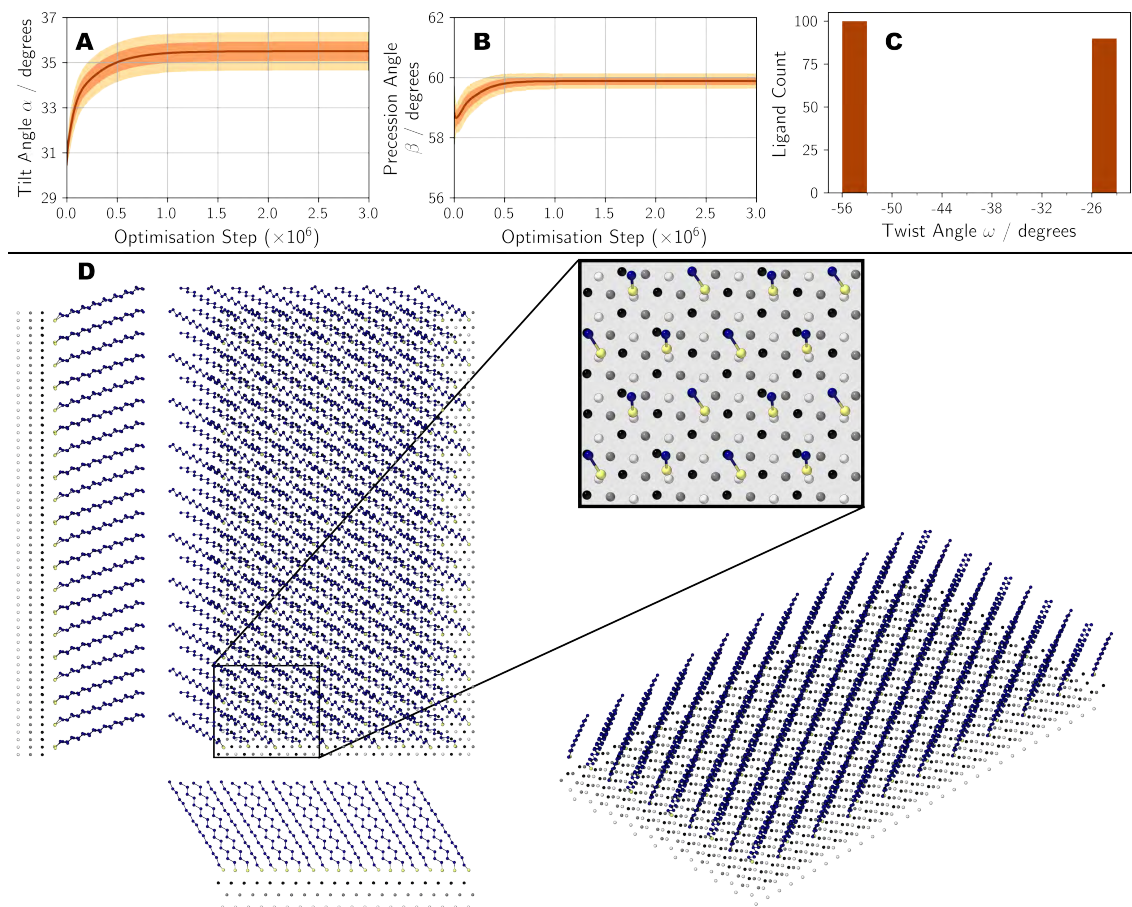


FIGURE 4.7 – Final HDT^{H} SAM model on Au(111) surface after 3 000 000 velocity quenching optimisation steps. The initial geometry replicates the $(\sqrt{3} \times \sqrt{3})$ R30° adsorption pattern and $c(4 \times 2)$ superlattice packing, consistent with Structure III from Zhang, Goddard, & Jiang [342]. Blue spheres: carbon; yellow spheres: sulphur; black, grey, and white spheres: top, middle, and bottom gold layers, respectively. (A) Evolution of the ligand tilt angle α during the optimisation; (B) evolution of the precession (azimuthal) angle β during the optimisation. In both cases, solid lines show mean values, while shaded areas represent one (orange) and two (yellow) standard deviations. (C) Histogram of the twist angles ω after optimisation. (D) Top and side orthographic projections, along with a perspective view, which illustrate the final system's geometry. The inset in (D) provides a closer view of the sulphur atom arrangement, showing only the carbon atoms directly attached to the sulphurs for clarity. Hydrogen atoms and the two bottommost gold layers are omitted for clarity. The edges of the system were trimmed for clearer visualisation.

the experimental value of 30°. Further reduction of the partial charges had a negligible effect on the overall structural ordering. We then further refined this analysis from 0.700 to 0.800 in steps of 0.025, obtaining the same stability observed at 0.7 up to 0.725, finally setting that as the optimum value (Figure 4.8). The need for a damping of the charges observed empirically can be understood in retrospect if we recall the fact that the CHARMM36 parameters are optimised for aqueous media [202], ie, a polarisable medium. Since we are

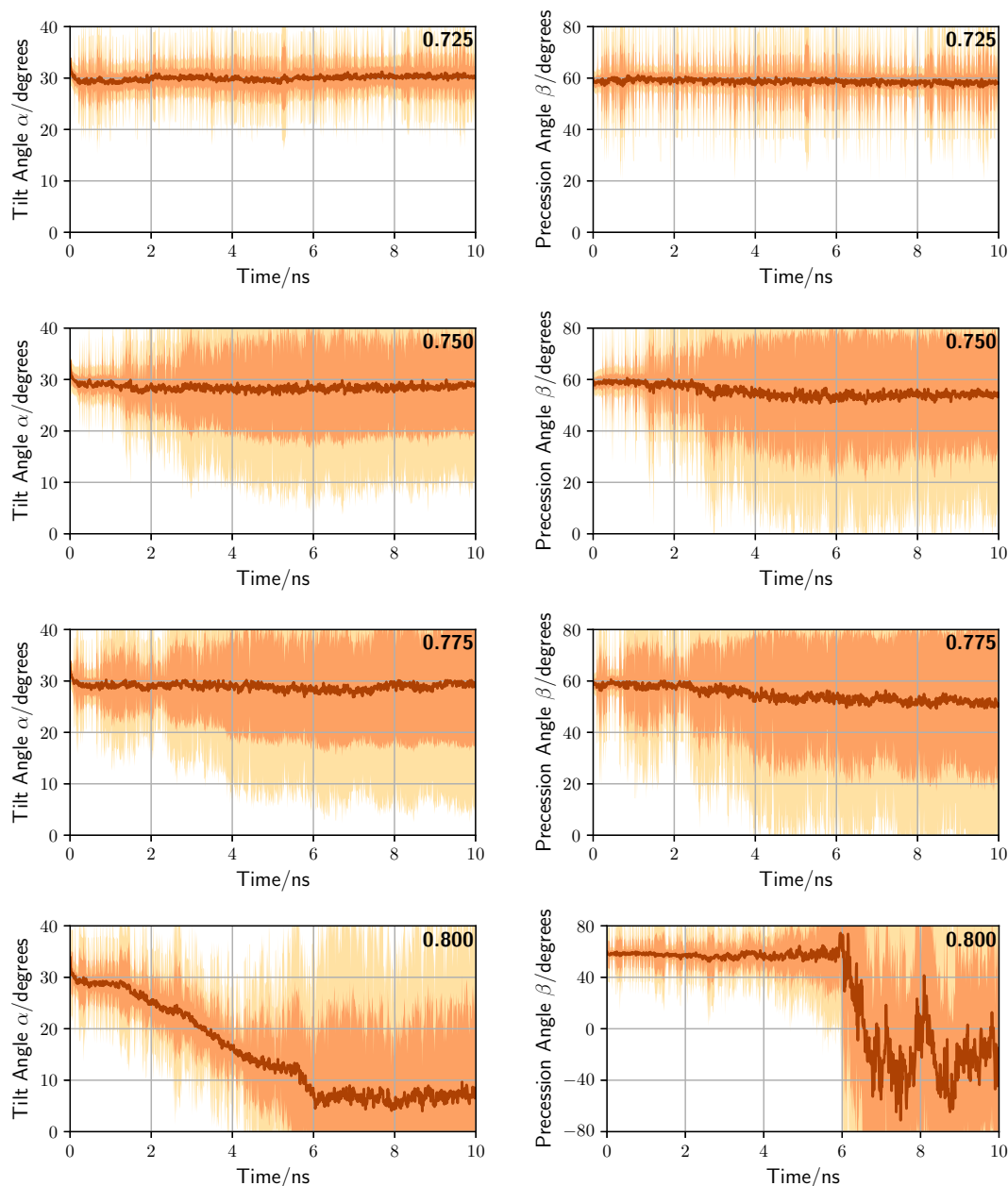


FIGURE 4.8 – Ligand tilt (α , left) and precession (β , right) angles vs 300 K MD simulation time for the final HDT^H SAM model on Au(111) surface for selected charge-damping factors (top right corners of each plot).

essentially simulating a system into a vacuum, the original charge distribution is overpolarised. The value of 0.725 is very close to the inverse-square-root of the high-frequency dielectric constant $\epsilon_{\infty} = 1.9$ for a long-chain hydrocarbon. The scaling by $1/\sqrt{\epsilon_{\infty}}$ is known to be important for parametrisations of nonpolarisable FFs such as CHARMM [382].

Besides the structural properties, another important property of SAM systems is their adsorption energy. Experimental estimates place the Au–S binding energy on Au(111) at approximately 44 kcal mol^{-1} , based on temperature-programmed desorption data [383]. Interchain interactions are estimated to contribute an additional 1 kcal mol^{-1} to 2 kcal mol^{-1} per methylene group [337, 351]. The final optimised geometry obtained with our selected FF parameters, including the adjusted partial charges, yields a total adsorption energy of $-61 \text{ kcal mol}^{-1}$, which falls within the expected range when both Au–S binding and interchain contributions are taken into account.

Through these investigations, we have successfully identified a set of force field parameters capable of accurately reproducing the experimentally observed features and previously reported computational results for three alkanethiol SAMs on Au(111). While the lack of well-defined structural data in the literature prevented explicit investigation of SAMs on Au(100), we expect the derived parameter set to reliably describe these systems as well. The strategy employed here can be extended to other functionalised alkanethiols, with different chain lengths and adsorbed on different surfaces. The complete final parameter sets are provided in Table B.2 as ready-to-use files. The final PSF files already include the correction to the partial charges.

4.4 CONCLUSIONS

IN THIS CHAPTER, WE proposed and demonstrated a systematic approach to evaluate how bonded interactions, atomic charges, and LJ parameters affect the geometrical and energetic characteristics of both pristine and functionalised alkanethiol SAMs on Au(100) and Au(111). To this end, we have performed an energy decomposition analysis as a function of the ligand tilt angle, which isolates the influence of each parameter on the overall behaviour of the SAM. Application of this framework allowed us to identify that the FF set combining CGenFF bonded parameters and charges with UFF LJ parameters consistently delivers superior performance, reproducing experimentally observed structural and energetic features with high accuracy. The LJ parameters effectively govern the equilibrium tilt angle of the alkanethiol chains, allowing the formation of well-defined energy minima that closely match experimental data, particularly for Au(111). This parametrisation also mitigates undesirable coupling between Coulomb and van der Waals interactions, enhancing the consistency and reliability of the model. The inclusion of carboxyl and hydroxyl ligands in our study addresses a notable limitation in the literature, which has mainly focused on unfunctionalised ligands in molecular-mechanics modelling of alkanethiol SAMs. Furthermore, our approach also paves the way for detailed investigations into the effect of varying surface nature, orientation, and ligand chain length.

Further analysis of surface coverage density and ligand packing reveals that simplistic rectangular grid arrangements inadequately capture the complexity of SAM organisation. A configuration reflecting the experimentally observed $(\sqrt{3} \times \sqrt{3})$ R30° hexagonal head-group arrangement and the $c(4 \times 2)$ superlattice patterns stabilises the system at realistic adsorption sites and chain orientations. The chosen parameter set effectively reproduces key experimental trends, including the distinct structural behaviours observed on Au(111) and Au(100). The systematically validated framework presented here provides an effective model for the simulation of SAM-coated substrates. The validation of the parametrisation over a range of ligands, densities, and lattice arrangements provides a basis for improving the predictive power of the simulations.

In recent years, complex many-body potentials, such as the charge-optimised many-body (COMB) framework [384], and reactive potentials, such as ReaxFF [219, 220] and rCHARMM [218], have been developed to model various metal–ligand systems. Recent advances in machine-learned interatomic potentials (MLIPs) have further expanded the capabilities for modelling metal–ligand systems, including Au–S interactions. MLIP methods like the spectral neighbour analysis potential (SNAP) [385] and DeepMD-kit [386] have demonstrated high accuracy across a variety of chemical environments. However, existing MLIPs are typically trained on small-molecule systems or ligand-protected nanoparticles [387, 388], and their direct applicability to densely packed, functionalised SAMs on extended crystalline gold surfaces remains limited. Moreover, incorporating such models into large-scale simulations that can resolve long-range ordering, surface patterning, and interchain interactions remains challenging, both computationally and in terms of practical implementation. In contrast, the classical parameter refinement strategy presented in this work provides a chemically interpretable, computationally efficient, and readily deployable alternative that is fully compatible with established simulation frameworks. A systematic comparison between classical and machine-learned approaches—once the latter are adapted to the context of SAMs—would represent a valuable direction for future research.

CHAPTER 5

CASE STUDIES

FEATURED WORKS

Í A O Bozzi, L A Machado, E B T Diogo, F G Delolo, L O F Barros, G A P Graça, M H Araujo, F T Martins, L F Pedrosa, L C da Luz, E S Moraes, F S Rodembusch, J S F Guimarães, A G Oliveira, S H Röttger, D B Werz, **C P Souza**, F Fantuzzi, J Han, T B Marder, H Braunschweig and E N da Silva Júnior, “Electrochemical Diselenation of BODIPY Fluorophores for Bioimaging Applications and Sensitization of $^1\text{O}_2$ ”, *Chem Eur J*, 2024, **30**, e202303883, DOI: 10.1002/chem.202303883.

C P Souza and F Fantuzzi, “Condensed-phase effects in the vacuum-ultraviolet spectra of H_2O and O_2 interstellar ice analogues”, *EPJ Web Conf*, 2026, **382**, 05003, DOI: 10.1051/epjconf/202638205003. 

A T Muiña, L E Borchert, Z Kaňuchová, D V Mifsud, **C P Souza**, A M Wilson, A T Hopkinson, M Mikkelsen, J Zhang, J C Santos, J G M Schrauwen, D Ramsamoedj, M Minissale, E Salomon, M Accolla, H Linnartz, B Redlich, M Zlatar, A Dawes, N J Mason, G Strazzulla, N C Jones, S V Hoffmann, L Hornekær, A M Cassidy, M S Gudipati, T Hempel, F Fantuzzi and S Ioppolo, “Survey of the Vacuum-Ultraviolet Spectroscopy and Absorption Cross-Sections of Astrophysical Ice Analogs: A Combined Experimental and Theoretical Study”, Unpublished draft manuscript, 2026.

K Cielinska, A V Verkhovtsev, **C P Souza**, M D Dickers, A V Solov'yov, N J Mason and F Fantuzzi, “Unpassivated edges as gateways to collision-driven topological transformations in finite graphene nanoflakes”, *The European Physical Journal D*, 2026, **80**, 134, DOI: 10.1140/epjd/s10053-026-01242-8. 

CONTENTS

5.1	INTRODUCTION	134
5.2	CASE STUDY 1: INVESTIGATION OF EXCITED STATES OF BODIPYs	134
5.3	CASE STUDY 2: SURVEY OF THE VACUUM-ULTRAVIOLET SPECTROSCOPY AND ABSORPTION CROSS-SECTIONS OF ASTROPHYSICAL ICE ANALOGUES AND THE MOLESS PROJECT	137
5.4	CASE STUDY 3: COLLISION-DRIVEN ALLOTROPIC TRANSFORMATION OF GRAPHENE	148
5.5	CONCLUSIONS	159

5.1 INTRODUCTION

IN CHAPTER 3, WE HAVE USED the range-separated hybrid GGA XC functional ω B97X to investigate the excited states and photodissociation channels of a series of (η^4 -diene)Ru(CO)₃ precursors for PACVD. The results are qualitatively in agreement with experimental investigations. In special, the absorption spectra match the overall shapes, band positions, and relative intensities of those experimentally measured. Nevertheless, the chosen method comes not without caveats, that we summarised in § 3.4.

In § 2.1, we introduced HF as the fundamental wavefunction molecular-orbital method for electronic structure. We discussed the flaws of this model and introduced a series of post-HF methods aimed at its improvement. Among these, coupled-cluster methods were introduced as the gold standard, providing systematic improvement of electronic correlation by inclusion of a series of excitation levels, while preserving size-extensivity and -consistency. Excited state calculations can be done at this level by applying the EOM approach (§ 2.1.4.3). This high-level of theory, however, comes with high computational cost and poor scaling with system size— $O(N^6)$ for CCSD. The DLPNO framework can be utilised with the EOM-CCSD to achieve near-linear scaling, thus making it comparable in computational cost to TDDFT. In Case Study 1 (§ 5.2), we put DLPNO-EOM-CCSD and TDDFT side-by-side in the investigation of excited states of boron-dipyrromethene molecules and discuss their different descriptions.

Throughout this text, we have emphasised the multiscale approach to molecular simulations. Indeed, it is our aim to develop a framework for the multiscale simulation of the PACVD process. The frequent necessity of simplifying the simulation model in order to access larger spatial and temporal scales has been discussed (§ 1.1). In this context, an important question arise: how far can one go in system size before a coarsening of theory level is necessary? In Case Study 2 (§ 5.3) we show the possibility of simulating solid-state vacuum-UV absorption spectra of molecular ices still at the TDDFT level using a cluster approach. We discuss important shortcomings of the method and open questions to be answered in order to clearly delineate its applicability.

Finally, essential to our model is the availability of a reactive molecular dynamics algorithm (§ 2.2.1.2). In Chapter 6 we delineate the implementation of a reactive FF model for the precursors based on the data presented in Chapter 3. Since we have not yet reached the stage of simulating the full deposition process, we bring in Case Study 3 (§ 5.4) an application of this approach to the collision-driven allotropic transformation of carbon nanoflakes into nanotubes. This study shows the interplay between a many-body potential and the rCHARMM reactive FF—a feature that is also present in the multiscale PACVD model developed here.

5.2 CASE STUDY 1: INVESTIGATION OF EXCITED STATES OF BODIPYS

BORON-DIPYRRROMETHENE (BODIPY) compounds are a well-known class of molecules that have high fluorescence quantum yields and good photostability, making them a popular

choice for a wide range of applications [389–394]. Notably, they play a crucial role in fluorescence microscopy for bioimaging and are utilised to label proteins, nucleic acids, cell membranes, and other cellular structures, enabling detailed visualisation and comprehensive analysis [395–397]. BODIPYs that exhibit red-shifted absorbance and photoluminescence in the red to near-IR region of the spectrum, often referred to as the biologically transparent window, have garnered significant attention. This attribute proves advantageous for biological and medical imaging applications as it allows for deeper tissue penetration (with less light absorption by the tissue) and reduced background autofluorescence when compared to dyes that absorb and emit in higher energy regions of the spectrum. However, most red-emitting BODIPYs demonstrate lower emission quantum yields compared to their blue-green-emitting counterparts, potentially constraining their effectiveness in specific contexts [398–400]. The emission properties of BODIPYs can be tailored by modifying the chromophore structure and introducing various functional groups [401–403]. Specifically, BODIPY derivatives decorated with chalcogens have been intensively studied to produce fluorescent probes for the detection of bioactive molecules [404–406]. In this work, a sustainable and versatile electrochemical approach for 2,6-diselenation of BODIPYs has been presented [407].

