X-ray spectroscopies through damped linear response theory

Thomas Fransson

Department of Physics, Chemistry, and Biology (IFM)
Linköping University, SE-581 83 Linköping, Sweden

Linköping 2016

ISBN 978-91-7685-908-7
ISSN 0345-7524

Printed by LiU-Tryck, Linköping 2016

To my Family.

Abstract

In order to reach a fundamental understanding of interactions between electromagnetic radiation and molecular materials, experimental measurements need to be supplemented with theoretical models and simulations. With the use of this combination, it is possible to characterize materials in terms of, *e.g.*, chemical composition and molecular structure, as well as achieve time-resolution in studies of chemical reactions. This doctoral thesis focuses on the development and evaluation of theoretical methods with which, amongst others, X-ray absorption and X-ray emission spectroscopies can be interpreted and predicted. In X-ray absorption spectroscopy the photon energy is tuned such that core electrons are targeted and excited to either bound or continuum states, and X-ray emission spectroscopy measures the subsequent decay from such an excited state. These core excitations/de-excitations exhibit strong relaxation effects, making theoretical considerations of the processes particularly challenging. While the removal of a valence electron leaves the remaining electrons relatively unaffected, removing core electrons has a substantial effect on the other electrons due to the significant change in the screening of the nucleus. Additionally, the core-excited states are embedded in a manifold of valence-excited states that needs to be considered by some computationally feasible method. In this thesis, a damped formalism of linear response theory, which is a perturbative manner of considering the interactions of (weak) external or internal fields with molecular systems, has been utilized to investigate mainly the X-ray absorption spectra of small- to medium-sized molecular systems.

Amongst the standard quantum chemical methods available, coupled cluster is perhaps the most accurate, with a well-defined, hierarchical manner of approaching the correct electronic wave function. Combined with response theory, it provides a reliable theoretical method in which relaxation effects are addressed by means of an accurate treatment of electron correlation. The first part of this thesis deals with the development and evaluation of such an approach, and it is shown that the relaxation effects can be addressed by the inclusion of double excitations in the coupled cluster manifold. However, these calculations are computationally very demanding, and in order to treat larger systems the performance of the coupled cluster approach has been compared to that of the less demanding method of time-density dependent functional theory (TDDFT). Both methods have been used to

investigate the X-ray absorption spectrum of water, which has been extensively debated in the scientific community following a relatively recent hypothesis concerning the underlying structure of liquid water. Water exhibits a great number of anomalous properties that stand out from those of most compounds, and the importance of reaching a fundamental understanding of this substance cannot be overstated. It has been demonstrated that TDDFT yields excellent results for liquid water, opening up possibilities of investigating the correlation between spectral features and local structures.

Furthermore, recent developments in damped linear response TDDFT in the four-component relativistic regime have enabled the inclusion of spin-orbit coupling in damped linear response calculations, making black-box calculations of absorption spectra in a relativistic setting practical. With this approach, it is possible to address the spin-orbit splitting in $L_{2,3}$ -edge X-ray absorption spectra, and the performance of such a method has been demonstrated for a set of small molecules. Excellent agreement with experiment is obtained in terms of relative features, but an anomalous error in absolute energy has been observed for silane derivatives featuring fluorine-substitutions. This is likely a result of the strong influence of the very electronegative fluorine atoms on the electron density of the core-excited atom.

Finally, the treatment of non-resonant X-ray emission spectroscopy using damped linear response theory is discussed. The expansion needed for the development of a simple method by which this spectroscopy can be treated using damped linear response theory at the TDDFT level of theory has been identified, and proof of principle calculations at the time-dependent Hartree–Fock level of theory are presented.

Populärvetenskaplig sammanfattning

Genom att studera hur material växelverkar med ljus av olika våglängder kan vi få information om hur detta material ser ut på en mikroskopisk nivå, och då exempelvis se vilka atomer som finns i provet och hur de är bundna till varandra. En grundläggande förståelse för detta är mycket viktigt för en mängd olika tillämpningar, exempelvis inom medicin och modern elektronik, både för analys och design av ny teknik. Våglängder som kan användas för sådana studier täcker stora delar av det elektromagnetiska spektrumet, och inom kemin används typiskt sett allt från infrarött ljus till högenergisk röntgenstrålning. För att kunna nå denna förståelse av interaktionen med materialet räcker dock inte experimentella mätningar och enklare fysikaliska beskrivningar, utan en kombination av experiment samt avancerade teoretiska modeller och simuleringar är nödvändiga. Med en sådan kombination går det att tolka experiment och att hitta nya material med önskade egenskaper med hjälp av beräkningar, något som kan bli mycket billigare än att försöka ta fram materialen enbart med hjälp av experiment. Denna doktorsavhandling behandlar utveckling och utvärdering av nya teoretiska metoder som bland annat kan användas till att tolka och förutsäga röntgenabsorptions- och röntgenemissionsspektra.

Inom röntgenabsorptionsspektroskopian används ljus för vilket energin är vald sådan att starkt bundna elektronerna fås att excitera till, eller att lyftas upp till, högre liggande molekylära orbitaler eller till icke-bundna tillstånd. Röntgenemissionsspektroskopian mäter sedan den efterföljande deexcitationen av valenselektroner ner till det tomma kärnhålet. Dessa excitationer/deexcitationer påverkas av starka relaxationseffekter, eftersom excitationen får det att se ut som att kärnladdningen har ökat med en enhet, vilket sätter särskilt hårda krav på de teoretiska modellerna. Utöver detta så döljs de intressanta excitationerna i en mångfald av valensjoniserade tillstånd, vilka i sin tur måste behandlas på något sätt som inte är för beräkningsmässigt krävande. I denna avhandling används en dämpad formalism av linjär responsteori, vilket är ett sätt att behandla hur systemet interagerar med externa eller interna fält med hjälp av kvantmekanisk störningsteori.

Av alla kvantkemiska modeller som är tillgängliga idag så är sannolikt *coupled cluster* den mest noggranna, och metoden erbjuder ett systematiskt sätt med vilken den korrekta fysikaliska beskrivningen kan närmas. Tillsammans med responsteori fås då ett pålitligt verktyg för att simulera interaktionen med röntgen-

strålning, och vi har kunnat visa att detta verktyg besitter bra egenskaper för beräkningar av röntgenabsorptionsspektra. Dessvärre är denna metod för beräkningsmässigt krävande för att kunna användas på större molekyllära system, och jämförelser har då gjorts mot mindre krävade beräkningar med *time-dependent density functional theory* (TDDFT). Dessa metoder har sedan använts för att simulera röntgenabsorptionsspektra för vatten, vilka har debatterats intensivt i det vetenskapliga samfundet till följd av nya tolkningar av vattens underliggande struktur. Vi har kunnat visa god överensstämmelse mellan experiment och TDDFT-beräkningar, vilket kommer att kunna användas för att undersöka sambanden mellan lokal struktur och spektras utseende.

För väldigt starkt bundna elektroner i en atom kommer elektronernas hastigheter att närma sig ljusets, vilket medför att relativistiska effekter blir allt viktigare att ta hänsyn till. Dessutom så kommer spinnbankopplingen att kunna ge en tydlig påverkan då vissa orbitaler delar upp sig i flera olika energier, och ger då spektra med fler detaljer än de orbitaler som saknar sådan stark spinnbankoppling. För dessa tillämpningar krävs ett relativistiskt ramverk, och vi har utvärderat responsteoretiska beräkningar i relativistisk fyrkomponentsteori. Det har uppnåtts utmärkt överensstämmelse med experiment, även om kisel tetrafluorid (SiF_4) påvisar ett avvikande fel i absolut energi. Detta är troligen ett resultat av den starka påverkan från de väldigt elektronegativa fluoratomerna — fluor är väldigt bra på att attrahera elektroner från andra atomer, så kiselatomen kommer i detta fall att förlora mycket av sin elektrontäthet, något som kan bli svårt att återskapa teoretiskt.

Slutligen så diskuteras behandlingen av icke-resonant röntgenemissionsspektroskopi, och vi identifierar framtida utvecklingar som behövs för att få tillgång till ett enkelt verktyg med vilken denna typ av spektroskopi kan behandlas med dämpad responsteori på TDDFT-nivå.

Acknowledgements

If I have seen further, it is by standing on the shoulders of giants.