For the context of this thesis, we discuss the computational excited-state investigation carried out in that work. To gain further insight into the electronic properties of these molecules, we conducted TDDFT calculations on a selected set of compounds (Figure 5.1). The appropriate level of theory was determined via benchmarking against the x-ray crystal structure of **3ha** and experimental spectra (see [407] for details). Geometry optimisations were carried out at the DFT/ ω B97X-D/cc-pVDZ, aug-cc-pVTZ(Se) level [408, 409] on GAUSSIAN 16 REV A.03. All geometries were confirmed as minima based on frequency calculations. TDDFT calculations of the singlet states were carried out on the optimised systems without TDA but with the inclusion of the RIJCOSX approximation, performed at the TDDFT/ ω B97X-D3BJ/def2-TZVP level. Solvation effects were considered through the implicit conductor-like polarisable continuum model (CPCM) [410], with dichloromethane (DCM) as solvent, on ORCA 5.0.3. The character of the transitions was interpreted using NTO analysis.

THE SIGNIFICANT ABSORPTION features observed in the visible region for all BODIPYs are attributed to the $S_0 \rightarrow S_1$ electronic transition. Although prior studies have underscored the disparities between calculated TDDFT excitation energies and experimental data for BODIPYs [411], the method retains its significance as a valuable tool for evaluating electronic transition characteristics and qualitative patterns in absorption features within the BODIPY family. In our calculations, deviations fall within the range of 0.30 eV to 0.53 eV, with the propynyloxyphenyl-substituted molecules (**1h**, **3ha**) exhibiting a slightly more accurate representation compared to those featuring the simpler phenyl group (**1a**, **3aa**). Furthermore, better agreement is observed for the precursor compounds (**1a**, **1h**) when contrasted with the

diselenide derivatives (**3aa**, **3ha**). All higher-energy transitions occur within the UV spectral range and are not relevant to our discussion. In light of the large excitation energy deviations observed with the TDDFT method, we employed a more accurate approach to better describe the excited states of these molecules. Specifically, we turned to the DLPNO-STEOM-CCSD method (see § 2.1.4.3), and conducted these calculations using ORCA 5.0.3. These were done at the DFT optimised geometries and also applying the CPCM implicit solvent model for DCM. A benchmark of basis sets indicated that employing the double- ζ quality def2-svp basis set sufficed (see [407] for details).

As anticipated, this higher-level theoretical approach yielded a more accurate description of singlet excitation energies compared to TDDFT (see Table 5.1). The discrepancies ranged from 0.11 eV to 0.18 eV. Consistent with the TDDFT results, a better agreement was observed for the precursor compounds compared to their diselenide derivatives. Furthermore, both TDDFT ($\Delta\lambda = 10$ nm) and DLPNO-STEOM-CCSD ($\Delta\lambda = 34$ nm) calculations indicated a bathochromic shift—a shift of the absorption bands towards longer wavelength or lower energy—when transitioning from precursor **1a** to its diselenide derivative **3aa**, aligning with experimental observations. Notably, the bathochromic effect aligns better with experimental data ($\Delta\lambda = 15$ nm) in the TDDFT perspective. One possible explanation for this discrepancy might be the lack of size-consistency introduced by the DLPNO scheme [412], even though CC methods are the golden choice specifically for its size-extensivity and -consistency (see § 2.1.1). This leads to more significant deviations in energy calculations for the larger derivatives compared to their respective precursors. This effect is not present in TDDFT.

TABLE 5.1 – TDDFT and STEOM-DLPNO-CCSD (CC) $S_0 \rightarrow S_1$ vertical excitation absorption wavelengths and energies compared with experimental (Exp) values, and the Kohn–Sham frontier molecular orbital energies, of **1a**, **1h**, **3aa**, and **3ha**. The values in parenthesis are deviations from the respective experimental values.

	$S_0 \rightarrow S_1$ absorption wavelength (nm)			$S_0 \rightarrow S_1$ absorption energy (eV)			Kohn–Sham frontier orbital energies (eV)		
	Exp	DFT	CC	Exp	DFT	CC	HOMO	LUMO	Gap
1a	500	413 (+87)	524 (+24)	2.48	3.00 (-0.52)	2.37 (-0.11)	-7.74	-0.90	6.84
1h	500	446 (+54)	525 (+25)	2.48	2.78 (-0.30)	2.36 (-0.12)	-7.73	-0.89	6.84
3aa	515	423 (+93)	558 (+43)	2.41	2.93 (-0.53)	2.22 (-0.18)	-7.88	-1.14	6.74
3ha	516	453 (+63)	548 (+32)	2.40	2.74 (-0.33)	2.26 (-0.14)	-7.89	-1.14	6.76

Despite the tendency of TDDFT to overestimate transition energies, the bathochromic effect induced by diselenide substitution is qualitatively captured. As previously discussed, and supported by existing literature [413], the $S_0 \rightarrow S_1$ transitions in BODIPYs are typically attributed to $^1\pi-\pi^*$ transition characterised by minimal charge transfer, typical for HOMO-LUMO transitions. The NTO analysis depicted in Figure 5.1 aligns with this picture. For all

of the molecules, the electron densities of the relevant orbitals are predominantly localised over the three-fused-ring moieties, with a minor contribution in the 8-Ph substituent and the nonbonding electron pairs of the fluorides on the acceptor orbitals. Of particular interest to our investigation is the influence of the Se-containing substituents. As it can be seen, Se atoms actively participate in both donor and acceptor orbitals. This leads to a more dispersed electron density in the Se-containing molecules when compared to the precursors, thereby narrowing their HOMO–LUMO gaps, an effect akin to what is observed with increased π -conjugation. Consequently, this reduction in the energy gap between the S_0 and S_1 states in the diselenated BODIPYS results in the observed bathochromic effect.

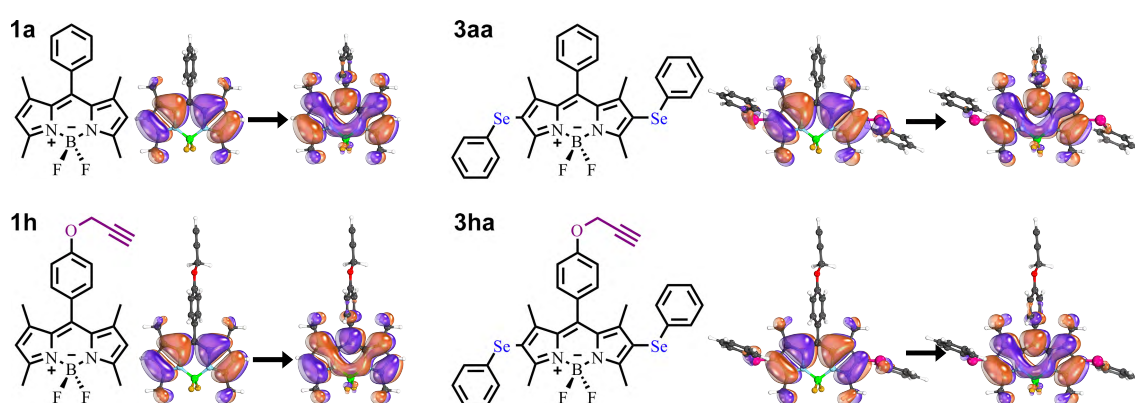


FIGURE 5.1 – Nomenclature and NTOs for the $S_0 \rightarrow S_1$, HOMO–LUMO electronic transitions of selected BODIPYS. NTO plots represent 90% of the density. Level of theory: TDDFT/ ω B97X–D3BJ/def2-TZVP.

5.3 CASE STUDY 2: SURVEY OF THE VACUUM-ULTRAVIOLET SPECTROSCOPY AND ABSORPTION CROSS-SECTIONS OF ASTROPHYSICAL ICE ANALOGUES AND THE MOLESS PROJECT

ASTRONOMICALLY-FAR ENVIRONMENTS, yet unreachable by probes and humans, can only be investigated by the information that reaches us on or near the Earth—mainly, light. Spectroscopy is the main technique via which we probe the molecular makeup of outer space regions. Gas-phase molecules have usually been detected by rotational emission spectroscopy with earth-based radio telescopes [414, 415]. Solid-phase material, where molecular rotation is hindered, on the other hand, are better studied via IR absorption spectroscopy. This technique has led to the detection of approximately 30 different molecules embedded within icy grain mantles in dense molecular clouds and star-forming regions [416–420], as well as on the surfaces of a number of icy outer Solar System moons [421–423]. Solid, particular icy, objects in space are believed to be the main phase in or on which complex molecules are formed through chemical reactions of smaller, trapped or adsorbed gas molecules [424–428].

However, with spectroscopy, seeing more is seeing better, and IR spectroscopy is not without its limitations. Higher energy regions of the electromagnetic spectrum have allowed for the detection of components of molecular ices that are invisible or difficult to observe in the IR regions. For instance, sulphur dioxide (SO_2) was famously detected on the surfaces of Jupiter's moons Europa and Callisto through observations in the UV region [429–432]. Moreover, UV–vis spectroscopy has been used to better understand the source of molecular oxygen (O_2) on the surface of Ganymede [433], while ozone (O_3) was recently detected on the surface of Callisto by making use of vacuum-UV (VUV) spectroscopy [434].

The interpretation of these complex spectral data is not straightforward. Laboratory spectra and theoretical calculations are essential to decode the molecular signatures embedded in the observational data. In the VUV region, however, laboratory data-acquisition for molecular ices demands expensive, specialised facilities with synchrotron light-sources and ultra-high vacuum chambers. An effort to construct a database of VUV absorption spectra of laboratory-grown astrophysical ice analogues and corresponding computational simulations and interpretation is being carried out by a group of scientists (including this author) at various institutions around the world [435].¹ In the same context of this work, the Molecular Excited State Spectroscopy (MOLESS) project was born [436].² The core objective of this international initiative is two-fold: to modernise and expand the material in Melvin Robin's classical "Higher Excited States of Polyatomic Molecules" series of books [437–439], and to assemble and host a comprehensive and authoritative database of laboratory measured and computationally simulated electronic excited state properties of molecules. The project aims not only to preserve historical data but also standardise future contributions following "findable, accessible, interoperable, and reusable" (FAIR) procedures.

Here, we present key computational results of simulations and interpretation of VUV spectra of molecular astrophysical ice analogues included in the scope of the aforementioned projects. While in § 5.2 we showed some flaws and successes of TDDFT (using the ωB97X functional) against EOM-CCSD of comparable computational expense thanks to the DLPNO approach for a main group molecule, here we want to push TDDFT to a challenging limit. The aim is to simulate high energy electronic transitions in the VUV, almost always leading to Rydberg states, not in isolated molecules, but in a solid (or as close as we can get to it). To do so, we utilise a molecular cluster approach. Besides the Rydberg states, transitions happening in collections of molecules often have high charge transfer character. Two key points are important for these cases: the DFT functional must be able to describe well long

¹The Aarhus University (Denmark), the University of Kent (UK), the Queen Mary University of London (UK), the Astronomical Institute of the Slovak Academy of Sciences (Slovakia), the HUN-REN Institute for Nuclear Research (Atomki; Hungary), the Leiden University (The Netherlands), the Radboud University (The Netherlands), the Aix Marseille Université (France), the INAF-Osservatorio Astrofisico di Catania (Italy), the University of Belgrade (Serbia), The Open University (UK), and the Jet Propulsion Laboratory of the California Institute of Technology (USA).

²The page for the MOLESS project is <https://www.moless-spectroscopy.org/>.

distance interactions, and the basis set must include enough polarisation and, more critically, diffusion. For that reason, we chose the TDDFT/ ω B97X-D3BJ/def2-QZVPPD level of theory for the excited state calculations [440].

The full protocol is as follows. The geometry of the isolated molecules were optimised at the DFT/ ω B97X-D3BJ/def2-TZVPPD level. Using this optimised geometries, molecular clusters of varying sizes (minimum six molecules) were constructed and the global minimum was obtained with the artificial bee colony algorithm for cluster global optimisation (ABCluster) [441]. This was achieved through the rigid molecular cluster optimisation module (rigidmol-optimizer), keeping the molecular internal degrees of freedom frozen while the intermolecular interactions were described by LJ and Coulomb potentials from the CGenFF or the universal force field (UFF) [368] (see discussion below). The parameters for the artificial bee colony algorithm were as follows: population size = 40, maximum generation = 100, scout limit = 4. All clusters' global minima were subsequently optimised at the DFT/ ω B97X-D3BJ/def2-SVPD level. The optimised geometries were then used to calculate absorption spectra at the TDDFT/ ω B97X-D3BJ/def2-QZVPPD level. For oxygen, clusters of 10, 14, and 18 molecular units with the monoclinic α crystal geometry (space group C2/m) were constructed from x-ray diffraction coordinates [442].³ This structure was utilised without optimisation in the calculation of the spectra at the same level utilised for the other clusters but employing the spin-flip method to reproduce the correct magnetic structure [443] (see Figure 5.5). All quantum mechanical calculations were performed using ORCA 5.0.3. The RIJCOSX approximation with the def2 auxiliary basis set was utilised throughout. The simulated spectra were generated according to the procedure described in § 3.2. NTO analysis with the THEODORE package was used to interpret the character of the transitions.

THE SPECTRUM OF CO ICE AT 20 K is dominated by a broad band associated with the $A^1\Pi \leftarrow X^1\Sigma^+$ electronic transition and sometimes referred to as the fourth positive band system [444–450]. The most notable feature of the fourth positive band system is the presence of a strong vibrational progression superimposed on the main absorption feature (see Figure 5.2). Another broad and intense band (though not as intense as the fourth positive band system) is typically visible at wavelengths below 120 nm [447, 449, 450] and has been attributed to an overlap between the $B^1\Sigma^+ \leftarrow X^1\Sigma^+$ system and, likely together, the $C^1\Sigma^+ \leftarrow X^1\Sigma^+$ and $E^1\Pi \leftarrow X^1\Sigma^+$ systems [447, 449]. At higher wavelengths of about 175 nm–210 nm, a significantly weaker set of forbidden bands known as the Cameron system has also been identified, and is associated with the $a^3\Pi \leftarrow X^1\Sigma^+$ electronic transition [444, 451]. The calculated spectrum for a cluster of six CO molecules is in excellent agreement with the experimental spectrum (Figure 5.2). The position of the fourth positive band is almost

³The structure is deposited in the Crystallography Open Database (COD) under ID 1528336: <https://www.crystallography.net/cod/1528336.html>

the same in both spectra and a band below 130 nm is predicted by the calculations. Since spin-orbit coupling is not accounted for in our calculations, transitions such as the Cameron system cannot be modelled at this level.

It is common practice to assign transition characters and symmetries from gas-phase spectra directly to the solid phase by analogy, although it is not technically correct. Electronic transitions in the condensed phase cannot generally be attributed to a single molecular centre and thus do not hold the symmetry of the isolated molecule. More often than not, transitions in condensed phase involve complex combinations of molecular centres and may exhibit large charge-transfer character across several molecular distances. Nevertheless, we will loosely correlate transitions in the clusters to those in the isolated molecules by comparing the orbitals involved in them. The fourth positive band system in the CO spectrum comprises six vertical transitions with appreciable oscillator strength (S_5 – S_9 and S_{11}) which are all characterised as collective, delocalised HOMO→LUMO-like transitions with no charge-transfer character on the basis of the orbital shapes. One representative NTO (S_7) is depicted in Figure 5.4, where it is possible to note that the donor (ie, hole) orbital resembles the HOMO $2\sigma^+$ orbital of the isolated molecule and that the acceptor (ie, particle) orbital is similar to the LUMO 2π orbitals of the isolated molecule. All other components of this transition are similar. This characterisation is compatible with the $A^1\Pi \leftarrow X^1\Sigma^+$ label attributed experimentally.

The absorption band below 120 nm was attributed to transitions to the excited Rydberg states $B^1\Sigma^+$, $C^1\Sigma^+$, and $E^1\Pi$. Our theoretical analysis suggests that the first, lower energy group of transitions are still of HOMO→LUMO character with higher energy π -like orbitals acting as acceptors. However, on progressing to higher energies, the transitions are better described as HOMO–1→LUMO, as exemplified by the S_{153} transition in Figure 5.4. Such an assignment correlates with transitions to the forbidden states Σ^- and Δ in the isolated molecule, and thus differs somewhat to attributions suggested by prior studies discussed above.

THE FIRST TRULY ASTROCHEMICAL study of the photo-absorption of solid H_2O studied an amorphous ice prepared by background condensation of the vapour at 25 K [448]. A hypsochromic shift from 167 nm to 144 nm was observed for the band corresponding to the $4a_1 : \tilde{A}^1B_1 \leftarrow 1b_1 : \tilde{X}^1A_1$ electronic transition when comparing to previous gas-phase studies. Later studies corroborated this observation, and also provided insight into the nature of the absorption at wavelengths below 132 nm, which was attributed to the $\tilde{B}^1A_1 \leftarrow \tilde{X}^1A_1$ transition [452, 453]. The experimental spectrum acquired for the present work is plotted alongside the calculated spectrum in Figure 5.2. The experimental spectrum exhibits the expected absorption bands that peak at 143.6 nm and below 120 nm. Moreover, a significantly less intense absorption peaking at 180 nm can be observed, which has been attributed to absorption by H_2O molecules on the ice surface and not within the bulk ice [454–458]. The

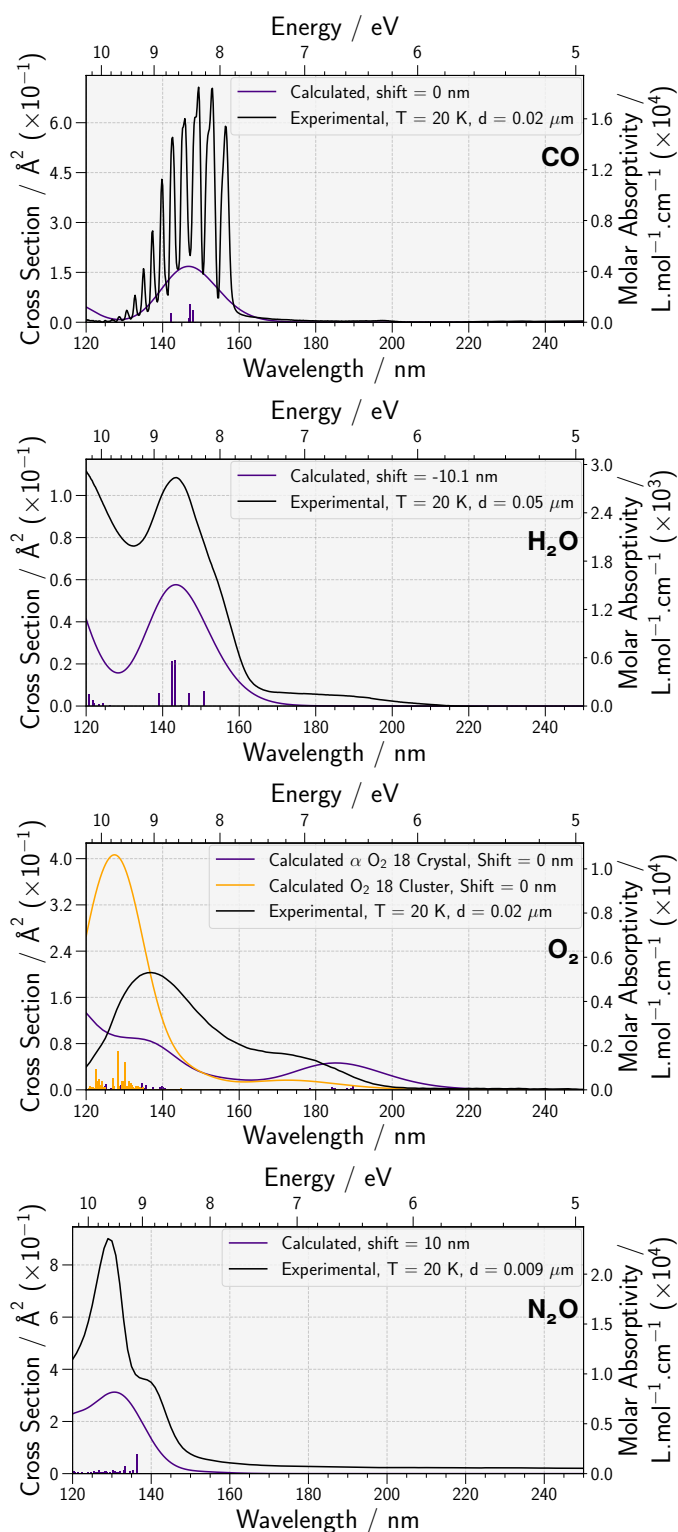


FIGURE 5.2 – Calculated and experimental vuv spectra of CO, H₂O, O₂, and N₂O. Calculated spectrum of O₂ is from an 18-molecule optimised cluster and an 18-molecule α -crystal slab. All others are from six-molecule optimised clusters. Level of theory: TDDFT/ ω B97X-D3BJ/def2-QZVPPD.

calculated spectrum agrees well with experiment after a hypsochromic shift of 10.1 nm. The first band in the calculated spectrum (between 130 nm–165 nm) is comprised of six vertical transitions. The two dominating transitions make up the main shape of the band, while the first two transitions, with smaller intensities, make up for the small shoulder observed experimentally. The second band (below 130 nm) is composed of several closely spaced, small intensity transitions.

Figure 5.3 shows a comparison of calculated spectra obtained for the isolated H_2O molecule, meant to represent the gas phase spectrum, and for clusters of six and twelve molecules, simulating the behaviour of the condensed phase spectrum. As the size of the systems increase, so does the hypsochromic shift. For the first band, there is a $\Delta\lambda_{\text{max}} = 13.7$ nm and a $\Delta\lambda_{\text{max}} = 19.2$ nm for the six-molecules and for the twelve-molecules clusters, respectively, in relation to the isolated molecule. The experimental shift is 22 nm. This result suggests that increasing the size of the cluster will result in a better match between the calculated and experimental spectra, bringing the calculated shift in line with the measured value. In contrast to the CO spectrum discussed above, we see here an important effect of cluster size on the quantitative accuracy of calculated spectra.

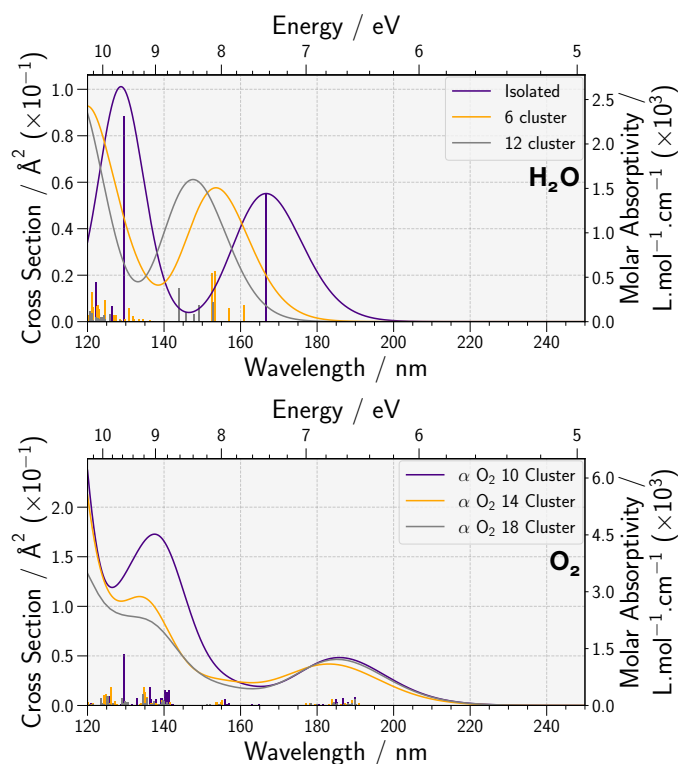


FIGURE 5.3 – Effect of cluster size on calculated vuv spectra of H_2O and $\alpha\text{-O}_2$. Level of theory: TDDFT/ $\omega\text{B97X-D3BJ/def2-QZVPPD}$.

The various orbitals and electronic transitions of the isolated H_2O molecule and the six-molecules cluster are shown in Figure 5.4. The six lowest-energy orbitals in the cluster are combinations of the $1a_1$ orbitals of the isolated molecule; while the next six orbitals are combinations of $2a_1$ orbitals of isolated water molecules, and so on. Negligible contamination of higher energy orbitals (eg, $2a_1$ among a $1a_1$ majority) is seen. For the virtual orbitals, however, the compositions are more complicated. To illustrate this point, the LUMO and LUMO+1 of the cluster are shown. The LUMO is mainly composed of the $4a_1$ orbitals of the isolated molecules with small contributions from the $5a_1$ orbitals. As such, it is possible to roughly correlate this LUMO with that of the isolated H_2O molecules. The LUMO+1, on the other hand, although being composed mostly of $4a_1$ orbitals of the isolated molecules, also has significant contributions from the $2b_2$ and $5a_1$ orbitals. Moving to higher energy orbitals, this mixing becomes more and more varied and spread out. Such mixing of virtual orbitals is a direct consequence of their Rydberg character; their higher spatial diffusiveness favouring their overlap. This effect is particularly pronounced in water.

To further complicate the interpretation, the electronic transitions are described by a combination of cluster orbitals. The six transitions responsible for the lowest energy band on the cluster spectrum are all broadly $4a_1 \leftarrow 1b_1$ transitions (cluster HOMO $\rightarrow$ LUMO transitions with some contributions of HOMO-1 $\rightarrow$ LUMO+1), comparable with the S_1 transition in the isolated molecule (see NTOs in Figure 5.4 for major contribution to S_5 in the cluster). However, since the LUMO+1 contains a significant contribution from the $2b_2$ orbital, the transition also possesses a $2b_2 \leftarrow 1b_1$ character, comparable to the dark S_2 transition in the isolated molecule. The transitions responsible for the second band in the cluster spectrum are more complicated as they have contributions from higher energy virtual orbitals, themselves mixing more of the virtual orbitals of the isolated molecules. The transitions in the twelve-molecules cluster can be characterised in a similar way, with a small difference: the transitions corresponding to the first band are more purely of the character $4a_1 \leftarrow 1b_1$. This indicates that, in terms of modelling the wave function and transition characters, smaller cluster sizes are sufficient, but not so much for prediction of quantitative properties.

Such an interpretation of the cluster spectrum helps in understanding the observed blueshift. Although the calculated HOMO-LUMO gap of the cluster is smaller than that for the isolated molecule by approximately 0.04 eV, none of the transitions is purely HOMO $\rightarrow$ LUMO. The three cluster virtual orbitals next in energy to the LUMO (itself combination of $4a_1$ orbitals of isolated molecules) are combinations of the higher energy orbitals from the isolated molecules, and contribute to the lowest energy transitions, thus increasing their energies. This blueshift has already been explained as a consequence of the “repulsion” of voluminous Rydberg orbitals which overlap with those of noble gas matrix atoms in the case of matrix-isolated H_2O samples, or with the surrounding H_2O molecules in ice samples [459].

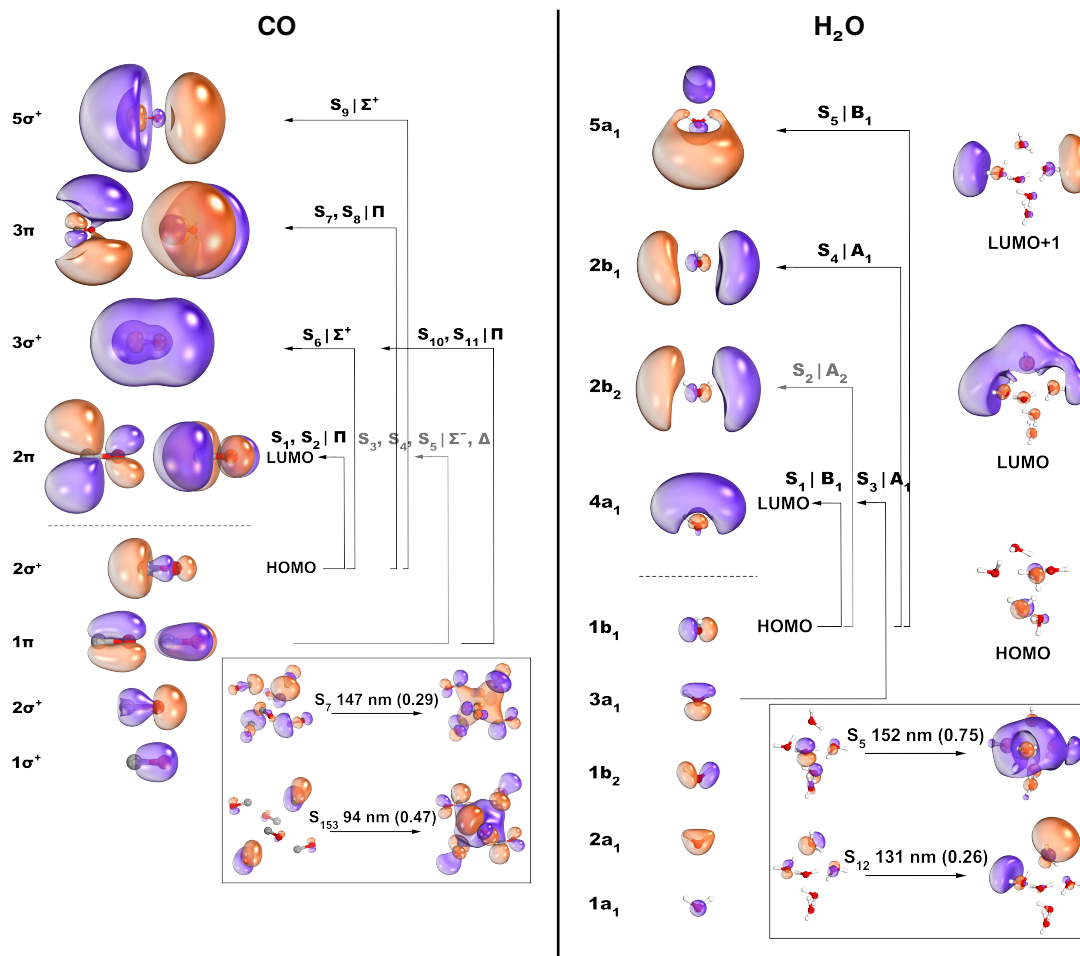


FIGURE 5.4 – Orbital analysis for CO (point group $C_{\infty v}$) and H_2O (point group C_{2v}) electronic transitions on the isolated molecules and the clusters. The orbitals for the isolated molecules (left of each panel) and cluster orbitals (for H_2O) are the Kohn-Sham. Orbital symmetries are designated to the left in each panel while electronic transitions are indicated by the arrows to the right and labelled by their order from lowest to highest transition energies followed by the symmetry of the transition. Grey indicates dark and black indicates bright transitions. In H_2O , the σ_v plane relative to which the 1 and 2 Mulliken symbols are defined is perpendicular to the molecular plane. NTOS for representative transitions in the clusters (inside rectangles) are shown for reference. Numbers in parenthesis are indicative of the electronic occupation number. Level of theory: TDDFT/ ω B97X-D3BJ/def2-QZVPPD.

EARLY ANALYSIS OF THE SOLID N_2O VUV absorption spectrum identified three absorption bands centred at about 127 nm, 138 nm, and 180 nm that were respectively attributed to the $^1\Sigma^+ \leftarrow ^1\Sigma^+$, the $^1\Pi \leftarrow ^1\Sigma^+$ and the $^1\Delta \leftarrow ^1\Sigma^+$ transitions [460]. Subsequent work identified a fourth band centred at about 113 nm [452], and still later work provided evidence of a fifth band at about 225 nm [461]. The experimental spectrum acquired as part of this study is shown in Figure 5.2 and clearly exhibits two major absorption features at 129 nm and 139 nm. Closer inspection of the higher wavelength regions of this spectrum reveals the presence of a

very weak absorbance feature at 183 nm which may be attributed to the $^1\Delta \leftarrow ^1\Sigma^+$ transition. The 225 nm feature observed in [461] may also be present, as a broad and weak band spanning from approximately 198 nm–272 nm.

The calculated spectrum, after a bathochromic shift of 10 nm, matches well the experimental spectrum, although the band shapes and intensities are not very accurate. The character of the bands are in agreement with the previous attribution discussed above. The broad, high intensity feature in the cluster spectrum comprises two main contributions compatible with the $^1\Pi \leftarrow ^1\Sigma^+$ and $^1\Sigma^+ \leftarrow ^1\Sigma^+$ assignment mentioned above. The former contribution is represented by the S_{20} transition in the cluster, whose NTOS are shown inside the rectangle in Figure 5.5, and is correlated with the S_4 and S_5 (HOMO→LUMO) transitions in the isolated molecule. The latter is represented by the cluster S_{32} transition, akin to the very-high-intensity S_6 (HOMO→LUMO+1) transition in the isolated molecule (in fact, the only bright transition above 120 nm). One interesting feature of this later transition is the mixing of the HOMO→LUMO+1 character with non-negligible contributions of HOMO→LUMO+4 of the same Δ symmetry. This mixing is present both in the isolated molecule and in the cluster, and may explain the prominent absorption intensity since the 4π Rydberg orbital will contribute more extended overlap in the transition density. At longer wavelengths (above 175 nm), a series of very-low-intensity transitions (molar absorptivity below $3 \text{ L mol}^{-1} \text{ cm}^{-1}$) exist in the calculated cluster spectrum. They are all of the $^1\Delta \leftarrow ^1\Sigma^+$ type (HOMO→LUMO+1 in the isolated molecule; see S_7 in Figure 5.5), in agreement with what has been hypothesised above.

FINALLY, WE DISCUSS THE SOLID O_2 absorption spectra. Previous studies have demonstrated that this spectrum is dominated by a broad absorption band ranging between 127 nm–177 nm and peaking at approximately 138 nm [448, 452, 461, 462]. This band is attributable to the $\tilde{\text{B}}^3\Sigma_u^- \leftarrow \tilde{\text{X}}^3\Sigma_g^-$ electronic transition, and may be thought of as a solid-phase equivalent of the Schumann–Runge bands and continuum observed in the gas-phase. Interestingly, a second, less intense absorption feature has also been observed, which appears as a shoulder to the lower energy side of the main Schumann–Runge band at about 173 nm [448, 452, 461–463]. The origin of this feature has been the subject of some debate in the literature. It was initially proposed that this could be a spectral signature of dimeric O_2 structures [448]; however, more recent work has suggested that this feature may arise as a result of the contamination of an amorphous O_2 ice by the crystalline α - and/or β -phases [463]. It was proposed that the main absorption peak at about 137 nm observed when an O_2 ice is prepared at low temperatures (ie, 10 K–20 K) is due to the presence of amorphous solid O_2 , whereas at temperatures below 24 K, the shoulder to this band is due to the presence of some quantity of α - O_2 . It is, therefore, evident that further studies using complementary experimental and theoretical techniques are required to fully comprehend this spectrum.

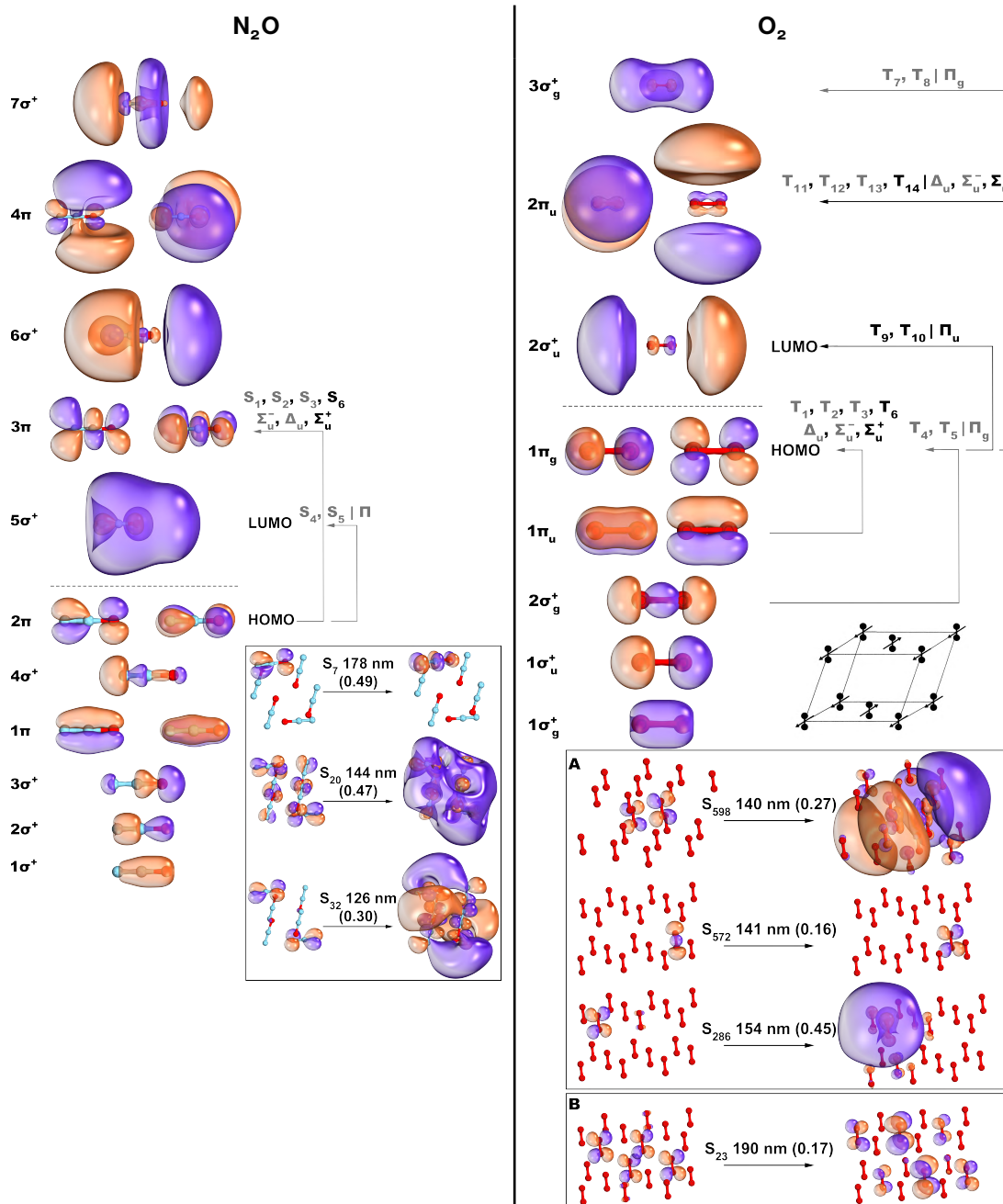


FIGURE 5.5 – Orbital analysis for N₂O (point group C_{∞v}) and O₂ (point group D_{∞h}) electronic transitions on the isolated molecules and the clusters. The orbitals for the isolated molecules (left of each panel) are the Kohn-Sham. Orbital symmetries are designated to the left in each panel while electronic transitions are indicated by the arrows to the right and labelled by their order from lowest to highest transition energies followed by the symmetry of the transition. Grey indicates dark and black indicates bright transitions. ntos for representative transitions in the clusters (inside rectangles) are shown for reference. Numbers in parenthesis are indicative of the electronic occupation number. A representation of the lattice and spin pairing in α O₂ is shown. Level of theory: TDDFT/ ω B97x-D3BJ/def2-QZVPPD.