I. Newton, 1676¹

There are numerous people I would like to acknowledge for making the writing of this thesis possible, or just for making the ride to a Ph.D. much more enjoyable. Let me start by thanking the past and present members of the group of theoretical chemistry (formerly known as computational physics) for the support and all the hours spent talking about something completely random during *fika*, as well as for our endless discussions on which restaurant has the most appealing meal of the day. For these latter points, a special thank should go to our former member Jonas Sjöqvist, whose list of random topics for discussions and opinions on restaurants seems all but endless. Another former member who also brought great joy to the group, as well as sweet deliciousness in the form of an assortment of pastries, is Joanna Kauczor, without whom half the results presented here would probably still be clogging up NSC's computers. In terms of present members, I'd like to extend special thanks to Tobias Fahleson for all the searches of sodium chloride and the camaraderie, Bo Durbeej for his caring and refreshing straightforwardness, and Mathieu Linares for his humour, enthusiasm and general frenchiness (rivalled only by that of our former member Florent Di Meo). A more recent addition to the group, Dirk Rehn, has my thanks for the beers and for making me feel welcome during my stays in the beautiful German city of Heidelberg.

Speaking of Heidelberg, I'd also like to thank Andreas Dreuw for making me feel welcome there — next time I'll try to remember *not* trying to keep up with the large, athletic, German when it comes to drinking beer. Another experienced scientist who has welcomed my visits and shared his great knowledge with me is my former Licentiate opponent Lars G. M. Pettersson. Thank you for this, and for introducing me to the mysteries of water. Two more wise seniors who deserve my thanks are Sonia Coriani and Trond Saue, for helping me understand coupled cluster theory and relativity, respectively.

Now, as a Ph.D. student comes into the world of research knowing very little, there are a number of schools I've attended, and teachers and participants there who deserve my thanks: from the summer school across the ocean in the humid campus of Virginia Tech in 2015, through the winter school in a surprisingly snowy

Stockholm in 2012, with additional stops at the summerschoolⁱ in Sicily in 2013 and the summer school in Geneva the same year, and finally to Linköping in 2012 to get a better grasp on how molecules actually move. For getting me to all those schools, as well as helping with all strange forms we get every now and then, our administrator Lejla Kronbäck definitely deserves my thanks. Without her we would probably be hopelessly lost.

During the course of my studies, I was enrolled in *Agora Materiae*, a multidisciplinary doctoral program at Linköping University, and the members and staff there deserve extra thanks for trying to turn me to the dark (*i.e.* solid state) side of science. Unfortunately, the attempts have so far been unsuccessful. And for other people at IFM, I should not forget all of you who have made these years fly by with relative ease. Here Rickard Gunnarsson and Mathias Forsberg should have special credit, for all our discussions on politics and random stuff, as well as all the hours lifting heavy objects up and down. Without you, I'd probably have less pain in my chest and core muscles.

As conducting research, going for *fika* and attending courses are only three of the four fundamental components of the life of a Ph.D. student, I would like to take this opportunity to thank my students in electromagnetism, for making teaching both a challenge and a joy. Also Daria Burdakova deserves my thanks, to whom I hopefully managed to illustrate some of the wondrous magics of basis set studies.

Moving away from academia, my family and friends should of course get huge credit for supporting me and making life in general more enjoyable — especially my parents, siblings, and old brothers-in-arms Christian Ström and Erik Karlsson. One day, I shall be sufficiently knowledgeable in the field to actually explain what I do. One day.

And finally, since I seem to have an very unpretentious tendency of including various quotes,ⁱⁱ I believe that it would be appropriate to dedicate one to the most important person for my scientific development. Patrick, thank you for your great knowledge, patience, and enthusiasm — I find it difficult to imagine a better mentor. Let us see if I turn out to be a worthy protégé.

Know what's weird? Day by day, nothing seems to change. But pretty soon, everything's different.

B. Watterson (creator of Calvin and Hobbes)

A handwritten signature in black ink, appearing to read 'Thomas Fransson', with a stylized, cursive script.

Thomas Fransson
Linköping, January 2016

ⁱNote the Scandinavian spelling.

ⁱⁱNot forgetting that *a witty saying proves nothing* — Voltaire.²

Contents

1	Introduction	1
1.1	Quantum chemistry	2
1.2	X-ray spectroscopy	4
1.3	Anomalous properties of liquid water	8
2	Electronic structure theory	13
2.1	Fundamentals of electronic structure theory	13
2.1.1	The one-particle wave function	15
2.1.2	The N -particle wave function	16
2.1.3	Relativistic effects	18
2.1.4	Approaching the correct wave function	21
2.2	Density functional theory	23
2.2.1	Basics of density functional theory	24
2.2.2	Approximate exchange-correlation functionals	26
2.2.3	The self-interaction error in density functional theory	30
2.3	Coupled cluster theory	31
2.3.1	The exponential <i>ansatz</i>	31
2.3.2	Approximate coupled cluster methods	34
2.4	Illustrations of concepts	35
2.4.1	Approaching the correct transition energies of ethene	35
2.4.2	Relativistic effects on orbital energies	38
2.4.3	Relativistic effects on valence properties	40
3	Molecular response theory	43
3.1	Exact state response theory	44
3.1.1	General response theory	44
3.1.2	Damped linear response theory	46
3.2	Coupled cluster response theory	51
3.2.1	Quasi-energy formalism	51

3.2.2	The coupled cluster linear response function	52
3.3	Time-dependent density functional theory	56
3.4	Computing the linear response function	60
3.4.1	Bottom-up calculation of eigenvalues	60
3.4.2	The Lanczos-chain method	61
3.4.3	Complex linear response equation solver	64
3.5	Limits of molecular response theory	66
3.5.1	High-intensity fields	67
3.5.2	Ultra-short pulses	69
3.5.3	Short-wavelength perturbations	69
4	K-edge X-ray absorption spectroscopy	73
4.1	Relaxation effects	73
4.1.1	Electron density of ground and core-ionized systems	74
4.1.2	Correlation effects of core electrons	75
4.1.3	Ionization potentials along the periodic table	77
4.1.4	Relaxation in the coupled cluster hierarchy	80
4.2	Treating larger systems	83
4.3	Calculating the X-ray absorption spectrum of water	85
4.3.1	Effects of hydrogen-bonding	85
4.3.2	The different phases of water	87
5	L-edge X-ray absorption spectroscopy	91
5.1	Reproducing experimental measurements	91
5.1.1	Electron correlation	92
5.1.2	Spin-orbit effects	93
5.2	Anomalous energy discrepancy of silicon tetrafluoride	95
6	K-edge X-ray emission spectroscopy	99
6.1	Damped linear response calculation of X-ray emission	99
6.2	Performance of Hartree-Fock and density functional theory	101
7	Conclusions	103
	Bibliography	105
	List of Figures	117
	List of Tables	119
	List of included Publications	121
	Paper I	123
	<i>Coupled-cluster response theory for near-edge X-ray-absorption fine structure of atoms and molecules</i>	

Paper II	133
<i>Asymmetric-Lanczos-chain-driven implementation of electronic resonance convergent coupled-cluster linear response theory</i>	
Paper III	149
<i>Carbon X-ray absorption spectra of fluoroethenes and acetone: A study at the coupled cluster, density functional, and static-exchange levels of theory</i>	
Paper IV	163
<i>Requirements of first-principles calculations of X-ray absorption spectra of liquid water</i>	
Paper V	189
<i>Four-component damped density functional response theory study of UV/vis absorption spectra and phosphorescence parameters of group 12 metal-substituted porphyrins</i>	
Paper VI	231
<i>K- and L-edge X-ray absorption spectrum calculations of closed-shell carbon, silicon, germanium, and sulfur compounds using damped four-component density functional response theory</i>	

CHAPTER 1

Introduction

In 1868 the French astronomer Pierre Jules César Janssen discovered an as of yet unknown line in the spectrum of the light from the chromosphere of the Sun, as can be observed by letting light pass through a prism. The optical spectrum is illustrated in Fig. 1.1, where dark lines are due to absorption of light by molecules and atoms in the Sun's atmosphere, and it was the D₃ feature at 587.56 nm which was the new line observed by Janssen. It was initially mistaken as an additional feature of sodium, but using theoretical arguments the two Englishmen Joseph Norman Lockyer and Edward Frankland concluded that it was instead the result of a new element. Inspired by the Greek word for the Sun, *helios*, they named it *helium*.

Figure 1.1. The Fraunhofer lines in the optical spectrum of the Sun. Public domain picture.

Their arguments were later shown to be correct, and in 1895 this element was isolated for the first time. We now know that helium is the sixth most common gas in the atmosphere, with a volume concentration of approximately 5 parts per

million, as well as the second most abundant element in the observable universe. This is thus an example in which the combination of measurements and theoretical considerations resulted in the discovery of a new material — in this case even a new element. Additionally, the element was discovered at a distance of approximately 1.5×10^{11} m, and it would take as much as 27 years before it could first be isolated on Earth.