The VUV absorption spectrum of solid O_2 measured at 20 K is shown in Figure 5.2, along with theoretically calculated spectra. It is possible to note that our experimentally acquired spectrum is similar to those of other spectroscopic studies conducted at low temperatures (ie, 9 K–22 K), and is characterised by the expected broad Schumann–Runge band peaking at 137 nm having a shoulder at 172 nm. To further address the character of the two bands and assess the participation of amorphous and crystalline phases, we obtained two calculated cluster spectra. The first is meant to represent the amorphous phase and was calculated from a cluster of 18 O_2 molecules in the usual way as described above. The total cluster was made spin singlet by flipping half of the molecules' spin at random from an initially all-parallel spin configuration ($S = 18$) using the spin-flip method. The second cluster, also with 18 molecules, was built from the monoclinic ($C2/m$) structure of an α -crystal obtained by X-ray diffractometry as described above. Both the α and the β phases of crystalline oxygen are antiferromagnetic. In the α -crystal, all the nearest-neighbours of each molecule in the face-centred cubic (fcc) lattice have opposite, collinear spin, and this magnetic structure was ensured in the construction of the cluster by means of the spin-flip method ($S = 6$), as shown in Figure 5.5. The magnetic structure of the rhombohedral ($R\bar{3}m$) β oxygen is more complicated, presenting a helical, noncollinear magnetic order without local antiferromagnetic domains, although the crystal is globally antiferromagnetic [443]. We, therefore, did not attempt to simulate the spectrum with such structure.

The higher intensity, higher energy band, seen in both the amorphous and in the crystalline clusters' spectra, are of similar nature, being composed of multiple types of transition according to the NTO characterisation. In the crystalline structure, however, this band is split into two major contributions and is blueshifted in relation to the amorphous spectrum. These two bands appear to merge as the cluster size increases (see Figure 5.3), indicating that they may become almost completely superimposed in the limit of an infinite crystal, as is seen experimentally. The NTOs for the major transitions composing this pair of bands is shown for the α -crystal inside rectangle A in Figure 5.5. At lower energies, the transitions are of the type ${}^3\Pi_g \leftarrow {}^3\Sigma_g^-$ (HOMO $\rightarrow$ LUMO+3; S_7 , S_6 in the isolated molecule) although they also extend to higher energy as their charge-transfer character increases. Transitions of the type ${}^3\Sigma_u^- \leftarrow {}^3\Sigma_g^-$ (or ${}^3\Sigma_u^+ \leftarrow {}^3\Sigma_g^-$, or ${}^3\Delta_u \leftarrow {}^3\Sigma_g^-$, all being of the HOMO $\rightarrow$ LUMO+2 type; S_{11} – S_{14} in the isolated molecule) appear in higher energies. Small intensity HOMO–2 $\rightarrow$ HOMO transitions (${}^3\Pi_g \leftarrow {}^3\Sigma_g^-$; S_4 , S_5 in the isolated molecule) are also present in the whole range of these bands.

The lower energy shoulder attributed to the crystal phases of O_2 is indeed characteristic of the α -crystal as suggested by the calculated spectrum. This transition is characterised by electron transfer from the HOMO orbital of one oxygen molecule to its nearest neighbour of opposite spin (rectangle B in Figure 5.5). Therefore, an initially triplet O_2 (say $M_S = 1$) becomes a doublet ($M_S = 1/2$) by populating the HOMO of a neighbouring O_2 (initially

$M_S = -1$) which also becomes a doublet with opposite spin ($M_S = -1/2$). Such transition is highly enhanced in the α -crystal geometry, where all nearest-neighbour to every molecule have opposite spin. In the amorphous case it would be much less probable that such spatial proximity would happen (although a faint band of the same character can be seen in the calculated spectrum for the amorphous cluster). We expect a similar effect to be possible in the β -phase as well.

THIS SURVEY, THEREFORE, SHOWED varying levels of challenges for the application of TDDFT for the multiscale simulation of VUV spectra of solids. CO is the most successful case, with bands matching very well the experimental spectrum. H_2O and N_2O offer a higher challenge, with calculated spectra showing bathochromic and hypsochromic shifts, respectively, in relation to experiments. The interpretation of the transitions for H_2O is complex and not completely clear and an effect of cluster size on the energy of the bands is clearly demonstrated. Finally, the case of O_2 shows an interesting interplay between amorphous and crystalline features whose characters were surprisingly well-described by the calculations, although the transition energies are not well reproduced with an 18-molecule cluster.

5.4 CASE STUDY 3: COLLISION-DRIVEN ALLOTROPIC TRANSFORMATION OF GRAPHENE

CARBON IS AN EXCEPTIONALLY versatile element, capable of forming a broad spectrum of allotropes whose structural, electronic, and mechanical properties span a wide range. These include three-dimensional networks such as diamond [464], layered and tubular structures such as graphite [465] and carbon nanotubes [466], as well as zero- and two-dimensional nanostructures including fullerenes [467, 468] and graphene [469]. This diversity originates from the ability of carbon to adopt multiple hybridisation states (sp , sp^2 , and sp^3) and to form stable covalent bonds across a wide range of coordination environments. Among these allotropes, graphene—a two-dimensional sheet of sp^2 -bonded carbon atoms arranged in a honeycomb lattice—has emerged as a paradigmatic low-dimensional material. Its massless Dirac-like charge carriers [470, 471], exceptionally high carrier mobility [469, 472–474], large thermal conductivity [475–477], mechanical robustness [478, 479], and maximal surface-to-volume ratio [480] have made it a central platform for the development of next-generation electronic [481], optoelectronic [482–484], and spintronic [485, 486] technologies [487, 488].

While much of the early research focused on extended graphene sheets, increasing attention has shifted toward finite graphene fragments, commonly referred to as graphene nanoflakes (GNS) [489] or graphene quantum dots [490]. In these systems, spatial confinement and the presence of edges introduce quantum and topological degrees of freedom that are

absent in the idealised bulk graphene: finite-size effects open electronic band gaps, while geometric shape and edge topology influence the spatial distribution of frontier orbitals, localised electronic states, and magnetic response [491–494]. As a consequence, the properties of GNs reflect not only the characteristics of the basal plane but also the interplay between size, shape, topology, and the chemical activity of their edges. In this broader context, graphene quantum dots have emerged as a distinct class of materials, exhibiting size- and shape-dependent optical, electronic, and optoelectronic properties that can be tuned through synthesis parameters and elemental doping [495].

From a structural and materials perspective, GNs occupy a unique position in the carbon allotrope landscape as intermediates between planar graphene, closed fullerene cages, and tubular carbon nanotubes. This dual role as both quantum-confined systems and structural building blocks has motivated long-standing hypotheses that finite graphene fragments may serve as precursors for other carbon nanostructures [496], provided that suitable nonequilibrium mechanisms exist to induce curvature, bond rearrangement, and topological closure. Computational and experimental studies have proposed multiple transformation routes linking finite graphene fragments, nanotube segments, and closed cages: large-radius carbon nanotube fragments can unfold into metastable graphene-like patches, while the inverse process can lead to the closure of finite fragments into fullerene cages through the progressive incorporation of nonhexagonal rings and local bending [497–499]. Complementary studies have further shown that polycyclic aromatic hydrocarbon and nanoflake intermediates can act as building blocks in the assembly of fullerenes and soot, with their geometry and flexibility influencing whether closure into cages or aggregation into extended networks is favoured [500–502].

Transformations between planar, tubular, and closed carbon nanostructures involve bond rearrangements such as Stone–Wales-type rotations and the incorporation of nonhexagonal rings, which induce bending and enable topological closure [503, 504]. These processes are typically associated with substantial activation barriers and strong coupling between mechanical strain and electronic structure [505]. Despite these theoretical pathways, both experimental and computational studies have demonstrated that GNs remain remarkably stable under near-equilibrium conditions, preserving their planar geometry through edge reconstructions and vibrational relaxation rather than transforming into closed or tubular forms [506]. This thermal robustness indicates that near-equilibrium pathways alone are insufficient to drive large-scale allotropic transformations in finite graphene systems.

Strongly nonequilibrium conditions, therefore, emerge as viable drivers of structural transformations in GNs. High-energy impacts at the nanoscale can generate intense, localised stimuli, including transient pressure spikes and rapid bond deformation, accompanied by ultrafast energy redistribution throughout the structure [507–509]. These effects activate bond-reorganisation pathways that remain inaccessible under steady-state conditions, making

ballistic collisions a powerful means of probing the energy landscape connecting different carbon allotropes [510]. Such mechanisms are also relevant in astrochemical and planetary environments, where carbonaceous species are exposed to cosmic rays, energetic ions, and grain-grain collisions at temperatures that can fall well below 10 K [511]. A central factor in these transformations is the chemical nature of graphene edges. In finite nanoflakes, undercoordinated edge atoms possess reactive dangling bonds that serve as nucleation sites for bond reconstruction, structural bending, and closure. Experimental and theoretical studies have shown that hydrogen-free edges exhibit enhanced reactivity, whereas hydrogen passivation suppresses the driving force for tubular formation [496, 512, 513].

In this context, the present study investigates collision-induced allotropic transformations in finite, hydrogen-free GNS using reactive MD simulations. We model high-energy impacts between a C_{60} fullerene projectile and a finite C_{296} nanoflake, systematically varying the impact energy and incidence angle to quantify edge-mediated effects, transformation statistics, and structural closure pathways [514]. By linking impact conditions, edge reactivity, and structural response, this work establishes an atomistic framework for understanding how finite graphene systems traverse the energy landscape connecting planar, tubular, and closed carbon allotropes, with implications for nanoscale materials processing and the nonequilibrium chemistry of carbon in astrophysical environments.

ALL SIMULATIONS WERE performed using MBN EXPLORER 5.0. The MBN STUDIO 5.0 toolkit was used to create the initial system's geometries and prepare the necessary input files. The simulated system consisted of a finite GN containing 296 carbon atoms (C_{296}) and a spherical fullerene projectile (C_{60}). The nanoflake was constructed as a planar square fragment with well-defined and evenly distributed armchair and zigzag edges (11 segments of each type), which were left unpassivated to retain chemically reactive dangling bonds and structural flexibility under impact (Figure 5.6).

The nanoflake dimensions (23.865 Å along the zigzag edge and 29.376 Å along the armchair edge) were selected to achieve an approximate target-to-projectile mass ratio of five. Initial nanoflake coordinates were adapted from a curated nanostructure dataset [515] and optimised using the velocity quenching algorithm prior to impact to eliminate residual strain and ensure structural stability. All numerical tolerances were set to 10^{-5} and were fully satisfied upon convergence. The C_{60} projectile was positioned at an initial separation of 40 Å from the nominal impact point, measured from its centroid. This impact point was placed at a distance equal to half the fullerene radius from the selected nanoflake edge in order to favour edge-mediated bending and bond formation rather than central perforation of the flake. An additional vertical offset of 2.0 Å above the nanoflake surface was introduced to account for the finite interaction range, suppressing van der Waals contact prior to the onset of the ballistic phase. Here, the term *ballistic* denotes inertia-driven motion in which the projectile

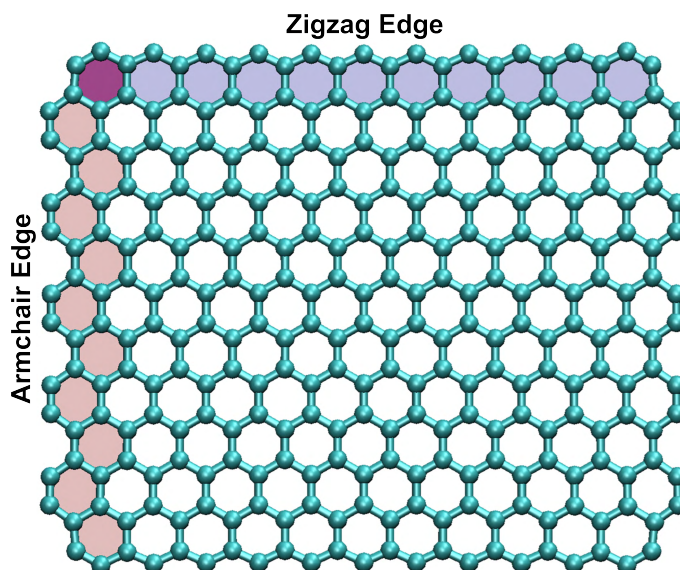


FIGURE 5.6 – Relaxed initial geometry of the square C_{296} graphene nanoflake used as the collision target. Armchair and zigzag edge segments (11 of each) are highlighted, illustrating the equal number of armchair and zigzag edge segments, ensuring an unbiased edge topology, as well as the planar structure prior to impact.

propagates freely under microcanonical (NVE) conditions without the influence of external fields or dissipative media, and does not imply penetration or permanent embedding into the target. To account for variations in the local atomic alignment and initial collision geometry, the impact point was randomly displaced along the direction of the projectile velocity vector projected onto the nanoflake plane within $\pm 0.71 \text{ \AA}$ (approximately half a C–C bond length in the flake), and the projectile was randomly rotated prior to each simulation. Collisions directed toward armchair- and zigzag-oriented edges were treated as separate ensembles.

The C–C bonded interactions within both the nanoflake and the fullerene were described using the many-body Brenner potential [516]. Long-range van der Waals interactions between the fullerene projectile and the graphene nanoflake were modelled using a LJ potential [517]. To monitor changes in molecular topology, an rCHARMM FF was introduced for bonded C–C interactions. Following the approach described in [510], a negligibly weak interaction was employed, characterised by a bond dissociation energy of $10^{-4} \text{ kcal mol}^{-1}$ and a bond-length threshold of $2.0 \text{ \AA}$. This setup allows monitoring and quantifying the dynamic processes of bond breakage and formation, enabling the development of nonhexagonal ring motifs and changes in local coordination under strongly nonequilibrium conditions, while the C–C interactions remain described solely by the nonreactive Brenner potential. The equations of motion were integrated using the velocity Verlet algorithm with a fixed time step of 1 fs in the NVE ensemble.

For a prescribed collision energy E , the projectile velocity was determined from $v = \sqrt{2E/m}$, where m is the mass of a carbon atom multiplied by 60, and decomposed according to the selected incidence angle. MD simulations were performed for 15 ps, which was sufficient to capture the ballistic phase, rapid nonequilibrium atomic dynamics, and subsequent relaxation into metastable or transformed morphologies. Selected cases were extended up to 200 ps to verify the post-formation structural stability of nanotube-like configurations. Collision energies were set in the range 100 eV–1000 eV in increments of 50 eV, and incidence angles were varied between 10° and 60° , measured with respect to the nanoflake plane, on a nonuniform grid. For each combination of edge type, energy, and angle, ten statistically independent trajectories were generated, yielding a total of 5700 collision events.

Structural classification was performed by aligning the final configurations to reference nanotube geometries using rigid-body transformations (translations and rotations only). The reference structures were constructed by topologically closing the same C_{296} nanoflake and relaxing the resulting geometries through velocity quenching. Owing to the finite dimensions of the parent nanoflake, these structures are not commensurate with ideal nanotubes of unique (n, m) chirality, but their diameters (approximately 8.2 Å and 9.8 Å, respectively) and local bonding patterns are closest to those of finite armchair-like (6,6) and zigzag-like (12,0) nanotubes, respectively, and are therefore used as geometric nanotube-like templates.

Atoms ejected from the nanoflake as a result of the fullerene impact were removed prior to analysis, and the RMSD to the reference structures was used as a quantitative similarity metric. A geometric attachment criterion based on the separation of the centres of mass of the projectile and nanoflake was used to locate persistent composite structures. Transformations into nanotube-like structures were identified using an RMSD threshold of 2 Å relative to the corresponding reference nanotube geometry, which provides a balanced criterion for capturing structurally coherent nanotube-like configurations while avoiding false positives associated with partially formed or highly distorted structures.

For each combination of collision energy E , incidence angle θ , and nanoflake edge orientation α , the resolved probability of nanotube-like formation was computed as

$$P_{\text{CNT}}(E, \theta, \alpha) = \frac{N_{\text{CNT}}(E, \theta, \alpha)}{N_{\text{total}}(E, \theta, \alpha)}, \quad (5.1)$$

where $N_{\text{CNT}}(E, \theta, \alpha)$ denotes the number of trajectories terminating in nanotube-like structures and $N_{\text{total}}(E, \theta, \alpha)$ is the total number of trajectories for the specified conditions. The probabilities of atom-ejection events, $P_{\text{ej}}(E, \theta, \alpha)$, and intact nontubular outcomes, $P_{\text{int}}(E, \theta, \alpha)$, are defined analogously. By construction, for each set of collision parameters (E, θ, α) , these probabilities form a complete partition of the observed outcomes, satisfying

$$P_{\text{CNT}}(E, \theta, \alpha) + P_{\text{ej}}(E, \theta, \alpha) + P_{\text{int}}(E, \theta, \alpha) = 1. \quad (5.2)$$

Since the outcome probabilities sum to unity within each (E, θ, α) ensemble, the probability P_{CNT} increases at the expense of competing channels, primarily atom ejection and intact non-tubular relaxation pathways, providing a direct measure of how different collision conditions lead to distinct structural transformations of the system.

WE PRESENT HERE THE MOST salient results, showcasing the effectiveness of the reactive MD approach in predicting the collisional allotropic transformations. A full account is given in [518]. The ensemble of collision trajectories reveals a rich landscape of structural outcomes. The finite GN evolves into a range of metastable structures that arise from the interplay between local bond reorganisation, global elastic deformation, and irreversible energy dissipation. Representative examples of these regimes are shown in Figure 5.7, which highlights the principal topological classes observed under collision conditions that do not preferentially promote coherent tubular closure. Although all structures in the figure are drawn from impacts towards the armchair edge, qualitatively similar morphologies are also observed for zigzag edge-aimed collisions.

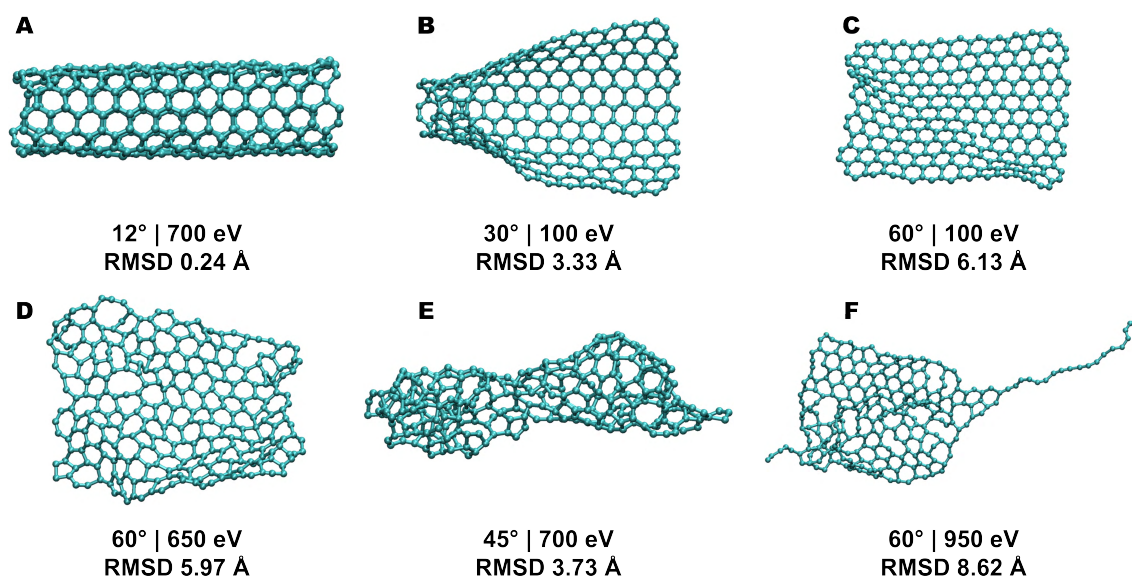


FIGURE 5.7 – Representative structural outcomes obtained from collision-driven transformations towards the armchair edge of C_{296} graphene nanoflakes, illustrating selected metastable morphologies with distinct topologies. The incidence angle θ and collision energy E for each trajectory are indicated. (A) Fully stitched nanotube exhibiting minimal deviation from the reference tubular geometry. (B) Partially closed tubular segment with incomplete seam propagation and one open end. (C) Non-planar nanoflake formed through bending without edge-to-edge bonding. (D) Non-planar flake with pronounced local defects and nonhexagonal ring motifs near the impact region. (E) Amorphous aggregate characterised by dense three-dimensional packing and loss of extended sheet or tubular topology. (F) Amorphous structure featuring extended, undercoordinated linear carbon tails protruding from a disordered core. RMSD values are reported relative to the corresponding reference nanotube geometry.

The first class (A) comprises fully stitched nanotubes, which yield the smallest RMSD relative to the reference tubular geometry across the entire dataset. In this regime, edge-to-edge contact is established across the full width of the nanoflake, and successive bond formation propagates away from the impact region to produce a continuous, low-defect seam and a nearly uniform cylindrical cross section. These structures exhibit the highest structural fidelity to the reference nanotube geometry across all simulated trajectories and serve as reference cases for successful collision-driven transformation from a nanoflake to a nanotube.

The remaining structures show a gradation of unsuccessful nanotube closures. The second class (B) comprises partially closed tubes. Here, local stitching is initiated near the collision site, but seam propagation terminates before spanning the full length. The third class (C) consists of nonplanar nanoflakes. In these structures, the dominant response is bending of the entire nanoflake rather than local bond rearrangement near the impact site. The flake adopts saddle-like or S-shaped conformations, with significant out-of-plane distortion but without the formation of persistent edge-to-edge bonds. The fourth class (D) includes nonplanar flakes with pronounced local defects. In this regime, bond rearrangements are concentrated near the impact region, leading to the formation of nonhexagonal rings and localised structural reconstruction, while the remainder of the flake undergoes out-of-plane bending similar to that observed in (C). The fifth class (E) corresponds to compact amorphous aggregates, which are characterised by dense, three-dimensional packing of carbon atoms, irregular coordination environments, and the loss of an identifiable sheet or tubular backbone. Finally, the sixth class (F) comprises amorphous shapes featuring extended, undercoordinated “linear” tails. In these configurations, compact disordered cores coexist with chain-like carbon fragments that were ripped off the main cluster.

Figure 5.8 summarises the probability of successful transformation to nanotube-like structures, $P_{\text{CNT}}(E, \theta, \alpha)$, across the explored collision parameter space. The maps are organised by edge orientation, with the left-side panel showing collisions to the armchair edge and the right-side panel, to the zigzag edge. For each edge type, the left-side map provides a coarse angular overview at representative incidence angles (15° , 30° , 45° , and 60°), while the right-side map resolves the low-angle regime (10° – 30°) at 2° increments. Each pixel corresponds to a single (E, θ) bin and is colour-coded according to P_{CNT} from 0 (white) to 1 (dark purple), where 1 indicates that all trajectories within the corresponding bin result in nanotube-like structures satisfying the RMSD-based success criterion.

Across both edge orientations, the maps display a pronounced nonmonotonic dependence on collision energy. At the lowest energy considered (100 eV), P_{CNT} is essentially zero across the entire angular range, indicating that the momentum transferred to the nanoflake during the collisions is insufficient to trigger the sequence of structural rearrangements required for nanotube closure. Already at 150 eV, however, pronounced high-probability domains emerge in collisions aimed at both armchair and zigzag edges. In the two-dimensional maps,

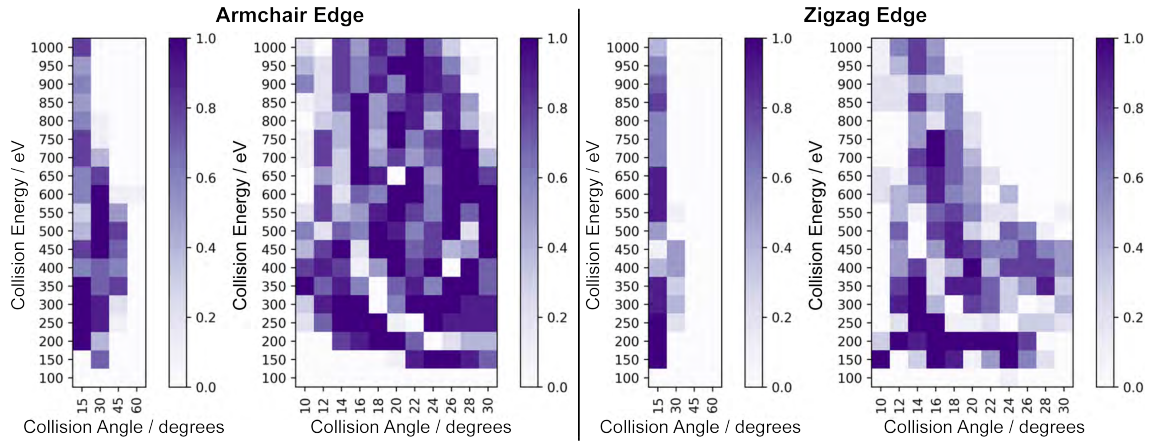


FIGURE 5.8 – Probability maps for successful transformation to nanotube-like structures, P_{CNT} , as a function of collision energy and incidence angle for armchair (left-side panel) and zigzag edge-aimed (right-side panel) collisions to the C_{296} graphene nanoflake. For each edge type, the left panel shows a coarse angular overview at representative angles of 15° , 30° , 45° , and 60° , while the right panel provides a high-resolution view of the low-angle regime (10° – 30°) sampled at 2° increments. Each bin corresponds to a single (E, θ) parameter set and is colour-coded according to the bar scale, representing the probability of satisfying the criterion for nanotube-like structure formation, ranging from 0 (white) to 1 (dark purple).

these localised regions reach P_{CNT} between 0.8 and 1 for selected collision angles, spanning θ between 22° – 30° for the armchair edge and occurring more sparsely for the zigzag edge (notably at $\theta \approx 10^\circ$, 15° – 18° , and 24°). Upon further increasing the collision energy, the armchair case develops a broad favourable window extending approximately from 250 eV to 750 eV, within which several angular regions exhibit $P_{\text{CNT}} > 0.8$, and the averaged probability remains in the range 0.60–0.77. In contrast, the zigzag case shows a narrower and more fragmented pattern, with its largest probabilities concentrated at 150 eV–200 eV and within a more restricted angular range of θ between 10° – 26° . At higher collision energies ($E \geq 750$ eV), the probability of nanotube-like formation decreases again, as evidenced by the re-emergence of low-probability regions in the maps and by the reduction of the averaged P_{CNT} to about 0.41–0.50 for armchair and 0.17–0.26 for zigzag at 800 eV–1000 eV. This trend reflects the increasing contribution of competing processes such as extensive bond rupture, atom ejection, and the formation of highly defective configurations that do not satisfy the criterion for nanotube-like structures. The region of largest P_{CNT} therefore lies at intermediate energies, but its angular extent and the continuity of high-probability regions depend strongly on edge orientation.

For the armchair edge, the coarse-angle overview indicates that successful transformation is concentrated at the smaller representative angles (15° – 30°), whereas large incidence angles strongly suppress closure. The high-resolution map for the armchair case reveals that the low-angle regime is not uniformly favourable but instead exhibits a structured distribution of

high- and low-probability regions. Several extended patches of moderate-to-high P_{CNT} ($0.5 \leq P_{\text{CNT}} \leq 1.0$) appear within 10° – 30° , separated by lighter “corridors” where the probability decreases markedly. The presence of these gaps indicates that, even within this nominally favourable angular range, small variations in θ can redirect the collision outcome towards competing channels that deviate from the reference nanotube topology. Part of this variability may also arise from the limited statistical sampling within individual (E, θ) bins. Notably, elevated P_{CNT} values are not confined to a narrow angular interval but extend across a substantial fraction of the 10° – 30° range, indicating that collisions directed at the armchair edge support successful nanotube closure over a broad set of incidence angles once the energy is sufficient to induce bending and initiate edge-to-edge stitching.

For the zigzag edge, the overall probability is confined to more selective regions of the parameter space. The coarse-angle overview already indicates a stronger sensitivity to the incidence angle θ : the probabilities at 60° and 45° remain effectively zero across the entire energy range. At 15° , however, the zigzag edge remains competitive with the armchair case, with extended energy intervals displaying moderate-to-high P_{CNT} values. This favourable behaviour is not maintained at 30° , for which the probability decreases much more strongly and high- P_{CNT} values become markedly less frequent than in the armchair case. This selectivity becomes clearer in the high-resolution zigzag map, which exhibits distinct, well-defined bands rather than a broad plateau. A prominent feature is a high-probability band at low energies (E roughly between 150 eV–200 eV), extending across small incidence angles (θ between 10° – 26°), indicating a regime where a modest collision-induced momentum transfer to the target can already promote nanotube closure when the geometry is favourable. At higher energies, the map resolves into inverted diagonal bands, in which the high-probability regions shift towards lower incidence angles as the collision energy increases.

Direct comparison of the two panels in Figure 5.8 shows that armchair edge-oriented collisions provide a wider low-angle parameter space over which high P_{CNT} can be achieved, whereas collisions towards the zigzag edge confine successful nanotube closure to narrower windows and more weakly connected regions. This contrast is particularly evident at higher energies, where the armchair configuration continues to support appreciable P_{CNT} across a broad angular range, while the zigzag case is largely suppressed outside a limited set of low-angle conditions. This trend is consistent with the edge-dependent mechanisms. Thus, the efficiency of seam formation depends not only on the availability of reactive, unpassivated edge atoms but also on the local topology of the edge segments, which determines the formation of bridging bonds during the final stitching stage. In practical terms, the probability maps indicate that successful nanotube formation is determined by a balance between (1) sufficient momentum transfer to induce bending and bring the opposing edges into contact, and (2) avoidance of excessive local energy deposition and tangential shear of the nanoflake, which promote competing processes and suppress coherent seam propagation.

Figure 5.9A illustrates the atomistic sequence by which a finite, hydrogen-free graphene nanoflake undergoes coherent topological closure following a ballistic impact, using a representative armchair-oriented case at an incidence angle of 26° and a collision energy of 150 eV. The time-resolved snapshots reveal a strongly localised, yet system-spanning, mechanism in which energy deposited at a single edge site is redistributed across the entire flake, ultimately driving a coordinated, edge-to-edge stitching process that converts a planar fragment into a fully connected nanotube.

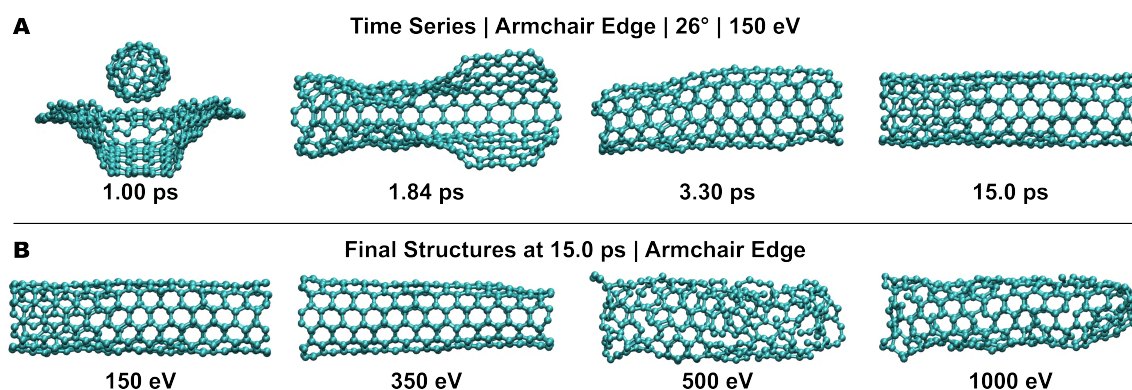


FIGURE 5.9 – Mechanism of edge-mediated topological closure of a graphene nanoflake from a fullerene collision aimed at the armchair edge of a C_{296} graphene nanoflake following ballistic impact. (A) Time-resolved snapshots for a representative trajectory at an incidence angle of 26° and a collision energy of 150 eV, illustrating the sequence from initial edge contact and grazing penetration of the C_{296} projectile, through local bending and progressive, zipper-like seam formation between opposing zigzag edges, to the emergence of a fully connected nanotube by $t = 15.0$ ps. The simulation snapshot at intermediate instant ($t \approx 1.84$ ps) highlights the systematic propagation of edge-to-edge bonding away from the impact region. (B) Final morphologies obtained at increasing collision energies for the same edge orientation, showing the transformation from open-ended nanotubes at lower energies to closed, cage-terminated nanotubes at higher energies, driven by enhanced post-closure energy redistribution and secondary bond reorganisation at the tube extremities.

At early simulation times ($t \approx 1.00$ ps), the C_{60} projectile makes initial contact with the nanoflake near the armchair edge and slides along the flake surface while partially penetrating the edge region. This grazing interaction maximises the normal component of the momentum transfer at the nanoflake edge without imparting the excessive local energy density associated with fragmentation. The immediate response is the formation of a shallow curvature and local rehybridisation at the impact site, accompanied by the nucleation of nonhexagonal motifs and transient sp^2 – sp^3 bonding that act as seeds for structural bending. By $t \approx 1.84$ ps, the deformation front has propagated away from the collision zone, and the opposing zigzag edges are drawn into close proximity. Rather than closing a nanotube at a single point, the snapshots show a progressive, zipper-like seam formation that initiates near the impact region and advances systematically along the length of the nanoflake. At intermediate times ($t \approx 3.30$ ps), the seam has propagated across the full width of the flake, yielding a fully

stitched nanotube-like structure. The residual kinetic energy is redistributed into global vibrational modes of the newly formed nanotube, leading to minor radial breathing and axial oscillations rather than further topological rearrangement. By the end of the simulated trajectory ($t = 15.0$ ps), the system has relaxed into a perfectly connected nanotube with no persistent projectile attachment and minimal residual defects.

Figure 5.9B compares the final morphologies obtained at various energies for armchair edge-oriented collisions at representative incidence angles. At the two lower energies (150 eV and 350 eV), the resulting nanotubes retain open ends. In these cases, the energy transfer is sufficient to induce bending and drive seam propagation along the opposing edges, but the remaining kinetic energy after closure is not sufficient to promote further bond rearrangements at the tube termini. The open rims therefore persist as metastable edge structures over the full simulation window. In contrast, at higher energies (500 eV and 1000 eV), the nanotubes undergo additional structural evolution at their ends, leading to complete closure. In these cases, the more intense initial energy deposition not only drives rapid seam formation across the entire nanoflake but also leaves a significant amount of internal energy within the newly formed nanotube. This excess energy is subsequently redistributed toward the open ends, where it promotes further bond rearrangements, the formation of nonhexagonal rings, and eventual cap formation. The result is the emergence of closed, cage-terminated nanotubes, indicating a transformation from edge-mediated seam propagation to a two-stage process in which seam formation is followed by end capping driven by internal energy redistribution.

IN SUMMARY, WE HAVE SHOWN how reactive MD seamlessly combining the rCHARMM framework with a many-body Brenner potential describes complex collision-driven topological transformations in finite, hydrogen-free graphene nanoflakes. This work helps elucidate how strongly nonequilibrium energy input enables access to regions of the carbon allotrope landscape that remain inaccessible near equilibrium, including pathways associated with structural bending, bond rearrangement, and edge-to-edge stitching. We mapped the outcome landscape of ballistic impacts between a C_{60} fullerene and a square C_{296} nanoflake containing equal numbers of armchair and zigzag edge segments and identified the conditions under which coherent nanotube-like formation becomes statistically favoured. The trajectory ensemble reveals a broad spectrum of metastable morphologies, including fully stitched nanotubes, partially stitched tubular segments, bent nonplanar flakes, locally reconstructed defective structures, compact amorphous geometries, and highly disordered carbon networks featuring undercoordinated chain-like tails. This diversity reflects a competition between cooperative bending and irreversible energy dissipation through bond rupture, defect formation, and atom ejection, the balance of which depends sensitively on incidence angle, collision energy, and edge topology.

Statistical analysis shows that armchair-oriented impacts sustain coherent tubular transformation over a substantially broader parameter window than zigzag-oriented impacts, as quantified by RMSD-based similarity to a reference nanotube and by the occurrence of atom ejection. The probability maps indicate a pronounced nonmonotonic dependence on collision energy, with successful nanotube-like closure confined to low-to-moderate oblique incidence angles ($\theta \approx 10^\circ\text{--}30^\circ$) and intermediate collision energies ($E \approx 200\text{--}700$ eV). In this regime, the transferred momentum is sufficient to induce bending and bring opposing edges into contact, while remaining moderate enough to preserve the structural integrity required for sustained stitching. At lower energies, deformation remains largely elastic and does not lead to edge-to-edge bonding, whereas at higher energies the increasing contribution of bond rupture, defect formation, and atom ejection suppresses coherent closure. Zigzag-oriented impacts display narrower and more fragmented regions of high P_{CNT} , together with a stronger reduction of P_{CNT} at high energies and systematically higher atom ejection counts, consistent with an increased tendency towards local bond rupture and defect accumulation that interrupts seam propagation.