This thesis deals with the development of theoretical methods by which we can understand the molecular properties of a material. These methods can be combined with experimental measurements in a manner similar to the above example in order to reach a fundamental understanding of the characteristics of the sample in consideration. Alternatively, such theoretical treatment can be used to guide the development of new molecular materials with some desired properties, an approach which can be far most cost- and time-effective than conducting trial and error experiments. In this thesis, focus is on the phenomena of absorption and emission of X-ray radiation, and in order to understand these properties we utilize the theoretical framework of quantum chemistry.

1.1 Quantum chemistry

Every attempt to employ mathematical methods to the study of chemical questions must be considered profoundly irrational and contrary to the spirit of chemistry. If mathematical analysis should ever hold a prominent place in chemistry — an aberration which is happily almost impossible — it would occasion a rapid and widespread degeneration of that science.

A. Comte, 1830³

In the light of the above statement this work would make little sense, as this thesis is entirely dedicated to employing mathematical methods to the study of chemical questions. Instead, the prediction of Auguste Comte failed monumentally, and mathematical considerations are now close to a necessity for the fundamental understanding of chemical questions. Intersecting physics and chemistry, the scientific field of quantum chemistry seek to investigate the behaviour of matter at a molecular scale, utilizing quantum mechanical methods. Such a description is necessary mainly for the electrons of a molecule, as they cannot be well described by classical mechanics. For even greater validity, it is sometimes necessary to also include relativistic effects, both because the potential exerted on tightly bound electrons is large enough such that scalar relativistic effects become important, and as spin-orbit couplings are influential, and sometimes an absolute necessity, for accurately describing chemical properties.

Having established a physical model which is able to accurately describe the chemical processes in question, it is then necessary to carry out the explicit, by Comte feared, mathematical operations in order to obtain the sought property. Here the field benefits greatly from the ever-continuing development of high-performance computer clusters, enabling the calculation of properties of ever larger chemical systems. But even with immense computational resources available, it

is still necessary to find appropriate approximate methods and computational schemes to carry out the calculation due to the huge complexity and technical demands of quantum chemical methods.ⁱ

In this thesis we will consider the description of molecular systems using both wave function based *ab initio* methods, in which the many-body electronic wave function is constructed, and density based methods, where the difficult many-body problem is simplified by instead focusing on the electronic density. Using these methods the electronic structure can be modeled in a manner by which the quantum mechanical nature of the system is explicitly accounted for.

In order to understand the interaction of electromagnetic radiation and molecules, electronic response theory offers a general framework in which a plethora of interactions can be understood. In this framework the interaction is studied by use of quantum mechanical perturbation theory, enabling the calculation of molecular properties which can be used to obtain a detailed understanding of the physical processes. Combined with experimental studies we thus have a powerful tool by which materials can be characterized at the molecular level.

In Fig. 1.2 the electromagnetic spectrum is illustrated, showing the approximate energies and wavelengths of the different categories of radiation. Also included are the manner by which some wavelengths interact with molecular systems. In this thesis we will focus on radiation in the soft X-ray region, with some additional discussions on ultraviolet and visible light. In accordance with the figure, light at these energies interacts with molecules through the excitations and de-excitations of core and valence electrons, respectively.

Figure 1.2. The electromagnetic spectrum and interactions with molecular materials at different energies.

ⁱAs an example, the largest molecular system considered in this thesis (a complex of 96 water molecules) required approximately 60 hours on 200 cores of 2.2 GHz each for the response calculations to finish. By comparison, a modern high-performance personal computer has in the order of 8 cores at 3.5 GHz each, so this would be comparable to having fifteen such computers working together on a single task for almost three days. To quote my esteemed supervisor,

*The modern slaves of today are the massive parallel supercomputers to which quantum chemistry has fully adapted to employing direct atomic orbital driven routines.*⁴

1.2 X-ray spectroscopy

In general terms, spectroscopy is the study of the interaction of matter with radiative energy as a function of its wavelength. In this thesis the radiative energy is in the form of electromagnetic radiation, and the wavelengths mainly correspond to those associated with core processes. For this field of X-ray spectroscopies, the development of advanced synchrotron facilities over the last few decades has been a great boon, and has lead to significant progress. Originally a byproduct in facilities dedicated to high-energy physics, modern third-generation synchrotrons offers tunable radiation covering the infrared to hard X-ray region of the electromagnetic spectrum of high intensity and well-known characteristics. Furthermore, the advent of fourth-generation synchrotron facilities, *e.g.* free-electron lasers, offers a new field of science with unprecedented intensities and time-resolution, which is yet relatively unexplored.⁵⁻⁷

Figure 1.3. Core spectroscopy processes of a prototypical π -conjugated system. X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), X-ray emission spectroscopy (XES), and resonant inelastic X-ray scattering (RIXS).

Some of the available X-ray spectroscopies are shown in Fig. 1.3, illustrating the physical processes being measured. The first two spectroscopies, X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS), both are single-step techniques with relatively high yield, and have been available for a long time. The other two techniques, X-ray emission spectroscopies (XES) and resonant inelastic X-ray scattering (RIXS), are both photon-in-photon-out techniques, with the latter being a comparatively young field of science, as it requires quite intense radiation sources to be viable. All these techniques involve processes affecting core orbitals, and due to the high specificity of core electron energies the methods are very element specific, and typically very sensitive to the local chemical environment of the core atom in question. The very short time (approximately attosecond) of the processes additionally ensures that the properties are investigated with atoms essentially frozen in space. With the high degree of element specificity,

the spectroscopies are termed after which element and core orbitals they seek to investigate, with reference to the electron binding energy, or edge, of the element. As such, they are indexed first by the shell in question (K , L , M ,...) and by the angular quantum number ($s = 1$, $p_{1/2} = 2$, $p_{3/2} = 3$,...). In the present work the main interest will be in transitions from $1s$, $2s$, $2p_{1/2}$, and $2p_{3/2}$ orbitals, *i.e.* the K -, L_1 , L_2 -, and L_3 -edges.

X-ray photoelectron spectroscopy measures the kinetic energy of photoejected electrons, as well as the angular dependence with respect to the orientation of the sample. From this, information on electron binding energy are obtained by probing the occupied core-orbitals. This spectroscopy will not be explicitly discussed in this work, even if some calculations on ionization potentials will be presented.

X-ray absorption spectroscopy⁸ is the main focus of this thesis, for which the absorption of photons are measured, exciting core electrons to bound or unbound (continuum) states. For the former the unoccupied states of the sample are probed, yielding an environmentally sensitive measure on the surface structure, chemical composition, and other properties. This region is referred to as the near-edge X-ray absorption fine structure (NEXAFS), or the X-ray absorption near-edge structure (XANES), region. Using energies above ionization the interaction of the photoelectrons with the environment is investigated, yielding features in the absorption spectrum due to constructive or destructive interference. This region is referred to as the extended X-ray absorption fine structure (EXAFS) region, typically beginning at 20–30 eV above the ionization threshold of the targeted elements.⁹ Together, NEXAFS and EXAFS form the X-ray absorption fine structure (XAFS), for which a prototypical K -edge spectrum of a π -conjugated system can be found in Fig. 1.5. X-ray absorption spectra can be measured by a number of different experimental techniques,¹⁰ the most direct of which being transmission mode. This is illustrated in Fig. 1.4 (left panel), where the intensity of the beam is seen to decrease in intensity exponentially with respect to the thickness of the sample x , the number density N , and the absorption cross section σ , all in accordance with the Beer–Lambert law. In this thesis it is thus our task of finding a reliable manner by which frequency-dependent microscopical molecular properties can be found and related to the macroscopic absorption cross section.

In order to relate the microscopical properties to experiments it is important to understand what we theoretically investigate and the actual experimental situation. In the right panel of Fig. 1.4, the potential energy surfaces (PES) of a ground state S_0 and an excited state S_i are illustrated. These surfaces show how the energy of the ground and excited state depend on the value of a geometry coordinate Q , and it is to be noted that neither the minima nor the curvature are identical for the two different potential energy surfaces. Overlaying each PES are also the energies of the lowest few vibrational states, exaggerated for illustrative purposes. The shape of the vibrational ground state of both S_0 and S_i are included, as well as third excited vibrational state of S_i . In a typical calculation the atoms of the molecules are considered frozen during the electronic excitation, and the energy difference is taken as the difference between the two potential energy surfaces, designated vertical in the figure. However, the experimental situation is more intricate than so, and a first improvement would be the inclusion of also the

Figure 1.4. (Left) Absorption in accordance to the Beer–Lambert law, with original intensity I_0 , number density N , thickness x of sample and absorption cross section σ . (Right) Potential energy surfaces of S_0 and S_i , indicating vertical and 0–0 transitions. Dotted grey lines signifying vibrational energy levels, full grey lines illustrating vibrational wave functions. Green line indicating vibrational states with strongest overlap.

vibrational overlap, illustrated with a green line in the figure. Here the overlap of the S_0 vibrational ground state and the third vibrational state of S_i is such that this transition will contribute more to the intensity than, for instance, vibrational ground state to vibrational ground state. Calculating the different contributions to the different ground states (the Franck–Condon factors) thus yields a good first improvement of the theoretical spectra, featuring a smoother spectrum. If the PES of S_0 and S_i are sufficiently close, the inclusion of only ground state to ground state may be sufficient, designated 0–0 in the figure. Experimentally, it may only be possible to resolve the 0–0 transition, or the wavelength corresponding to the maximum of absorption, $\lambda_{\max}$. The vertical transition energy thus gives only a rough estimate of the actual physical situation, but it is in most cases sufficiently accurate.

With X-ray emission spectroscopy the decay of a core-excited state is measured, probing the occupied states through the transition of valence electrons to the empty core-orbital. If the excited core electron was given sufficient energy to leave the molecular system, leaving behind a core-ionized state, the spectroscopy is referred to as non-resonant XES. If the excitation energy is tuned such that the core electron instead is excited to a bound state, resonant XES is instead obtained, also designated as resonant inelastic X-ray scattering. In the present work only non-resonant XES will be considered, as this is theoretically easier since do not need to be concerned over where the excited electron is. Reliably calculating such non-resonant X-ray emission spectra would thus be a first step towards a more general treatment of emission processes.

The many theoretical challenges posed by core processes — largely related to

Figure 1.5. Prototypical X-ray absorption spectrum of π -conjugated system, with an intense π^* transition lowest in energy, weak Rydberg resonances next and broader σ^* features above the ionization potential.^{8,11} At 20–30 eV the near-edge X-ray fine structure region mix with the extended X-ray fine structure region, in which scattering of the photoelectrons by the its environment gives features corresponding to constructive and destructive interference.¹²

influential relaxation effects, as will be described later — have spawned a number of theoretical methods by which these spectroscopies can be considered. Focusing on X-ray absorption spectroscopies, these include transition potential density functional theory,^{13,14} Slater transition-state density functional theory,^{15,16} the static exchange method,^{17–19} the many-body perturbative Bethe–Salpeter equation approach,^{20–22} equation of motion coupled cluster,^{23–25} the symmetry-adapted cluster configuration interaction approach,^{26,27} the algebraic-diagrammatic construction approach,^{28,29} as well as the here considered methods of time-dependent density functional theory^{9,30–36,III,IV,VI} and linear response coupled cluster theory.^{I–III} Still, there is always room for improvements.

Before closing this discussion on the general aspects of X-ray spectroscopies, it is worth considering the fate of an irradiated molecule, especially in the context of the influence on any living organism. A core-excited state is inherently unstable and a valence electron will quickly fill up the core-hole. The excess energy from this de-excitation will have to be released by some means, and the system will get rid of the main contributions of the energy by either emitting a photon (fluorescence) or by ejecting a valence electron (Auger decay). If the emitted photon has sufficiently high energy it may in turn excite core electrons, possibly leading to a cascade of absorption processes. However, if this was the only decay channel, X-ray radiation would not have such an adverse effect as it has, leading mainly to an increase in temperature of the irradiated region. The Auger electrons are instead the more dangerous decay channel, as both the electrons and the ionized molecular system are highly chemically reactive, and can break bonds or ionize other molecules in tissue, possibly leading to a cascade of bond-breaking and radical creation. This

will have adverse effects on living cells and on DNA molecules. Unfortunately for us, the Auger decay dominates for low- Z elements, while the fluorescence channel dominates for high- Z elements.

1.3 Anomalous properties of liquid water

It's in the anomalies that nature reveals its secrets.

J. W. von Goethe³⁷

Of all the compounds important for the existence of life as we know it, water stands out as the most vital. Indeed, when searching for extraterrestrial life in the universe, signals of an abundance of liquid water is one of the main fingerprints that are sought after. The reasons for this are manifold, with water possessing a number of favourable properties, including availability,ⁱⁱ the behaviour of its density at different conditions, its heat capacity and ability to solvate. As such, the importance of reaching a fundamental understanding of this compound can hardly be overstated.

In our attempts of understand this liquid, a number of anomalous properties have been identified — properties which would not usually be expected, deviating from that of most other compounds. In everyday life, the most easily observable ones are the simple facts that water is a liquid at room temperatureⁱⁱⁱ and that ice floats. Both these properties are most fortunate for Life,^{iv} as a divergence from the former would mean that Earth would be a barren rock planet, and the latter would mean that ice would be formed from the bottom of the lakes, making the survival of sea life in winter times difficult. Other anomalous properties include a decrease in viscosity under pressure, high surface tension, unusual compressibility trends, high heat capacity and many more.³⁸ These anomalies are typically more pronounced in the supercooled region — *i.e.* for liquid water with a temperature of less than 0°C — but they appear also under ambient conditions.³⁹

The exact origin of all of these properties is yet to be understood, but it can be expected to be found in the minute details of the hydrogen-bonding network.³⁹ With a water molecule possessing two bonds between hydrogens and the very electronegative oxygen atom, water has the potential of forming four strong hydrogen bonds, but the details of the dynamics and structure of the resulting network is not yet understood. The development of new experimental and theoretical tools is essential for the elucidation of these questions. The standard view of liquid water is that it has an underlying tetrahedral structure, similar to that of ice, but possessing more dynamics.^{40,41} This view was challenged in 2004, following the publication of new X-ray spectrum measurements and interpretations of the experimental results.⁴² In this study it was hypothesized that water does not possess an

ⁱⁱBeing composed of the most and third most abundant elements in the observable universe.

ⁱⁱⁱMost compounds of similar weight is in gas phase at room temperature.

^{iv}Of course, making any such prediction is fraught with danger, as it is exceedingly difficult to know all consequences such thought experiments could imply — after all, for water to possess different properties, some changes in the fundamental laws of the universe would have to be carried out, and who can tell what would be the result?

underlying heterogeneous structure, but rather thermal fluctuations around two separate underlying structural motifs. This hypothesis has later been expanded upon, with those motifs being discussed in terms of, amongst others,^v low-density liquid (LDL) and high-density liquid (HDL). In this two-structure model it is hypothesized that liquid water consists of patches of ice-like, tetrahedrally coordinated low-density liquid, embedded in a sea of more disordered high-density liquid exhibiting more weakened or broken H-bonds.³⁹ The LDL patches are estimated to be of a size of approximately 1 nm^{43,44} and driven by directionally strong H-bonds and favoured by enthalpy. In contrast, the HDL water is driven by isotropic van der Waals interactions and favoured by entropy, as quantized librational modes are now available for excitation. The structure is thus a competition between entropy and enthalpy,⁴⁵ with tetrahedral patches growing weakly in size and occurrence as the temperature is decreased.¹⁰ A schematic illustration of the two different structures is given in Fig. 1.6, where it is seen that the breaking of H-bonds in HDL enables water molecules to be closer to each other. It is important to note that the two-structure hypothesis does not presuppose two well-defined species in equilibrium with each other, but rather a continuum distribution of HDL-like structures with fluctuations into LDL-like structures.³⁹

Figure 1.6. Schematic illustration of hypothesized structural motifs of liquid.

This two-structure model was initially based on results from studies of the X-ray absorption spectrum of liquid water, as this gives a very local probe sensitive to the closest environment. However, the experimental measurements and theoretical calculations required to make a definitive interpretation of, amongst others, the X-ray absorption spectrum of liquid water are challenging, and the correct interpretation is still in debate.