Time-resolved trajectory analysis reveals an atomistic sequence for coherent edge-mediated closure. A grazing impact at the nanoflake edge initiates local bonding rearrangement and bending, after which elastic strain redistribution across the nanoflake brings distant edge segments into proximity. Nanotube closure proceeds through a zipper-like stitching process that propagates away from the impact region, forming a continuous seam and a structurally coherent nanotube. After the tubular topology is established, the remaining internal energy redistributes into collective vibrational motion of the nascent nanotube, which stabilises open-ended morphologies at lower collision energies but can promote closure of the nanotube ends at higher energies.

5.5 CONCLUSIONS

THE WORKS EXPLORED IN THIS chapter expands on the application of the methods chosen for the construction of the PACVD multiscale simulation model. The strengths and weaknesses of the TDDFT/ ω B97X-D method in dealing with electronic excited-state investigations is further assessed in two contexts. Firstly, we have shown that the linear scaling version of coupled cluster for excited states, the DLPNO-EOM-CCSD method, may suffer from lack of size-consistency and can sometimes give poorer results compared to TDDFT (§ 5.2). These results serve as a cautionary tale against blindly trusting any level of theory, and demands careful judgement of methods and interpretations from the scientist. In this sense, the work presented in Chapter 3, although fairly comprehensive in its scope, is far from final, leaving room for improvement and further critical evaluation.

Secondly, we have shown that, even purely within the higher QM level of theory, moving towards multiscale properties is possible (§ 5.3). The VUV spectral features of molecular solids of astrochemical interest has been quite well predicted with the cluster approach including only vertical excitations with artificial Gaussian broadening. NTO analyses proved adequate to assign the transition characters in comparison with those for the isolated molecules. It is even possible to differentiate amorphous from crystalline solids, as has been shown for O₂. The limitations of the method were also delineated. The accuracy of the transition energies is system-dependent and improves with the increasing of cluster sizes, but the larger the clusters, the costlier the computations. Here as well, improvements are possible still at the TDDFT level by inclusion of other effects, neglected in the model for the time being.

Finally, we have demonstrated the synergy between the Brenner many-body potential and the rCHARMM reactive FF in the description of an extreme-energy chemical transformation. Complex collision-driven transformations of extended carbon networks have been shown with atomistic details, producing several types of transformations of carbon nanoflakes. The method showed a balanced description of carbon local topological transformations without any noticeable nonphysical effect. Although the results are not to be taken as definitive validation, they at least serve as another test-case for the algorithm implemented in MBN EXPLORER, in lieu of its application to our final model, which we discuss in the next chapter.

CHAPTER 6

TOWARDS THE SIMULATION OF THE PACVD PROCESS

CONTENTS

6.1	METHOD PROPOSAL-----	162
6.1.1	A MM/MD MODEL FOR THE PRECURSORS -----	162
6.1.2	IDMD APPROACHES-----	165
6.2	IMPROVING THE MODEL AND FUTURE PERSPECTIVES -----	166
6.3	FINAL REMARKS -----	167

THIS CHAPTER FUNCTIONS as a Janus.¹ It looks back at the photochemical investigations of the PACVD precursors discussed in Chapter 3 and at the MM/MD model of alkanethiol SAMs presented in Chapter 4, and moves towards the main objective of assembling these results into the multiscale simulation of the PACVD process in the general context laid out in Chapter 1 and using the methods described in Chapter 2. At the same time, it looks into the future, discussing the prospects of such endeavour that has not been fully realised yet.

To be more specific, in § 6.1 we propose a method for the reactive MD modelling of the precursors including excited states with an rCHARMM parametrisation. The probability inputs to the IDMD module from the data acquired in the photochemical investigations (Chapter 3) so far is discussed. We also propose a simple solution for the interaction of the various precursor fragments with the substrate. We then discuss the limitations of the proposed model and offer insight into avenues leading to its improvement in § 6.2. The model is devised in such a way that allows for the progressive and systematic increase in complexity and accuracy as new knowledge about the system is gained through further theoretical and experimental investigations.

6.1 METHOD PROPOSAL

THE ATOMISTIC ELEMENTS of the PACVD simulation we propose are an alkanethiol SAM substrate as modelled by the strategy presented in Chapter 4 and a particular Ru-containing precursor from the set discussed in Chapter 3. The substrate model is very close to complete. We only need to define the reactive potentials of the alkanethiol terminals with the various precursor fragments. We discuss this strategy further below. We have not yet presented a MM/MD model of the precursors themselves, which we discuss now.

6.1.1 A MM/MD MODEL FOR THE PRECURSORS

THE GREATEST COMPLEXITY that needs to be more carefully addressed for our selected precursors is the description of the polyhapto Ru–diene bonds and the bonded and free diene moieties. There are several ways one can choose to model the Ru–diene bonds for molecular FF parametrisation purposes. Wahlers *et al* [519] discuss four alternatives in the context of a ferrocene model. Two of them are nonbonded approaches: (1) the ligands are treated as rigid bodies with a fixed position relative to the metal centre, or (2) the ligands interact with the metal centre through nonbonded interactions (Coulomb and van der Waals potentials). Neither of these approaches is suitable for our purposes since we need covalent interactions in order to keep track of the topology of the molecules via PSF files and to assign dissociation

¹Janus (Latin: Iānus) is the Roman god of beginnings, ends, gates, transitions, time, duality. He is usually depicted with two heads fused together back-to-back, one face looking back or into the past, the other looking forward or into the future. The month of January, as the beginning of a new year or a transition, is named after this mythological figure.

probabilities and changes in the interaction parameters (see below). Besides that, describing what is essentially a covalently bonded system (see § 3.3.2) by nonbonded interactions is conceptually inadequate.

There remains the two covalent options. (3) The most intuitive way is to consider a covalent bond between Ru and each of the carbon atoms (four if an η^4 bond) involved in the interaction. This strategy offers a more flexible and granular description that can easily account for changes in hapticity such as those discussed for **3COT** in § 3.3.1. The disadvantages for our purposes are too many, though: the parametrisations of this high number of bonds and the various implied angles is cumbersome and can generate artefacts; rotation of the ligand is impeded, which may result in a molecule that is too stiff; and, most importantly, the assignment of a bond centre for dissociation in the IDMD approach, with changes of topologies and probabilities of dissociation becomes too complex. There remains (4) the dummy-atom approach, in which a dummy atom is positioned at the centroid of the diene carbon atoms involved in the bonding to the metal. The dummy atom is bonded to each of those diene carbon atoms and to the metal centre. A single Ru–diene bond interaction potential is assigned to the dummy–metal bond. This method simplifies the description of the bonding, allowing for a single set of bond parameters for the Ru–diene interaction—consistent with the simple PEC description of the bond dissociation discussed in Chapter 3—and a single dissociation probability for the IDMD simulation. It also allows for easy rotation of the diene, that can be controlled by nonbonded interactions with the CO ligands. The disadvantage is the introduction of an extraneous atom whose bonds to the diene need to be parametrised. If not done correctly, this can introduce artefacts. Nevertheless, the dummy-atom approach has been preconised by several authors for various polyhapto molecules [519–522], and we also propose the use of such a model here, as exemplified in Figure 6.1.

The next step in modelling the precursors is the definition of FF parameters. The Ru–C–O moieties in the various precursors are straightforward to describe. The bond stretch parameters can be directly obtained from the DFT scans. Bond angle and dihedral torsion parameters can also be obtained from DFT scans, but will preferably be sourced from existing databases or previous work, such as the ones already developed within the scope of FEBID simulations with metal-carbonyl precursors using MBN EXPLORER [221, 222, 224, 274, 282]. With the dummy-atom approach, it is also a simple task to fit bonded parameters to the Ru–dummy bond from the PEC calculated in Chapter 3, as exemplified in Figure 6.1. The internal FF parameters describing the bonded atoms in the dienes can be obtained through various means. An interesting *ab initio* approach is the Seminario method that only uses the information contained in the QM Hessian matrix of a molecular system [523]. This method has been adapted for parametrisation of metal-containing molecules for the assisted model building with energy refinement (AMBER) FF [524]. Our initial suggestion, though, is to extract these parameters from the CGenFF engine for the free dienes, as we

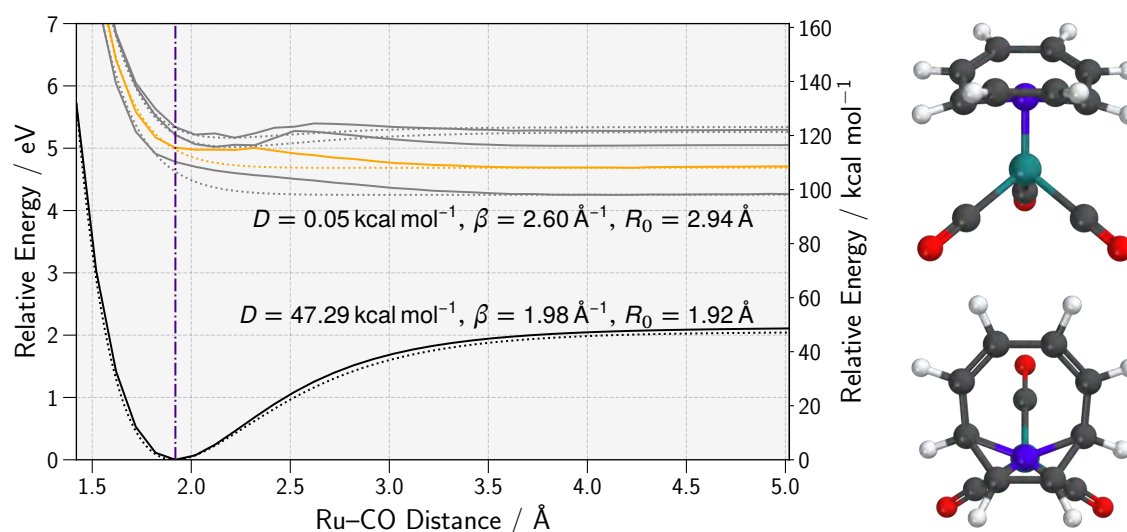


FIGURE 6.1 – Representative PACVD precursor PECS fitted with Morse potentials (dotted curves) for rCHARMM FF parametrisation and two views of a dummy-atom (purple sphere) model of the Ru–diene bond in **3cot**. Morse parameters for the GS and for the first (dark), dissociative excited state PECS are shown.

have done for the alkanethiols (see Chapter 4), and keep them unchanged in the various diene-containing fragments. Since these parameters will not be crucial for the objectives of our PACVD simulation, any small inaccuracy in them should have negligible impact. The interaction parameters of the dummy atom with the diene carbon atoms are also not as crucial. It is sufficient that it properly keeps the diene equilibrium geometry correct with a small amount of flexibility. This parametrisation will need to be tested. The reactive bonds (Ru–CO and Ru–diene) will be described by a Morse potential while the remaining ones will be modelled by the usual harmonic potential. For any missing LJ parameter in our model (eg, for Ru) we propose the use of those in the UFF, as it has already been successfully used for the alkanethiols.

Finally, the reactive interactions of the various precursor fragments with the alkanethiol chains need to be defined. The mechanism by which the Ru deposits form on the substrate has not been elucidated in details yet. However, we suppose that the metal forms a bond with the hydroxyl oxygens of either the alcohol or the carboxylic acid terminals of the chains, with release of hydrogen. We do not need to model this reaction in its full detail. We propose the removal of all H atoms from the hydroxy groups, leaving the oxygen atoms with a free valence to form bonds with the metal. We then define a Morse potential for the Ru–O bond. The parameters of this potential can be calibrated against quantitative experimental PACVD data or through additional DFT calculations.

6.1.2 IDMD APPROACHES

WITH THE MOLECULAR MODEL defined, the approach to the stochastic irradiation step must be decided. The IDMD module in MBN EXPLORER allows for two modes relevant to our problem: the use of *random dissociation* events and of *random atom type change* events. In the former approach, the user assigns a set of probabilities for the dissociation of each active bond in the system, together with an energy that will be deposited into the atoms of the bond in case the event is accepted. In the latter mode, the probabilities set by the user are for the change of atom types for the atoms associated with each active bond. If the event is accepted, the atom types are changed, and with that, the interactions parameters will be changed accordingly, provided they are adequately defined in the FF files.

With the random dissociation strategy, the idea is to model the entire dissociation process as a fast local event. Some control of the process is possible by considering the amount of energy deposited in the bonds. To use this approach, one needs to know the dissociation cross section of each photodissociation event. We do not have access to this information with the data generated in our investigations discussed in Chapter 3. This is because the full dissociation process is dynamical, following a series of events after the absorption of a photon that can culminate in dissociation or in the relaxation of the system back to the GS. The only calculated cross section we have access to is the photoabsorption cross section for the various vertical transitions (§ 3.3.3). We can start from these values for the relevant excited states leading to dissociation channels as we have identified and further refine the values against experimental quantum yields. However, the solution phase quantum yields available for the precursors so far [266] are not comprehensive and likely do not reflect the gas-phase values. More experimental data is needed to validate the probabilities for this method.

A more direct approach from the theory perspective would be the use of the random atom type change mode. Changing atom types in a bond amounts to switching the PES related to that pair of atoms. If the initial parameters for the initial atom pair type are fitted from the GS PEC and those for the new atom types are fitted for a given excited state (see Figure 6.1), the random event is akin to a photoexcitation. After that, during the MD stage at a finite temperature, the system would then evolve on the excited state potential with a possible dissociation depending on the BDE. For dissociative states it is possible to obtain a reasonable Morse potential with essentially null BDE. Although the Morse potential has not been devised to describe dissociative PEC, the approximation is good enough for our purposes, as the example in Figure 6.1 shows. In the case of more complex dissociation channels where a series of internal conversions are necessary to achieve dissociation, one can use an effective Morse potential with the estimated barriers as those shown in Table 3.7. Of course, this model must also be validated against experimental data and the photoabsorption cross sections and the BDEs can be adjusted accordingly.

6.2 IMPROVING THE MODEL AND FUTURE PERSPECTIVES

THE METHOD PROPOSED above can already be put into effect, particularly if the random atom type change approach is utilised in the IDMD simulations. However, the proper validation of the model depends on quantitative experimental data not yet available. Without validation, the model cannot be trusted for any prediction. The necessary experimental data are gas-phase dissociation quantum yields for the precursors, detailed time-resolved chemical mapping of PACVD deposits on the substrates of interest during the experiment, gas-phase transient (time-dependent) spectroscopic analysis of the precursors and fragments, among others.

The IDMD model proposed in § 6.1.2 above has also some limiting assumptions that must be carefully considered. The approach using the random atom type change assumes that there is a small number of dominant dissociative channels for each fragmentation event. Indeed, that can be assumed from the investigations we have done in Chapter 3: only a few bright excited states exist in the photon energy range we considered, and of these, a few dissociation channels have been identified. For systems where a large number of dissociation channels from various different excited states exist, our model would easily become too complicated to parametrise. The existence of events leading to nonradiative deactivation of the precursors with a high probability competing against dissociation channels are also a problem. This is because the IDMD model implemented on MBN EXPLORER has no way of accounting for a change back to the original atom types of the GS.

For the description of more complex cases, the random dissociation approach is more suitable because a single net cross section is utilised for each photodissociation event. The photodissociation process can be thought of as a series of possible events. A molecule initially in the ground state absorbs a photon and reaches a given excited state. The probability of this event is measured by the photoabsorption cross section σ_{abs} . Once in the excited state, the nuclear coordinates of the molecule evolve on the excited state PES for a while. We are here still considering the BO approximation. The system may reach a conical intersection with another state of same spin multiplicity, leading to an internal conversion, or cross a PES of different spin multiplicity, leading to an intersystem crossing (non-BO events). Indeed, many such events can happen in the course of this evolution, and we have proposed many of them in Chapter 3. We can assign a probability P_{cross} for each crossing event. After possibly several of these events, the system may dissociate, decay back to the GS, or even undergo an undesirable reaction with other molecules. Only the dissociation outcome is important for our case, to which we can assign a final probability P_{diss} . The total photodissociation cross section for a channel in this scenario is given by

$$\sigma = \sigma_{\text{abs}} \times \prod_j P_{\text{cross},j} \times P_{\text{diss}}. \quad (6.1)$$

The various $P_{\text{cross},j}$ can be obtained from nonadiabatic quantum dynamics calculations using either trajectory ensemble methods (eg, surface hopping, *ab initio* multiple spawning) or fully quantum methods (eg, wavepacket dynamics) [525–532]. In trajectory approaches, the probability is inferred from the fraction of trajectories undergoing a surface hop; in wavefunction-based methods, it is obtained from the projected state populations after the crossing region. Transient spectroscopy experiments are often utilised in parallel to such simulations to better interpret the data [533–536]. Such investigations are complex and time-consuming but have the potential to greatly improve our multiscale model and offer invaluable insight into the photochemistry of these precursors.

In summary, the near-future progression of this project is: (1) production of better quantitative data for the PACVD process to be used in the validation of the model; (2) time-resolved spectroscopy (ultrafast pump-probe experiments) studies of the precursors' photodissociation; (3) nonadiabatic dynamics simulations of relevant photodissociation pathways as identified in Chapter 3 and from the aforementioned experiments; (4) improvement of the model by inclusion of this new information and further validation. With a robust model and a well-established protocol, there is potential for this work to result in a dedicated module for PACVD simulations implemented in a future version of MBN EXPLORER. Such tool would be an attractive resource for academic and industrial sectors interested in the application and investigation of PACVD. Therefore, the work presented in this text, far from concluded, is the beginning of a much greater task, to be carried further into the future.

6.3 FINAL REMARKS

THIS BODY OF WORK ENCOMPASSES a proof-of-concept application of various computational methods for the simulation of a photoassisted chemical vapour deposition process. The details of the project were introduced in the context of multiscale modelling in Chapter 1. The theoretical and computational bases underpinning this project were then detailed in Chapter 2.

This foundational work was followed, in Chapter 3, by a detailed QM-based investigation of the photodissociation chemistry of five (η^4 -diene) $\text{Ru}(\text{CO})_3$ precursors for PACVD: diene = butadiene (BUD), isoprene or 2-methyl-1,3-butadiene (MBUD), cyclooctatetraene (COT), 1,3-cyclohexadiene (CHD), cyclobutadiene (CBUD). We applied DFT to investigate all pertinent equilibrium geometries and coordination for all precursors and their fragments. EDA-NOCV aided in interpreting the Ru-diene bond situation of the pristine precursors. Ground-state DFT optimisations and Ru–ligand scans were then combined with TDDFT excitations and adiabatic singlet PES profiles to identify CO- and diene-loss pathways. NTO analysis was utilised to assign the character of the excited states involved in the photoreactivity of the chemical species and to help in the identification of potential IC pathways. The calculated

UV-vis spectra reproduced experimental trends, including the markedly higher absorptivity and extended wavelength coverage of the COT-containing complex and serving as a validation for the choice of method. We concluded that CO loss is generally enabled by a range of localised metal-ligand or charge-transfer excitations and IC-assisted channels. In contrast, diene loss is strongly ligand dependent: BuD, MBuD, and CHD showed accessible pathways, CBuD remained resistant, and COT exhibited additional complexity due to ligand flexibility and coordination changes.