From an experimental point of view,¹⁰ the advent of third-generation synchrotron radiation sources has been pivotal for the measurement of high-quality X-ray absorption spectra of water, especially using X-ray Raman scattering (XRS). In terms of experimental challenges, XAS measurements of liquid water are diffi-

^vOther designations include tetrahedral and distorted, symmetrical and asymmetrical, and locally favoured and normal, but they all refer to the same two general structural classes.⁴³

cult due to, *e.g.*, ultra high vacuum requirements and the need to avoid saturation effects. Alternatively, X-ray absorption spectra can be measured by use of XRS, if momentum transfer q is low (using small scattering angles) and nondipolar contributions to the spectrum are thus avoided. Here the energy loss in scattering is used to construct the absorption spectrum, and the use of hard X-ray beams removes some concerns on vacuum environment. However, this latter technique suffers from an extremely small scattering cross section, such that significant development in radiation sources and spectrometers were required for this method to yield a significant impact.¹⁰ The continuing development of fourth-generation synchrotron facilities, *e.g.* free-electron lasers, will provide even more opportunities for novel experimental studies of the behaviour of water, such as the recent investigation of the liquid water structure at temperatures below that of homogeneous ice nucleation.⁴⁶

From a theoretical point of view,¹⁴ the calculation of X-ray absorption spectra for liquid water is challenging, partially due to the difficulties in performing accurate molecular dynamics simulations and partially due to the challenges of modeling core-excitation processes. The former difficulty will not be discussed further in this work, but we note that high-quality *ab initio* molecular dynamics simulations with van der Waals interactions reliably accounted for are necessary for accurate properties,³⁹ whereas a classical force field cannot properly account for cooperation effects and, for example, tends to yield overstructured MD snapshots.⁴⁷ It is also important to note that it is not clear if the inability to, as of yet, obtain good theoretical X-ray absorption spectra of liquid water is due to deficiencies in the molecular dynamics simulations or in the spectral calculations.

The correct interpretation of the experimental observations is contested, where theory is needed to, ideally, give quantitative measures of the disorder of the H-bonding network. The two most prominent interpretations of the X-ray absorption spectrum rationalize the observed behaviours either in terms of fluctuations around an underlying homogenous tetrahedral structure,^{40,48–54} or as arising from fluctuations around two separate structural motifs.^{10,14,42,55–59} It is to be noted that it may not be necessary to reproduce the exact spectral features under the different conditions, but reliably capturing the correct trends is a priority. In order to investigate the validity of the different models, what is needed is to correlate the spectral features to local geometries using some reliable and unambiguous categorization. Details on the features of the X-ray absorption spectra of water in all three phases can be found in Paper [IV] and Section 4.3, but it is important to note here that the behaviour of the spectrum is well investigated experimentally, and what is needed in order to reach a fundamental understanding of the structure and dynamics of the hydrogen-bonding network is mainly theoretical considerations.

Additionally, measurements on water using XES have been keenly debated in the scientific community, with interpretations of spectral signals including dynamics^{60–62} or the two-structure model.^{63–65} Other measurement have also been invoked to support the two-structure model, *e.g.* small angle X-ray scattering,^{43,45} and in the end it is important to formulate a theory which can account for the many different properties and measurements.³⁹

Remark

The material presented in this doctoral thesis have in parts been reused from a licentiate thesis written by the author,⁶⁶ adapted where appropriate.

CHAPTER 2

Electronic structure theory

The nature of the chemical bond is the problem at the heart of all chemistry.

B. Crawford, 1957⁶⁷

In this chapter we will discuss, in general terms, the challenges Nature provides for us when attempting to understand the interaction of matter on a microscopic scale. Focus will be on the construction of accurate electronic structures, either in terms of many-particle wave functions or as electron densities, allowing us to unravel the mysteries of the mentioned chemical bonds. It will here be assumed that the Reader has some familiarity with quantum chemistry, at least in terms of the Hartree–Fock method, as described in, *e.g.*, Refs. [68–71].

2.1 Fundamentals of electronic structure theory

I think I can safely say that nobody understands quantum mechanics.

R. Feynman, 1965⁷²

For the description of any quantum mechanical system, the wave function satisfies the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{H} |\Psi\rangle. \quad (2.1)$$

In the case of an unperturbed molecular system consisting of N electrons and M nuclei, the non-relativistic molecular Hamiltonian can be expressed asⁱ

$$\begin{aligned}\hat{H} &= -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \\ &= \hat{T}_e + \hat{T}_n + \hat{V}_{en} + \hat{V}_{ee} + \hat{V}_{nn}.\end{aligned}\tag{2.2}$$

Here the first two terms describe the kinetic energy of the electrons and nuclei, and the last three terms contain the Coulombic interaction between the electrons and nuclei, electrons and electrons, and nuclei and nuclei, respectively. The solution of the Schrödinger equation for a molecular system then requires the calculation of a many-body wave function with $3N \times 3M$ degrees of freedomⁱⁱ, which can be solved analytically for only the smallest of systems. In order to treat large systems numerical methods are thus necessary, and approximations must be made to decrease the level of complexity.

Of all simplifications used in quantum chemistry, the Born–Oppenheimer approximation is likely the most common. It enables the separation of the electron and nuclear degrees of freedom and thus gives a foundation of concepts such as potential energy surfaces — without which it would be difficult to discuss, *e.g.*, chemical reactions, as molecules would only be a collection of moving, charged particles — by dividing the total many-body wave function into nuclear and electronic components

$$\Psi(\mathbf{r}, \mathbf{R}) = \Psi_e(\mathbf{r}, \mathbf{R}) \Psi_n(\mathbf{R}),\tag{2.3}$$

where the electronic wave function Ψ_e depends explicitly on the positions of the electrons and parametrically on the positions of the nuclei. Time-independence is assumed, for brevity. The electronic wave function is calculated by use of the Schrödinger equation with the electronic Hamiltonian

$$\hat{H}_e = \hat{T}_e + \hat{V}_{en} + \hat{V}_{ee},\tag{2.4}$$

yielding eigenvalues

$$\hat{H}_e \Psi_e(\mathbf{r}, \mathbf{R}) = \varepsilon_e \Psi_e(\mathbf{r}, \mathbf{R}),\tag{2.5}$$

and the nuclear Hamiltonian becomes

$$\hat{H}_n = \hat{T}_n + \hat{V}_{nn} + \varepsilon_e.\tag{2.6}$$

The validity of this approximation lies mainly in the large difference in the mass of the nuclei as compared to the mass of the electrons, differing by a factor of over

ⁱAs expressed in atomic units (a.u.), for which the numerical values of fundamental parameters of Nature becomes $\hbar = e = m_e = 4\pi\epsilon_0 = 1$, and the speed of light $c = \alpha^{-1} \approx 137.04$. For comparison, the values of the 1 length unit (a_0), 1 energy unit (E_h), and 1 electric field strength unit in a.u. is approximately 5.29×10^{-11} m, 4.36×10^{-18} J, and 5.14×10^{11} V/m, respectively, as expressed in SI units. Finally, $1 E_h \approx 27.2$ eV.

ⁱⁱDisregarding the spin degree of freedom, for simplicity, as will be done for most of our discussion.

1800 for the lightest of elements. By comparison, the electrons thereby responds close to instantaneously to any change in the positions of the nuclei.

Example: Illustration of the Born–Oppenheimer approximation

Operating with the full Hamiltonian from Eq. (2.2) on the wave function of Eq. (2.3) yields

$$\begin{aligned}\hat{H}\Psi_e(\mathbf{r},\mathbf{R})\Psi_n(\mathbf{R}) &= \left(\hat{T}_n + \hat{V}_{nn} + \hat{H}_e\right)\Psi_e(\mathbf{r},\mathbf{R})\Psi_n(\mathbf{R}) \\ &= \left(\hat{T}_n + \hat{V}_{nn}\right)\Psi_e(\mathbf{r},\mathbf{R})\Psi_n(\mathbf{R}) + \varepsilon_0\Psi_n(\mathbf{R}) \\ &= \hat{T}_n\Psi_e(\mathbf{r},\mathbf{R})\Psi_n(\mathbf{R}) + \Psi_e(\mathbf{r},\mathbf{R})\hat{V}_{nn}\Psi_n(\mathbf{R}) + \varepsilon_0\Psi_n(\mathbf{R}),\end{aligned}$$

for which the last two terms are unproblematic, and the first term can be expanded as

$$\begin{aligned}\hat{T}_n\Psi_e(\mathbf{r},\mathbf{R})\Psi_n(\mathbf{R}) &= -\sum_{A=1}^M \frac{1}{2M_A} \left([\nabla_A^2\Psi_e(\mathbf{r},\mathbf{R})]\Psi_n(\mathbf{R}) + \Psi_e(\mathbf{r},\mathbf{R})\nabla_A^2\Psi_n(\mathbf{R}) \right. \\ &\quad \left. + 2\nabla_A\Psi_e(\mathbf{r},\mathbf{R})\nabla_A\Psi_n(\mathbf{R}) \right).\end{aligned}$$

Here the second term is in line with the Born–Oppenheimer approximation, and the other two terms — containing $\nabla_A\Psi_e(\mathbf{r},\mathbf{R})$ — need to be small if the approximation is to be accurate. For most cases this is the case due to the small pre-factor, but if the electronic wave function changes rapidly with the positions of the nuclei this term can no longer be neglected, as is the case when two electronic states are nearly degenerate.

2.1.1 The one-particle wave function

In order to construct a many-body wave function a description of the spatial distribution of the electrons is needed. This construction is more effectively done by considering the behaviour of the electrons in question — for solid state physics the use of plane waves is advantageous, while for chemistry a basis of atom-centered functions is favourable. Using the latter, molecular orbitals are optimized using a set of atomic orbitals, as

$$\psi_i(\mathbf{r}) = \sum_j C_{ij}\chi_j(\mathbf{r}). \quad (2.7)$$

The exact atomic orbitals are only available for hydrogenic atoms, expressed in atomic units as⁷³

$$\Psi_{nlm}(R, \theta, \phi) = N_{nl}e^{-R/2}R^l L_{n+l}^{2l+1}(R)Y_{lm}(\theta, \phi), \quad (2.8)$$

where $R = 2Zr/n$, L_{n+l}^{2l+1} are the associated Laguerre polynomials, and Y_{lm} are the spherical harmonics.

Suitable radial functions to be used include functions with exponential asymptotic behavior, so-called Slater-type orbitals

$$\chi^{\text{STO}}(\mathbf{r}) = P(r)e^{-\xi r}Y_{lm}(\theta, \phi), \quad (2.9)$$

with basis set exponent ξ . However, for technical reasons concerning the calculation of integrals, it is computationally more efficient to use basis functions with a $e^{-\xi r^2}$ behaviour, *i.e.*, using Gaussian basis functions (GTO:s). Several such basis functions can be combined, or contracted, in order to get a smaller number of basis functions which approximate the behaviour of STO:s. Choosing the appropriate basis sets corresponds then to the one-electron description, and this choice should be balanced against the selected electronic structure method. In this thesis the correlation-consistent polarized valence X- ζ (cc-pVXZ) basis sets developed by Dunning and coworkers⁷⁴ have been used for the majority of the calculations. To better describe core relaxation these basis sets have been augmented with core-polarizing functions,⁷⁵ and additional augmentation using diffuse functions have been used to better describe excited states.⁷⁶ Finally, as many of the excited states studied are of Rydberg character, we have adopted the proposition of Kaufmann *et al.*⁷⁷ and supplemented the basis sets with Rydberg functions.

2.1.2 The N -particle wave function

For the construction of the electronic many-particle wave function, a plethora of electronic structure methods are available, with widely varying computational cost and accuracy. As a first approximation, the electron-electron interaction can be modeled as an interaction between single electrons and the mean-field of the other electrons. This corresponds to the Hartree-Fock (HF) method and yields results that include the main contributions to the electronic energy. The wave function is constructed using a single Slater determinant

$$|\Psi\rangle = \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix}. \quad (2.10)$$

The HF approach requires no parametrization from experiment or other calculations, and is thus an example of an *ab initio* wave function method. However, as the electrons interact in manners that cannot be described by a mean-field approximation, the HF energy (E_{HF}) lacks important electron correlation, and the retrieval of this constitutes one of the major issues in quantum chemistry. Correlation effects can be subdivided into two different effects, static and dynamic correlation, where the latter is the main issue for the calculations discussed in this thesis.

Static correlation is important when a molecule requires several (nearly) degenerate determinants for a good description of the electronic state. Cases when this becomes important include, *e.g.*, bond breaking and quasi-degenerate ground

states with low lying excited states. In order to capture these effects, multi-reference methods are necessary, which will not be described here. Static correlation will thus not be considered any further, and all correlation discussed is hereby understood to mean dynamic correlation.

Dynamic correlation arises from the correlation in the movement of the electrons, resulting in an energy difference compared to HF as

$$E_{\text{corr}} = E_0 - E_{\text{HF}}. \quad (2.11)$$

In accordance with the variational principle, E_{HF} is always larger than the exact energy (E_0), and the correlation energy is thus negative. In order to capture the effects of this correlation, a number of post-HF methods have been developed — methods that builds upon HF, taking the HF wave function as a starting point for a more accurate treatment of the electron-electron interaction.

One such method is configuration interaction (CI), in which correlation is accounted for by means of exciting the electrons in a reference determinant to virtual orbitals, forming a CI wave function as a sum of this reference, all singly excited determinants, all doubly excited determinants, and so on. This is done variationally, and if the CI excitation space is included up to excited determinants of order N (*i.e.* the number of electrons in the system), the resulting wave function is exact (under the restriction of the other approximations, *e.g.* the Born–Oppenheimer approximation). However, constructing this full CI wave function is unfeasible for most systems, and the CI excitation space is truncated by necessity. Unfortunately, owing to the linear nature of the CI expansion, the wave function resulting from such a truncation is no longer size-consistent, meaning that the energy of two infinitely separate molecules is different from that of the sum of the energies of the two molecules.

A methodology similar to CI is that of coupled cluster (CC) theory, for which a non-linear (exponential) expansion of excited determinants is used to form the CC wave function, thus yielding size-consistency. The method is hierarchical in the inclusion of electron correlation and stands out as one of the most accurate approaches in quantum chemistry. As for negative aspects, it is non-variational in most implementations and very computationally demanding, but these concerns will be discussed in more detail in Section 2.3.

Alternatively, it is possible to take a different approach than the Hartree–Fock and related *ab initio* wave function methods, by instead focusing on the electron density. By doing so, it would in principle be possible to remove the degrees of freedom from $3N$ to 3, and this is the basic idea underlying density functional theory (DFT). Unfortunately, as will be discussed in more detail in Section 2.2, the solution of the electronic density requires the knowledge of a entity known as the exchange-correlation functional, for which the correct expression is not known. As a result of this, the results from any DFT calculation strongly depends on the exchange-correlation functional in use, and the predictability of the method is thus put in some doubt.

2.1.3 Relativistic effects

Next to the Born–Oppenheimer approximation, the most commonly used simplification in quantum chemistry is likely the disregard of, or only scalar inclusion of, relativistic effects. This approximation is for many properties warranted, but we will later see how relativity can have a profound effect already for quite light elements. We will here briefly discuss the theory of relativistic quantum chemistry, and thorough discussions there are several relevant books,^{70,78} as well as review articles,^{79–82} which can be consulted.

For the discussion of molecular properties, the most influential effects of relativity are those of special relativity, which is of interest mainly at high velocities, *i.e.*, high kinetic energies — as such, they are definitely of relevance for a treatment of the core electrons and especially for heavy elements. It is however to be noted that relativistic effects of the valence electrons also increase with the full, and not the screened, charge of the nuclei.⁸⁰ Additionally, the magnetic interaction between electron current and electron spin breaks symmetries of non-relativistic theory, yielding, amongst others, new allowed electronic transitions. Relativistic effects can be highly influential — as an everyday example it has, for example, been calculated that of the 2.1 V per cell of a lead-acid battery, over 1.7 V comes from relativistic effects.⁸³

In relativistic theory the space and time coordinates are coupled, and thus forms a four-dimensional space-time which needs to be considered. Any physical processes must here be Lorentz-transformable, and it is clear that the Schrödinger equation in 2.1 is not — the time and space variables are not treated at equal order of differentiation. For the construction of a Lorentz-invariant wave function the spin of the particles has to be accounted for, and we here demonstrate a simple derivationⁱⁱⁱ of the spin-zero Klein–Gordon equation.⁷⁸

For spin-1/2 particles the relativistic wave equation is a bit too cumbersome to be repeated here, and we instead move directly to the resulting Dirac equation for a spin-1/2 particle in an electromagnetic field:

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \hat{h}_D \Psi(\mathbf{r}, t) = \left(\hat{\beta} mc^2 + e\phi(\mathbf{r}) + c\hat{\alpha} \cdot \hat{\pi} \right) \Psi(\mathbf{r}, t). \quad (2.12)$$

Here, the wave function $\Psi(\mathbf{r}, t)$ is required to be a four-component vector, written in the standard representation as

$$\Psi = \begin{pmatrix} \Psi^{\alpha L} \\ \Psi^{\beta L} \\ \Psi^{\alpha S} \\ \Psi^{\beta S} \end{pmatrix}, \quad (2.13)$$

where L and S denote the large and small components, and α and β denote the different spins. These components will be discussed shortly, but first we need to consider the operators in the Dirac Hamiltonian.

ⁱⁱⁱOr rather demonstration of, as this is by now means a formal proof.