We then discussed the task of building a MM/MD model of the alkanethiol SAM substrates in Chapter 4. We tackled the challenge of providing a consistent computational description of the unique structural features of these systems, such as adsorption patterns, chain conformations, and superlattice arrangements. We systematically analysed MM FF parameters for bonded and nonbonded (van der Waals and Coulomb) interactions in alkanethiol SAMs with different terminal groups. Using structure optimisation and energy decomposition analysis, we assessed the impact of FF parameters on key properties, such as the equilibrium tilt angle, ligand packing density, and nanoscale structural organisation. An optimal set of FF parameters that reproduces the experimentally determined structural and energetic properties of these systems was identified. We demonstrated that the final set ensures the dynamic stability of the structures at room temperature. This investigation provided a validated general framework for simulating pristine and functionalised alkanethiol-coated substrates under thermal conditions relevant to experimental applications, in particular as substrates for the PACVD process.

In the spirit of complementing the methodological discussions, we included three case studies showing different facets of the methods in Chapter 5. In § 5.2 we showed a comparison of TDDFT with a linear-scaling version of the CCSD method for electronic excited states (DLPNO-EOM-CCSD). While the CC method predicted transition energies closer to the experimental values, it was outperformed by TDDFT in predicting band shifts for related BODIPY molecules of different sizes, possibly because of the lack of size consistency introduced by the DLPNO approach, which is otherwise absent in standard CC methods, as we discussed in § 2.1.1. Since at the multiscale level we often need to describe and compare systems of large and varying sizes, such errors must be handled judiciously.

In § 5.3 we showed the possibility of moving from the molecular towards the condensed-phase level for the calculation of excited-state properties still at the QM level. Four cases (CO, H₂O, O₂, and N₂O) illustrated the successes and challenges of an approach applying TDDFT to molecular clusters to predict the VUV spectra of molecular ices of astrochemical interest. We showed the clear fitness of the method for the prediction and assignment (when combined with NTO analysis) of most experimentally detected bands, usually with good quantitative accuracy in the spectra. We also showed that spectral differences between amorphous and crystal O₂ solids can be predicted and explained by the method. On the other hand, we highlighted two drawbacks of the method. (1) The case of H₂O demonstrated

that quantitative accuracy may require increasing cluster size beyond what is computationally feasible. (2) The collected data demonstrated that the performance of the method is strongly system-dependent.

A last case study concluded the chapter showcasing the ability of the reactive CHARMM FF combined with a many-body Brenner potential in predicting allotropic transformations of carbon materials in collision processes. In this investigation, we modelled energetic collisions involving a C_{60} fullerene projectile and a finite C_{296} graphene nanoflake across a broad parameter space of collision energies, incidence angles, and edge terminations. The structural response was analysed through statistical transformation maps that quantified the probability of nanoflake bending, edge stitching, and the formation of nanotube-like structures. We identified a regime of collision energies and oblique incidence angles under which localised energy deposition at unpassivated edges promotes bond rearrangement, cooperative bending, and covalent stitching between opposing edges. We found that armchair and zigzag edge-directed impacts result in different probability distributions for nanotube formation. These results established a non-equilibrium framework linking local edge chemistry and collision-induced energy deposition to topological evolution in finite graphene systems. They also showed the generality and versatility of the reactive MD approach in the description of complex chemical transformations, necessary for our main objective in this work.

Finally, in this chapter, we brought the results of the investigations discussed in Chapter 3 and Chapter 4 together by proposing a model of the multiscale IDMD simulation of the PACVD process. We discussed how the large dataset obtained as a result of the investigations in Chapter 3 allow us to obtain parameters for the stochastic step of the IDMD simulations and to parametrise rCHARMM FFs for the precursors. We proposed a dummy-atom description of the Ru–diene bond that allows for simple assignment of dissociative Morse parameters and for one-step probabilistic dissociations. We presented two approaches to IDMD: the random dissociation and the random atom type change modes. We discussed the scenarios where each of them are more appropriate, and we stressed the necessity for experimental data to validate our final model. We concluded proposing ways in which the method can be improved, and outlining the future plans for this endeavour.

REFERENCES

- [1] J Tabilo Alvarez and P Ramírez-Correa, “A Brief Review of Systems, Cybernetics, and Complexity”, *Complexity*, 2023, **2023**, 8205320, DOI: 10.1155/2023/8205320. 
- [2] S Kesić, “Systems biology, emergence and antireductionism”, *Saudi J Biol Sci*, 2016, **23**, 584–591, DOI: 10.1016/j.sjbs.2015.06.015. 
- [3] S M Manson, “Simplifying complexity: a review of complexity theory”, *Geoforum*, 2001, **32**, 405–414, DOI: 10.1016/S0016-7185(00)00035-X.
- [4] S Wolfram, “Complex Systems Theory”, in *Emerging Syntheses In Science*, ed D Pines, CRC Press, 2018, vol 1.
- [5] M Fuentes, “Complexity Measures”, in *Complexity, Emergence and the Evolution of Scientific Theories: Towards a Predictive Epistemology*, Springer Nature Switzerland, Cham, 2025, pp 21–44, DOI: 10.1007/978-3-031-99994-9_2.
- [6] F A Rodrigues, “Prediction and inference in complex networks: A brief review and perspectives”, *Europhys Lett*, 2026, **153**, 21002, DOI: 10.1209/0295-5075/ae2950. 
- [7] M Gosak, R Markovič, J Dolenšek, M Slak Rupnik, M Marhl, A Stožer and M Perc, “Network science of biological systems at different scales: A review”, *Phys Life Rev*, 2018, **24**, 118–135, DOI: 10.1016/j.plrev.2017.11.003.
- [8] J Dupré, *The Disorder of Things: Metaphysical Foundations of the Disunity of Science*, Harvard University Press, London, UK, 1st ed, 1993.
- [9] D G Witmer, “Dupré’s Anti-Essentialist Objection to Reductionism”, *Philos Q*, 2003, **53**, 181–200, DOI: 10.1111/1467-9213.00305.
- [10] J A Fodor, “Special Sciences (or: The Disunity of Science as a Working Hypothesis)”, *Synthese*, 1974, **28**, 97–115.
- [11] J Fodor, “Special Sciences: Still Autonomous After All These Years”, *Philos Perspect*, 1997, **11**, 149–163.
- [12] T E Jones, “Special Sciences: still a flawed argument after all these years”, *Cogn Sci*, 2004, **28**, 409–432, DOI: 10.1207/s15516709cog2803_5.
- [13] H F Spinner, “Science without reduction”, *Inquiry*, 1973, **16**, 16–94, DOI: 10.1080/00201747308601681.
- [14] M J Nathan, “Between Scylla and Charybdis”, in *Black Boxes: How Science Turns Ignorance Into Knowledge*, Oxford University Press, 2021, DOI: 10.1093/oso/9780190095482.003.0002.

- [15] *The Re-Emergence of Emergence: The Emergentist Hypothesis from Science to Religion*, ed P C W Davies and P Clayton, Oxford University Press, New York, NY, USA, 1st ed, 2006.
- [16] J A Walker and T E Cloete, “Reductionism or holism? The two faces of biology”, *HTS Teol Stud*, 2023, **79**, DOI: 10.4102/hts.v79i1.8336. 
- [17] A Rosenberg, “Reductionism (and Antireductionism) in Biology”, in *The Cambridge Companion to the Philosophy of Biology*, ed D L Hull and M Ruse, Cambridge University Press, 2007, pp 120–138, DOI: 10.1017/CCOL9780521851282.007.
- [18] A Rosenberg and D M Kaplan, “How to Reconcile Physicalism and Antireductionism about Biology”, *Philos Sci*, 2005, **72**, 43–68, DOI: 10.1086/428389.
- [19] R H Jones, *Analysis & the Fullness of Reality: An Introduction to Reductionism & Emergence*, Jackson Square Books, New York, NY, USA, 1st ed, 2013.
- [20] R W Batterman, *The Devil in the Details: Asymptotic Reasoning in Explanation, Reduction, and Emergence*, Oxford University Press, New York, NY, USA, 2001.
- [21] W C Wimsatt, *Re-Engineering Philosophy for Limited Beings: Piecewise Approximations to Reality*, Harvard University Press, Cambridge, MA, USA, annotated edition, 2007.
- [22] P W Anderson, “More Is Different”, *Science*, 1972, **177**, 393–396, DOI: 10.1126/science.177.4047.393.
- [23] R B Laughlin, “Nobel Lecture: Fractional quantization”, *Rev Mod Phys*, 1999, **71**, 863–874, DOI: 10.1103/RevModPhys.71.863. 
- [24] R B Laughlin and D Pines, “The Theory of Everything”, *Proc Natl Acad Sci USA*, 2000, **97**, 28–31, DOI: 10.1073/pnas.97.1.28. 
- [25] E B Davies, *Epistemological Pluralism*, This is a substantially rewritten and expanded version of a paper called “Scientific Understanding”, 2006.
- [26] V Havlik, *Hierarchical Emergent Ontology and the Universal Principle of Emergence*, Springer, Cham, Switzerland, 2022, DOI: 10.1007/978-3-030-98148-8.
- [27] D Kondepudi and I Prigogine, *Modern Thermodynamics: From Heat Engines to Dissipative Structures*, Wiley, West Sussex, UK, 2nd ed, 2015, DOI: 10.1002/9781118698723.
- [28] L D Landau and E Lifshitz, *Statistical Physics, Part 1*, Pergamon Press, Oxford, UK, 3rd ed, 1980, vol 5.
- [29] H B Callen, *Thermodynamics And an Introduction to Thermostatistics*, Wiley, New York, NY, USA, 2nd ed, 1985.
- [30] J S Dugdale, *Entropy and its Physical Meaning*, Taylor & Francis, London, UK, 2nd ed, 1996, DOI: 10.1201/9781315274324.
- [31] M A Bedau, “Weak Emergence”, *Philos Perspect*, 1997, **11**, 375–399.
- [32] M A Bedau, “Is Weak Emergence Just in the Mind?”, *Minds Mach*, 2008, **18**, 443–459, DOI: 10.1007/s11023-008-9122-6.
- [33] D J Chalmers, “Strong and Weak Emergence”, in *The re-emergence of emergence: the emergentist hypothesis from science to religion*, ed P Clayton and P Davies, Oxford University Press, 2006.

- [34] P Clayton, *Mind and Emergence: From Quantum to Consciousness*, Oxford University Press, New York, NY, USA, 2005.
- [35] S Gibb, R F Hendry and T Lancaster, *The Routledge Handbook of Emergence*, Routledge, London, UK, 1st ed, 2019.
- [36] *Emergence: Contemporary Readings in Philosophy and Science*, ed M A Bedau and P Humphreys, MIT Press, 1st ed, 2008, DOI: 10.7551/mitpress/9780262026215.001.0001.
- [37] J M Wilson, *Metaphysical Emergence*, Oxford University Press, Oxford, UK, 2021.
- [38] T Nagel, *What Is it Like to Be a Bat?*, Oxford University Press, New York, NY, USA, 2024, DOI: 10.1093/oso/9780197752791.001.0001.
- [39] T Nagel, *Mind and Cosmos: Why the Materialist Neo-Darwinian Conception of Nature Is Almost Certainly False*, Oxford University Press, New York, NY, USA, 2012.
- [40] M A Bedau, “Weak Emergence and Computer Simulation”, in *Models, Simulations, and Representations*, ed P Humphreys and C Imbert, Routledge, 2012.
- [41] S Wolfram, “Computation theory of cellular automata”, *Commun Math Phys*, 1984, **96**, 15–57, DOI: 10.1007/BF01217347.
- [42] S Wolfram, *A New Kind of Science*, Wolfram Media, Inc, Champaign, IL, USA, 2022.
- [43] S Wolfram, *Cellular Automata and Complexity : Collected Papers*, CRC Press, Boca Raton, FL, USA, 2018.
- [44] D Fan and B Zheng, “Diachronic Emergence and its Characteristics from the Viewpoint of Complexity Science”, *Front Philos China*, 2020, **15**, 653–674, DOI: 10.3868/s030-009-020-0037-0.
- [45] C Szabo and L Birdsey, “Toward the Automated Detection of Emergent Behaviour”, in *Emergent Behavior in Complex Systems Engineering*, John Wiley & Sons, Ltd, 2018, chap 11, pp 228–261, DOI: 10.1002/9781119378952.ch11.
- [46] R Penrose, “Gravitational Collapse and Space-Time Singularities”, *Phys Rev Lett*, 1965, **14**, 57–59, DOI: 10.1103/PhysRevLett.14.57. 
- [47] S W Hawking and R Penrose, “The singularities of gravitational collapse and cosmology”, *Proc R Soc Lond A Math Phys Sci*, 1970, **314**, 529–548, DOI: 10.1098/rspa.1970.0021. 
- [48] S Vargas-Serdio and H Quevedo, “Singularity theorems in Schwarzschild spacetimes”, *Eur Phys J Plus*, 2020, **135**, 636, DOI: 10.1140/epjp/s13360-020-00636-w.
- [49] C Kiefer, “Conceptual Problems in Quantum Gravity and Quantum Cosmology”, *Int Sch Res Notices*, 2013, **2013**, 509316, DOI: 10.1155/2013/509316. 
- [50] J F Donoghue, “Quantum General Relativity and Effective Field Theory”, in *Handbook of Quantum Gravity*, ed C Bambi, L Modesto and I Shapiro, Springer Nature Singapore, Singapore, 2024, pp 3–26, DOI: 10.1007/978-981-99-7681-2_1.
- [51] J Giné, “Towards a quantum universe”, *Astrophys Space Sci*, 2012, **339**, 25–30, DOI: 10.1007/s10509-012-0978-9.

- [52] M K E L Planck, “Über eine Verbesserung der Wienschen Spectralgleichung”, *Verhandl Dtsch Phys Ges*, 1900, **2**, 202, DOI: 10.1007/978-3-663-13885-3_15.
- [53] A Einstein, “Über einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtspunkt”, *Ann Phys (Berlin)*, 1905, **322**, 132–148, DOI: 10.1002/andp.19053220607. 
- [54] P Ehrenfest, “Welche Züge der Lichtquantenhypothese spielen in der Theorie der Wärmestrahlung eine wesentliche Rolle?”, *Ann Phys (Berlin)*, 1911, **341**, 91–118, DOI: 10.1002/andp.19113411106.
- [55] T S Kuhn, *Black-Body Theory and the Quantum Discontinuity, 1894-1912*, University of Chicago Press, London, UK, 1987.
- [56] P Ehrenfest, “Bemerkung über die angenäherte Gültigkeit der klassischen Mechanik innerhalb der Quantenmechanik”, *Z Phys*, 1927, **45**, 455–457, DOI: 10.1007/BF01329203.
- [57] G Friesecke and M Koppen, “On the Ehrenfest theorem of quantum mechanics”, *J Math Phys*, 2009, **50**, 082102, DOI: 10.1063/1.3191679.
- [58] V Sahni, “On Ehrenfest’s theorem”, *Int J Quantum Chem*, 2004, **97**, 953–960, DOI: 10.1002/qua.10824.
- [59] D Sen, S K Das, A N Basu and S Sengupta, “Significance of Ehrenfest theorem in quantum–classical relationship”, *Curr Sci*, 2001, **80**, 536–541.
- [60] L E Ballentine, Y Yang and J P Zibin, “Inadequacy of Ehrenfest’s theorem to characterize the classical regime”, *Phys Rev A*, 1994, **50**, 2854–2859, DOI: 10.1103/PhysRevA.50.2854.
- [61] A V Solov’yov, A V Verkhovtsev, N J Mason, R A Amos, I Bald, G Baldacchino, B Dromey, M Falk, J Fedor, L Gerhards, M Hausmann, G Hildenbrand, M Hrabovský, S Kadlec, J Kočíšek, F Lépine, S Ming, A Nisbet, K Ricketts, L Sala, T Schlathölter, A E H Wheatley and I A Solov’yov, “Condensed Matter Systems Exposed to Radiation: Multiscale Theory, Simulations, and Experiment”, *Chem Rev*, 2024, **124**, 8014–8129, DOI: 10.1021/acs.chemrev.3c00902. 
- [62] T Karakasidis and C Charitidis, “Multiscale modeling in nanomaterials science”, *Mater Sci Eng C*, 2007, **27**, EMRS 2006 Symposium A: Current Trends in Nanoscience - from Materials to Applications, 1082–1089, DOI: 10.1016/j.msec.2006.06.029.
- [63] E van der Giessen, P A Schultz, N Bertin, V V Bulatov, W Cai, G Csányi, S M Foiles, M G D Geers, C González, M Hütter, W K Kim, D M Kochmann, J LLorca, A E Mattsson, J Rottler, A Schluger, R B Sills, I Steinbach, A Strachan and E B Tadmor, “Roadmap on multiscale materials modeling”, *Model Simul Mater Sci Eng*, 2020, **28**, 043001, DOI: 10.1088/1361-651X/ab7150. 
- [64] J Fish, G J Wagner and S Keten, “Mesoscopic and multiscale modelling in materials”, *Nat Mater*, 2021, **20**, 774–786, DOI: 10.1038/s41563-020-00913-0.
- [65] M F Horstemeyer, “Multiscale Modeling: A Review”, in *Practical Aspects of Computational Chemistry: Methods, Concepts and Applications*, ed J Leszczynski and M K Shukla, Springer Netherlands, Dordrecht, 2010, pp 87–135, DOI: 10.1007/978-90-481-2687-3_4.

- [66] W E, *Principles of Multiscale Modeling*, Cambridge University Press, Cambridge, MA, USA, 1st ed, 2011.
- [67] W E, B Engquist and Z Huang, “Heterogeneous multiscale method: A general methodology for multiscale modeling”, *Phys Rev B*, 2003, **67**, 092101, DOI: 10.1103/PhysRevB.67.092101.
- [68] B Singh, T Fischer and S Mathur, “Field-enhanced chemical vapor deposition: new perspectives for thin film growth”, *J Mater Chem A*, 2025, **13**, 20104–20142, DOI: 10.1039/D5TA01081K. 
- [69] K R Johnson, P Arevalo Rodriguez, C R Brewer, J A Brannaka, Z Shi, J Yang, B Salazar, L McElwee-White and A V Walker, “Photochemical CVD of Ru on functionalized self-assembled monolayers from organometallic precursors”, *J Chem Phys*, 2016, **146**, 052816, DOI: 10.1063/1.4971434. 
- [70] B G Salazar, H Liu, A V Walker and L McElwee-White, “Low temperature platinum chemical vapor deposition on functionalized self-assembled monolayers”, *J Vac Sci Technol A*, 2020, **38**, 033404, DOI: 10.1116/6.0000087.
- [71] B G Salazar, C R Brewer, L McElwee-White and A V Walker, “Photoactivated Ru chemical vapor deposition using (η^3 -allyl)Ru(CO)₃X (X = Cl, Br, I): From molecular adsorption to Ru thin film deposition”, *J Vac Sci Technol A*, 2022, **40**, 023404, DOI: 10.1116/6.0001490.
- [72] C R Brewer, B Das, R Singh, D Caretti, D Bhattacharyya, O Oni, X Kang, J Perry, L McElwee-White and A V Walker, “Photoassisted Chemical Vapor Deposition Using (η^4 -Diene)Ru(CO)₃ Precursors”, *ACS Appl Mater Interfaces*, 2025, **17**, 55034–55044, DOI: 10.1021/acsmi.5c11415.
- [73] A C Jones and M L Hitchman, *Chemical Vapour Deposition: Precursors, Processes and Applications*, The Royal Society of Chemistry, 2008, DOI: 10.1039/9781847558794.
- [74] P Wang, Y Huan, P Yang, M Cheng, J Shi and Y Zhang, “Controlled Syntheses and Multifunctional Applications of Two-Dimensional Metallic Transition Metal Dichalcogenides”, *Acc Mater Res*, 2021, **2**, 751–763, DOI: 10.1021/accountsmr.1c00092.
- [75] T Kang, T W Tang, B Pan, H Liu, K Zhang and Z Luo, “Strategies for Controlled Growth of Transition Metal Dichalcogenides by Chemical Vapor Deposition for Integrated Electronics”, *ACS Mater Au*, 2022, **2**, 665–685, DOI: 10.1021/acsmaterialsau.2c00029. 
- [76] J R Creighton and J E Parmeter, “Metal CVD for microelectronic applications: An examination of surface chemistry and kinetics”, *Crit Rev Solid State Mater Sci*, 1993, **18**, 175–237, DOI: 10.1080/10408439308242560.
- [77] M L Green and R A Levy, “Chemical Vapor Deposition of Metals for Integrated Circuit Applications”, *JOM*, 1985, **37**, 63–71, DOI: 10.1007/BF03257716.
- [78] G Zhang, F R Lin, F Qi, T Heumüller, A Distler, H-J Egelhaaf, N Li, P C Y Chow, C J Brabec, A K-Y Jen and H-L Yip, “Renewed Prospects for Organic Photovoltaics”, *Chem Rev*, 2022, **122**, 14180–14274, DOI: 10.1021/acs.chemrev.1c00955.
- [79] J Janata and M Josowicz, “Conducting polymers in electronic chemical sensors”, *Nat Mater*, 2003, **2**, 19–24, DOI: 10.1038/nmat768.