Example: The Klein–Gordon equation

The energy of a relativistic free particle is given as

$$W = \sqrt{p^2 c^2 + m^2 c^4}, \quad (2.14)$$

which in the rest-frame reduces to what is likely the most famous equation in all of science

$$W = E = mc^2. \quad (2.15)$$

Substituting the momentum and total energy with the quantum mechanical operators

$$\hat{W} = i\hbar \frac{\delta}{\delta t} \quad \text{and} \quad \hat{p} = \frac{\hbar}{i} \nabla,$$

we get

$$i\hbar \frac{\delta \Psi(\mathbf{r}, t)}{\delta t} = (-\hbar^2 c^2 \nabla^2 + m^2 c^4)^{1/2} \Psi(\mathbf{r}, t). \quad (2.16)$$

Moving all terms to the left-hand side and using the identity $a^2 - b^2 = (a + b)(a - b)$, we get

$$\left(-\frac{1}{c^2} \frac{\delta^2}{\delta t^2} + \nabla^2 - \frac{m^2 c^2}{\hbar^2} \right) \Psi(\mathbf{r}, t) = 0, \quad (2.17)$$

which is the free-particle Klein–Gordon equation. Note here that both time and space coordinates are operated on at the same order, such that this equation is now Lorentz-invariant. However, it is only valid for spin-zero particles and can thus not be used here, as electrons are the particles of interest.

The external field enters into the Hamiltonian through minimal substitution of the mechanical momentum, *i.e.*

$$\hat{\pi} = \hat{p} - e\bar{A}(\mathbf{r}, t), \quad (2.18)$$

with the external vector field $\bar{A}(\mathbf{r}, t)$. Additionally, we add scalar effects through the electrostatic potential $\phi(\mathbf{r}, t)$. The $\hat{\alpha}$ and $\hat{\beta}$ operators are now defined as

$$\hat{\alpha} = \begin{pmatrix} 0 & \hat{\sigma}_i \\ \hat{\sigma}_i & 0 \end{pmatrix} \quad \text{and} \quad \hat{\beta} = \begin{pmatrix} \hat{I}_2 & 0 \\ 0 & \hat{I}_2 \end{pmatrix}, \quad (2.19)$$

with the two-dimensional unit matrix $\hat{I}_2$ and the Pauli spin matrices $\hat{\sigma}_i$. This yields the one-particle Dirac Hamiltonian for four-component spinors

$$\bar{h}_D = \begin{pmatrix} (mc^2 + e\phi)\hat{I}_2 & c\hat{\sigma} \cdot \hat{\pi} \\ c\hat{\sigma} \cdot \hat{\pi} & (-mc^2 + e\phi)\hat{I}_2 \end{pmatrix}. \quad (2.20)$$

For a molecular many-electron system, the Hamiltonian can now be written as

$$\hat{H} = \sum_i \hat{h}_D + \frac{1}{2} \sum_{i \neq j} \hat{g}(i, j) + \hat{V}_{en}, \quad (2.21)$$

with the one-electron, two-electron operators, and the electron-nuclear interactions. The Dirac equation satisfies the requirements of special relativity, not of general relativity⁷¹ — for this we need quantum gravity which is not yet known, but this yields a negligible effect beyond the accuracy of the present work. Spin is often considered to arise from relativistic effects, but it can be shown⁷¹ to arise also in the non-relativistic limit of the Dirac equation — in fact, if we rewrite $\vec{p}^2$ as the equivalent factor $(\vec{\sigma} \cdot \vec{p})^2$, electron spin is present in the Schrödinger equation.

For many-body interactions the electronic structure should be described by models derived from relativistic quantum field theory. However, this is currently not viable, and more approximate methods are instead used. For this, there are no closed forms of the electron-electron interaction, which can instead be expanded in order of the inverse of the speed of light, with leading terms

$$\hat{g}(i, j) = \frac{1}{\hat{r}_{ij}} - \frac{\hat{\alpha}_i \cdot \hat{\alpha}_j}{2\hat{r}_{ij}} - \frac{(\hat{\alpha}_i \cdot \hat{r}_{ij})(\hat{\alpha}_j \cdot \hat{r}_{ij})}{2\hat{r}_{ij}^3} + \mathcal{O}(c^{-3}), \quad (2.22)$$

for the interaction of electrons i and j . Here the first term is the (non-relativistic) instantaneous Coulomb interaction between the electrons, which is corrected by the retardation effect in the third term — the electromagnetic interaction is mediated by photons and should thus not be instantaneous. Finally, the second term indicates the magnetic (spin) interaction. If only the first term is included this yields the Dirac–Coulomb Hamiltonian, if both the first and the second terms are included we get the Dirac–Coulomb–Gaunt Hamiltonian, and finally if all three terms are included we have the Dirac–Coulomb–Breit Hamiltonian. Relativistic effects on nuclear-electron interactions are of the order of c^{-3} , and are thus neglected at this order of approximation. A fully relativistic treatment starts from quantum electrodynamics, with perturbative expansions. Dirac–Coulomb most used four-component many-electron Hamiltonian, when coupled with the Dirac operator above. It is to be noted that this Hamiltonian is, in general, not Lorentz-invariant, but any improvements beyond typically lies in the realm of quantum electrodynamics.⁸⁰ More on electrodynamics in Ref. [79].

One of the most striking differences as compared to the non-relativistic wave equation, the free Hamiltonian given here has a spectrum of infinitely many negative energy solutions, separated from the positive solutions by $2mc^2$ — the positronic solutions. For the positive energy solutions the small component of the spinor is coupled to the momentum of the electron, and for weak potentials this has the consequence that the small components are of the order of $1/c$.⁸¹ times the large component, explaining the origin of the small/large names. For hydrogenic wave functions we get,⁷¹ in the non-relativistic limit (*i.e.* in the limit of infinite speed of light)

$$\Psi^S \approx \frac{Z}{2c} \Psi^L, \quad (2.23)$$

i.e. negligible for small systems. From this the basis set of the small component is typically chosen to fulfill the kinetic balance condition

$$\chi^S = \vec{\sigma} \cdot \vec{p} \chi^L. \quad (2.24)$$

From this condition we see that the small component basis set contains derivatives of the large component basis set, making the approximately twice as big as the latter. Compared non-relativistic calculations we thus get ~ 8 times more small-large two-electron integrals, ~ 16 times more small-small — *i.e.* totally approximately 25 times more two-electron integrals than for a non-relativistic calculation. As such, in order to decrease the computational costs of relativistic calculations, it is possible to approximate some of the integrals — in this thesis we employ an approximation in which all (SS|SS) integrals are replaced by tabulated values.⁸⁴

A complication of using relativistic theory is that a point-charge in the nuclei becomes problematic (in reality, protons and neutrons are distributed in volume of a radius of $2 - 6 \text{ fm}^{70}$), due to the singularity that now appears there — by comparison a non-relativistic calculation only exhibits a cusp there. As such, a finite charge distribution should be used, and for the calculations reported here we have utilized Gaussian charge distributions. Also note that the real, more complicated, charge distribution will depend on the isotope, and we thus have a (weak) isotope dependence occurring here.

In order to decrease the computational costs of solving the Dirac equation a plethora of approximate Hamiltonians can be found in the literature, which typically seek to reduce the equation from a four-vector form to a one- or two-vector form. In general, scalar relativistic effects can be incorporated at little extra cost for a one-component wave function — this is done, *e.g.* using the perturbative Douglas–Kroll–Hess approach^{85–87} — while the spin-orbit interactions require a two component wave function, as is done in, *e.g.* exact two-component (X2C) calculations.⁸⁸ In this thesis we will discuss the use of X2C for *L*-edge spectroscopy, but as the additional cost when using relativistic Hamiltonians lies in the pre-factor, and not in the scaling, we in general advocate the use of the full Dirac–Coulomb–Breit Hamiltonian for any relativistic calculations. Alternative ways of including relativistic effects include the use of relativistic effective core potentials, where the core electrons are replaced by a potential mimicking the correct relativistic behaviour, and (provided that the interaction is sufficiently weak) the use of perturbative spin-orbit corrections.

2.1.4 Approaching the correct wave function

As has been seen in Sections 2.1.1–2.1.3, the construction of an accurate wave functions have three manners in which an appropriate description must be found: the one-particle wave functions, the *N*-electron wave function, and the relativistic effects. This can be visualized as in Fig. 2.1, where the correct wave function is approached by moving simultaneously along the three axes. A step along any of the axes will increase the computational cost of any calculation, and the treatment of large molecules is thus restricted to the volume close to origin. Hence, schemes by which the effects of an improved description can be estimated are a major priority in quantum chemistry.