- [80] R L Carroll and C B Gorman, “The Genesis of Molecular Electronics”, *Angew Chem Int Ed*, 2002, **41**, 4378–4400, DOI: 10.1002/1521-3773(20021202)41:23<4378::AID-ANIE4378>3.0.CO;2-A.
- [81] R H Friend, R W Gymer, A B Holmes, J H Burroughes, R N Marks, C Taliani, D D C Bradley, D A D Santos, J L Brédas, M Lögdlund and W R Salaneck, “Electroluminescence in conjugated polymers”, *Nature*, 1999, **397**, 121–128, DOI: 10.1038/16393.
- [82] I A Solov’yov, A V Yakubovich, P V Nikolaev, I Volkovets and A V Solov’yov, “MesoBioNano Explorer—A universal program for multiscale computer simulations of complex molecular structure and dynamics”, *J Comput Chem*, 2012, **33**, 2412–2439, DOI: 10.1002/jcc.23086.
- [83] **C P Souza** and F Fantuzzi, “Computational strategies for modelling excited states in organometallic chemistry”, in *Organometallic Chemistry*, ed C Bakewell, G R Owen, N Costa and R Musgrave, Royal Society of Chemistry, London, 2024, vol 45, chap 9, pp 271–316, DOI: 10.1039/9781837676200-00271. 
- [84] I N Levine, *Quantum Chemistry*, Pearson, Upper Saddle River, NJ, USA, 7th ed, 2014.
- [85] P A M Dirac, “The quantum theory of the electron”, *Proc R Soc Lond Ser A Math Phys Character*, 1928, **117**, 610–624, DOI: 10.1098/rspa.1928.0023. 
- [86] P A M Dirac, “The quantum theory of the Electron. Part II”, *Proc R Soc Lond Ser A Math Phys Character*, 1928, **118**, 351–361, DOI: 10.1098/rspa.1928.0056. 
- [87] E A Hylleraas, “Über den Grundzustand des Heliumatoms”, *Z Phys*, 1928, **48**, 469–494, DOI: 10.1007/BF01340013.
- [88] E A Hylleraas, “Neue Berechnung der Energie des Heliums im Grundzustande, sowie des tiefsten Terms von Ortho-Helium”, *Z Phys*, 1929, **54**, 347–366, DOI: 10.1007/BF01375457.
- [89] E A Hylleraas, “Über den Grundterm der Zweielektronenprobleme von H^- , He, Li^+ , Be^{++} usw.”, *Z Phys*, 1930, **65**, 209–225, DOI: 10.1007/BF01397032.
- [90] E A Hylleraas, “The Schrödinger Two-Electron Atomic Problem”, in *Advances in Quantum Chemistry*, ed P-O Löwdin, Academic Press, 1964, vol 1, pp 1–33, DOI: 10.1016/S0065-3276(08)60373-1.
- [91] A Szabo and N S Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*, Dover Publications, Inc, Mineola, NY, USA, 1st ed, 1996.
- [92] G A Worth and L S Cederbaum, “Beyond Born–Oppenheimer: Molecular Dynamics Through a Conical Intersection”, *Annu Rev Phys Chem*, 2004, **55**, 127–158, DOI: 10.1146/annurev.physchem.55.091602.094335.
- [93] M Born and R Oppenheimer, “Zur Quantentheorie der Molekeln”, *Ann Phys (Berlin)*, 1927, **389**, 457–484, DOI: 10.1002/andp.19273892002. 
- [94] J von Neuman and E Wigner, “Über merkwürdige diskrete Eigenwerte. Über das Verhalten von Eigenwerten bei adiabatischen Prozessen”, *Phys Z*, 1929, **30**, 467–470.
- [95] L D Landau and E M Lifshitz, *Quantum Mechanics Non-Relativistic Theory*, Pergamon Press, Oxford, UK, 3rd ed, 1981, vol 3.

- [96] T F O'Malley, "Diabatic States of Molecules– Quasistationary Electronic States", in *Advances in Atomic and Molecular Physics*, ed D Bates and I Esterman, Academic Press, 1971, vol 7, pp 223–249, DOI: 10.1016/S0065-2199(08)60361-9.
- [97] D J Tannor, *Introduction to Quantum Mechanics: A Time-Dependent Perspective*, University Science, Sausalito, CA, USA, 2007.
- [98] H Köppel, "Diabatic Representation: Methods for the Construction of Diabatic Electronic States", in *Conical Intersections*, ed W Domcke, D R Yarkony and H Köppel, World Scientific, 2004, chap 4, pp 175–204, DOI: 10.1142/9789812565464_0004.
- [99] E G Lewars, "The Concept of the Potential Energy Surface", in *Computational Chemistry: Introduction to the Theory and Applications of Molecular and Quantum Mechanics*, Springer International Publishing, Cham, 2024, pp 11–54, DOI: 10.1007/978-3-031-51443-2_2.
- [100] F Jensen, *Introduction to Computational Chemistry*, John Wiley & Sons, Ltd, Chichester, UK, 3rd ed, 2017.
- [101] A R Leach, *Molecular Modelling: Principles and Applications*, Prentice Hall, Harlow, UK, 2nd ed, 2001.
- [102] *Methods of Electronic Structure Theory*, ed H F Schaefer III, Springer, New York, NY, USA, 1st ed, 1977, vol 3, DOI: 10.1007/978-1-4757-0887-5.
- [103] T M Cardozo, D W O D Sousa, F Fantuzzi and M A Nascimento, "The Chemical Bond as a Manifestation of Quantum Mechanical Interference: Theory and Applications of the Interference Energy Analysis Using SCGVB Wave Functions", in *Comprehensive Computational Chemistry*, Elsevier, 2024, pp 552–588, DOI: 10.1016/B978-0-12-821978-2.00027-1.
- [104] M Hamermesh, *Group Theory and its Application to Physical Problems*, Addison-Wesley Pub Co, Reading, MA, USA, 1962.
- [105] R Pauncz, *The Symmetric Group in Quantum Chemistry*, CRC Press, Boca Raton, FL, USA, 1995.
- [106] R Pauncz, *Spin Eigenfunctions: Construction and Use*, Plenum Press, New York, NY, USA, 1979.
- [107] J Gerratt and W N Lipscomb, "Spin-Coupled Wave Functions for Atoms and Molecules", *Proc Natl Acad Sci USA*, 1968, **59**, 332–335, DOI: 10.1073/pnas.59.2.332.
- [108] J Gerratt, "General Theory of Spin-Coupled Wave Functions for Atoms and Molecules", in *Advances in Atomic and Molecular Physics*, 1971, pp 141–221, DOI: 10.1016/S0065-2199(08)60360-7.
- [109] J Gerratt, D L Cooper, P B Karadakov and M Raimondi, "Modern valence bond theory", *Chem Soc Rev*, 1997, **26**, 87, DOI: 10.1039/cs9972600087.
- [110] R C Ladner and W A Goddard III, "Improved Quantum Theory of Many-Electron Systems. V. The Spin-Coupling Optimized GI Method", *J Chem Phys*, 1969, **51**, 1073–1087, DOI: 10.1063/1.1672106.
- [111] W A Goddard III, T H Dunning, W J Hunt and P J Hay, "Generalized valence bond description of bonding in low-lying states of molecules", *Acc Chem Res*, 1973, **6**, 368–376, DOI: 10.1021/ar50071a002.

- [112] M M Goodgame and W A Goddard III, “Modified Generalized Valence-Bond Method: A Simple Correction for the Electron Correlation Missing in Generalized Valence-Bond Wave Functions; Prediction of Double-Well States for Cr_2 and Mo_2 ”, *Phys Rev Lett*, 1985, **54**, 661–664, DOI: 10.1103/PhysRevLett.54.661.
- [113] T H Dunning, L T Xu, D L Cooper and P B Karadakov, “Spin-Coupled Generalized Valence Bond Theory: New Perspect on the Electronic Structure of Molecules and Chemical Bonds”, *J Phys Chem A*, 2021, **125**, 2021–2050, DOI: 10.1021/acs.jpca.0c10472.
- [114] P Pulay, “Convergence acceleration of iterative sequences. the case of scf iteration”, *Chem Phys Lett*, 1980, **73**, 393–398, DOI: 10.1016/0009-2614(80)80396-4.
- [115] P Pulay, “Improved SCF convergence acceleration”, *J Comp Chem*, 1982, **3**, 556–560, DOI: 10.1002/jcc.540030413.
- [116] T P Hamilton and P Pulay, “Direct inversion in the iterative subspace (DIIS) optimization of open-shell, excited-state, and small multiconfiguration SCF wave functions”, *J Chem Phys*, 1986, **84**, 5728–5734, DOI: 10.1063/1.449880.
- [117] P Hohenberg and W Kohn, “Inhomogeneous Electron Gas”, *Phys Rev*, 1964, **136**, B864–B871, DOI: 10.1103/PhysRev.136.B864. 
- [118] L H Thomas, “The calculation of atomic fields”, *Math Proc Camb Philos Soc*, 1927, **23**, 542–548, DOI: 10.1017/S0305004100011683.
- [119] E Fermi, “Un metodo statistico per la determinazione di alcune priorieta dell’atome”, *Rend Accad Naz Lincei*, 1927, **6**, 32.
- [120] E Fermi, “Eine statistische Methode zur Bestimmung einiger Eigenschaften des Atoms und ihre Anwendung auf die Theorie des periodischen Systems der Elemente”, *Z Phys*, 1928, **48**, 73–79, DOI: 10.1007/BF01351576.
- [121] E Fermi, “Sulla deduzione statistica di alcune proprietà dell’atomo. Applicazione alla teoria del sistema periodico degli elementi”, *Rend Lincei*, 1928, **7**, 342.
- [122] R G Parr and Y Weitao, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford, UK, 1994, vol 16.
- [123] R G Parr and W Yang, “Density-Functional Theory of the Electronic Structure of Molecules”, *Annu Rev Phys Chem*, 1995, **46**, 701–728, DOI: 10.1146/annurev.pc.46.100195.003413.
- [124] W Koch and M C Holthausen, *A Chemist’s Guide to Density Functional Theory*, Wiley - VCH, Weinheim, NY, USA, 2nd, 2001, DOI: 10.1002/3527600043.
- [125] E Engel and R M Dreizler, *Density Functional Theory: An Advanced Course*, Springer-Verlag, Heidelberg, Germany, 1st ed, 2011, DOI: 10.1007/978-3-642-14090-7.
- [126] J P Perdew and K Schmidt, “Jacob’s ladder of density functional approximations for the exchange-correlation energy”, *AIP Conf Proc*, 2001, **577**, 1–20, DOI: 10.1063/1.1390175.
- [127] E Livshits and R Baer, “A well-tempered density functional theory of electrons in molecules”, *Phys Chem Chem Phys*, 2007, **9**, 2932–2941, DOI: 10.1039/B617919C.

- [128] S Grimme, J Antony, S Ehrlich and H Krieg, “A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu”, *J Chem Phys*, 2010, **132**, 154104, DOI: 10.1063/1.3382344.
- [129] S Grimme, S Ehrlich and L Goerigk, “Effect of the damping function in dispersion corrected density functional theory”, *J Comput Chem*, 2011, **32**, 1456–1465, DOI: 10.1002/jcc.21759.
- [130] E Caldeweyher, S Ehlert, A Hansen, H Neugebauer, S Spicher, C Bannwarth and S Grimme, “A generally applicable atomic-charge dependent London dispersion correction”, *J Chem Phys*, 2019, **150**, 154122, DOI: 10.1063/1.5090222.
- [131] P J Hay and W R Wadt, “Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals”, *J Chem Phys*, 1985, **82**, 299–310, DOI: 10.1063/1.448975.
- [132] F Weigend and R Ahlrichs, “Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy”, *Phys Chem Chem Phys*, 2005, **7**, 3297–3305, DOI: 10.1039/B508541A.
- [133] C Chang, M Pelissier and P Durand, “Regular Two-Component Pauli-Like Effective Hamiltonians in Dirac Theory”, *Phys Scr*, 1986, **34**, 394, DOI: 10.1088/0031-8949/34/5/007.
- [134] J-L Heully, I Lindgren, E Lindroth, S Lundqvist and A-M Martensson-Pendrill, “Diagonalisation of the Dirac Hamiltonian as a basis for a relativistic many-body procedure”, *J Phys B: At Mol Phys*, 1986, **19**, 2799, DOI: 10.1088/0022-3700/19/18/011.
- [135] E van Lenthe, E J Baerends and J G Snijders, “Relativistic regular two-component Hamiltonians”, *J Chem Phys*, 1993, **99**, 4597–4610, DOI: 10.1063/1.466059.
- [136] R van Leeuwen, E van Lenthe, E J Baerends and J G Snijders, “Exact solutions of regular approximate relativistic wave equations for hydrogen-like atoms”, *J Chem Phys*, 1994, **101**, 1272–1281, DOI: 10.1063/1.467819.
- [137] E van Lenthe, E J Baerends and J G Snijders, “Relativistic total energy using regular approximations”, *J Chem Phys*, 1994, **101**, 9783–9792, DOI: 10.1063/1.467943.
- [138] E van Lenthe, J G Snijders and E J Baerends, “The zero-order regular approximation for relativistic effects: The effect of spin–orbit coupling in closed shell molecules”, *J Chem Phys*, 1996, **105**, 6505–6516, DOI: 10.1063/1.472460.
- [139] K G Dyall and E van Lenthe, “Relativistic regular approximations revisited: An infinite-order relativistic approximation”, *J Chem Phys*, 1999, **111**, 1366–1372, DOI: 10.1063/1.479395.
- [140] W Liu, “With-Pair Relativistic Hamiltonians”, in *Handbook of Relativistic Quantum Chemistry*, ed W Liu, Springer Berlin Heidelberg, Berlin, Heidelberg, 2014, pp 1–29, DOI: 10.1007/978-3-642-41611-8_1-2.
- [141] W Kutzelnigg and W Liu, “Quasirelativistic theory equivalent to fully relativistic theory”, *J Chem Phys*, 2005, **123**, 241102, DOI: 10.1063/1.2137315.
- [142] M Iliaš and T Saue, “An infinite-order two-component relativistic Hamiltonian by a simple one-step transformation”, *J Chem Phys*, 2007, **126**, 064102, DOI: 10.1063/1.2436882.

- [143] W Liu and W Kutzelnigg, “Quasirelativistic theory. II. Theory at matrix level”, *J Chem Phys*, 2007, **126**, 114107, DOI: 10.1063/1.2710258.
- [144] T Saue, “Relativistic Hamiltonians for Chemistry: A Primer”, *ChemPhysChem*, 2011, **12**, 3077–3094, DOI: 10.1002/cphc.201100682.
- [145] B A Hess, “Relativistic electronic-structure calculations employing a two-component no-pair formalism with external-field projection operators”, *Phys Rev A*, 1986, **33**, 3742–3748, DOI: 10.1103/PhysRevA.33.3742.
- [146] M Douglas and N M Kroll, “Quantum electrodynamical corrections to the fine structure of helium”, *Ann Phys (NY)*, 1974, **82**, 89–155, DOI: 10.1016/0003-4916(74)90333-9.
- [147] J J Sakurai and J Napolitano, *Modern Quantum Mechanics*, Cambridge University Press, Cambridge, MA, USA, 3rd ed, 2021, DOI: 10.1017/9781108587280.
- [148] V Barone, S Alessandrini, M Biczysko, J R Cheeseman, D C Clary, A B McCoy, R J DiRisio, F Neese, M Melosso and C Puzzarini, “Computational molecular spectroscopy”, *Nat Rev Methods Primers*, 2021, **1**, 38, DOI: 10.1038/s43586-021-00034-1.
- [149] R C Hilborn, “Einstein coefficients, cross sections, f values, dipole moments, and all that”, *Am J Phys*, 1982, **50**, 982–986, DOI: 10.1119/1.12937.
- [150] T J Zuehlsdorff and C M Isborn, “Modeling absorption spectra of molecules in solution”, *Int J Quantum Chem*, 2019, **119**, e25719, DOI: 10.1002/qua.25719. 
- [151] E Benassi, C Cappelli, B Carlotti and V Barone, “An integrated computational tool to model the broadening of the absorption bands of flexible dyes in solution: cationic chromophores as test cases”, *Phys Chem Chem Phys*, 2014, **16**, 26963–26973, DOI: 10.1039/C4CP03419H.
- [152] J Bednarska, R Zaleśny, G Tian, N Murugan, H Ågren and W Bartkowiak, “Nonempirical Simulations of Inhomogeneous Broadening of Electronic Transitions in Solution: Predicting Band Shapes in One- and Two-Photon Absorption Spectra of Chalcones”, *Molecules*, 2017, **22**, 1643, DOI: 10.3390/molecules22101643. 
- [153] T Petrenko and F Neese, “Analysis and prediction of absorption band shapes, fluorescence band shapes, resonance Raman intensities, and excitation profiles using the time-dependent theory of electronic spectroscopy”, *J Chem Phys*, 2007, **127**, 164319, DOI: 10.1063/1.2770706.
- [154] F J A Ferrer, J Cerezo, J Soto, R Improta and F Santoro, “First-principle computation of absorption and fluorescence spectra in solution accounting for vibronic structure, temperature effects and solvent inhomogeneous broadening”, *Comput Theor Chem*, 2014, **1040-1041**, 328–337, DOI: 10.1016/j.comptc.2014.03.003.
- [155] P P Fehér, Á Madarász and A Stirling, “Multiscale Modeling of Electronic Spectra Including Nuclear Quantum Effects”, *J Chem Theory Comput*, 2021, **17**, 6340–6352, DOI: 10.1021/acs.jctc.1c00531. 
- [156] R Crespo-Otero and M Barbatti, “Spectrum simulation and decomposition with nuclear ensemble: formal derivation and application to benzene, furan and 2-phenylfuran”, in *Marco Antonio Chaer Nascimento*, 2014, pp 89–102, DOI: 10.1007/978-3-642-41163-2_9.