Two remarks should be added in concern with this model. First, the axes with the relativistic models and the basis sets^{iv} are hierarchical, meaning that moving

^{iv}At least when adding more basis functions to the set at hand — changing from a double- ζ

Figure 2.1. Approximate ordering of theoretical models for describing electron structure. Model partially adopted from Ref. [89].

outwards along them improves the description of the wave function. However, this is not always the case for the N -particle axis, as some properties may be better described with a electronic structure method lower in the ordering, as a result of cancellation of errors or other effects. This is especially true for Kohn–Sham density functional theory (KS-DFT), as will be discussed in the following section. Secondly, the model may give the impression that variations along these three axes are decoupled. This is not the case, especially for the basis sets and electronic structure methods. In order to properly account for electron correlation the basis set needs to be sufficiently flexible. If this is not the case the results can actually be less reliable than using a more approximate electronic structure method. Further, relativistic effects and electron correlation effects are not additive, so these needs to be considered simultaneously as well.

In conclusion, the approximations on the different axes needs to be balanced in order to approach the correct wave function in a reliable, efficient manner.

basis set optimized for specific types of calculations to a triple- ζ basis set optimized for a different situation might not be an improvement.

2.2 Density functional theory

When teaching chemistry students, I explain that DFT is some algorithm meaning unreliable, while ab initio is Latin for too expensive.

K. Burke, 2012⁹⁰

In order to account for the correlation effects in an efficient manner, a good balance between quality and computational cost is typically achieved using density functional theory (DFT). Here, the idea is to focus on the electron density rather than the wave function, and while DFT has some problems in terms of the account for exchange-correlation energies, and thus lacks a clear predictability, its tremendous influence on the field of quantum chemistry cannot be denied. In this section we will discuss the basics of (Kohn–Sham) density functional theory, the problem concerning the exchange-correlation energy and some issues for core-excitations. A more in-depth discussion of the theory can be found in, *e.g.*, Refs. [70, 71], as well as a multitude of reviews on the subject.^{90–93}

When estimating the importance and influence of DFT, it can be noted that a study on the 100 top cited research papers of all time conducted in 2014,⁹⁴ identified DFT as “easily the most heavily cited concept in the physical sciences”, with twelve papers in the top 100 and two in the top ten.^v Another measure can be given by an analysis of the number of DFT-related papers per year, as is found in Fig. 2.2 — it is readily apparent that DFT has experienced a huge development in the last two decades. Included here is also the number of papers with the keyword B3LYP, which can be considered to be the go-to exchange-correlation functional (more on this below) in quantum chemistry.

Figure 2.2. Number of published papers associated with the keywords DFT (black) or B3LYP (red), as obtained on the 5:th of December 2015 on Web of Science.

^vIt should be noted that these highly cited papers do not necessarily include the most influential papers in science, but a majority rather consists of description of experimental or theoretical methods. Still, it is a clear indication of the importance of the respective methods.

2.2.1 Basics of density functional theory

Solving the Schrödinger equation with the electronic Hamiltonian in Eq. (2.4) involves solving a system of $4N$ degrees of freedom, or $3N$ if the spin degrees of freedom are neglected. An alternative approach is to focus on the electron density, which in general is given as

$$\rho(\mathbf{r}_1) = N \int \dots \int |\Psi_e(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 d\mathbf{r}_1 d\mathbf{x}_2 \dots d\mathbf{x}_N, \quad (2.25)$$

giving the electron density in $d\mathbf{r}_1$. The total number of electrons is obtained by integrating the density as

$$N = \int \rho(\mathbf{x}) d\mathbf{x}. \quad (2.26)$$

In this notation $\mathbf{x}_i = (\mathbf{r}_i, \sigma_i)$, *i.e.* represents both the spatial and spin degrees of freedom for the orbital. In the remainder of this section we will focus on the spatial orbitals, thus leaving out the spin degrees of freedom for brevity.

It was long unclear if the density contains the necessary information for a good description of electronic structure. Initial attempts of using the electron density was too approximate to be practically useful — attempts to express kinetic and exchange energies as functionals dates back to works of Thomas,⁹⁵ Fermi,⁹⁶ and Dirac⁹⁷ in the 1920s–1930s — mainly due to unacceptably large errors in the kinetic energies. The theoretical foundations of modern density functional theory was laid down by Hohenberg and Kohn in their ground-breaking paper of 1964,⁹⁸ in which they demonstrated that

1. For any system of interacting particles in an external potential $V_{\text{ext}}(\mathbf{r})$, the potential $V_{\text{ext}}(\mathbf{r})$ is determined uniquely, up to a trivial constant, by the ground state density $\rho_o(\mathbf{r})$.
2. A universal functional^{vi} for the energy $E[\rho]$ can be defined, valid for any external potential $V_{\text{ext}}(\mathbf{r})$. The exact ground state energy is given by the global minimum value of this functional, with the corresponding density amounting to the exact ground state density $\rho_0(\mathbf{r})$.

These are the two Hohenberg–Kohn theorems, from which the Hamiltonian can be fully reconstructed from only the electron density. As such, the density contains the exact same information as the wave function. That the Hamiltonian is fully known from density can be conceptually understood as follows: in order to obtain this knowledge we need to know the number of electrons and the external potential, *i.e.* the positions and charges of the nuclei. The number of electrons is obtained from the integration in Eq. (2.26), and the cusps in the density indicates the position of the nuclei, with the slope corresponding to nuclear charge.

^{vi}A functional is a function of a function — in this case the energy is a function of the density, which in turn is determined by the position.

The energy functional can be written as a sum of terms

$$\begin{aligned} E[\rho] &= T[\rho] + V_{ee}[\rho] + \int \rho(\mathbf{r})V_{\text{ext}}(\mathbf{r})d\mathbf{r} \\ &= F[\rho] + \int \rho(\mathbf{r})V_{\text{ext}}(\mathbf{r})d\mathbf{r}, \end{aligned} \quad (2.27)$$

where the kinetic energy and the Coulomb repulsion between the electrons are combined into a single functional $F[\rho]$. This division of terms is chosen such that $F[\rho]$ contains no dependencies on V_{ext} , and is thus system independent. However, as the correct form of the (universal) functional $F[\rho]$ is not known, this formulation of DFT is in practice seldom used. Instead, the next step towards a practical computational method was presented by Kohn and Sham in 1965.⁹⁹ They proposed that the system of interacting electrons can be replaced by an auxiliary system of non-interacting particles with the same ground state density. This auxiliary system is then significantly easier to consider, with a universal functional written as

$$F[\rho] = T_s[\rho] + J[\rho] + E_{\text{xc}}[\rho], \quad (2.28)$$

where $T_s[\rho]$ is the kinetic energy of the non-interacting particle and $J[\rho]$ is the Coulombic interaction of the particle density with itself. Here, the poor representation of the kinetic energy in orbital-free models is redeemed by splitting it into two parts — one which can be calculated exactly plus a small correction. The disadvantage of this approach is the re-introduction of orbitals, which again bring up the complexity to $3N$ variables — but even so, the computational scaling is still far more favorable than for most *ab initio* methods. The most noteworthy term in $F[\rho]$ is the so-called exchange–correlation energy, which can be written as

$$E_{\text{xc}}[\rho] = T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho]. \quad (2.29)$$

This exchange–correlation term thus contains the difference between the kinetic and Coulombic energy of the real system and the auxiliary system of non-interacting particles — for the latter we now have *exact* expressions, with the kinetic energy given as

$$T_s[\rho] = \sum_i \langle \Psi_i | -\frac{1}{2}\nabla^2 | \Psi_i \rangle, \quad (2.30)$$

and the Coulomb self-energy

$$J(\rho) = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (2.31)$$

Inserting the functional of the system of non-interacting particles in the energy functional

$$E = T_s[\rho] + J[\rho] + E_{\text{xc}}[\rho] + \int \rho(\mathbf{r})V_{\text{ext}}(\mathbf{r})d\mathbf{r}, \quad (2.32)$$

which is the total electronic energy to be calculated. Applying the variational

principle, we get

$$\begin{aligned}
 \frac{\delta E}{\delta \rho} &= \frac{\delta}{\delta \rho} \left(T_s[\rho] + J[\rho] + E_{\text{xc}}[\rho] + \int \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r} \right) \\
 &= \frac{\delta T_s[\rho]}{\delta \rho} + \frac{\delta J[\rho]}{\delta \rho} + \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho} + V_{\text{ext}}(\mathbf{r}) \\
 &= \frac{\delta T_s[\rho]}{\delta \rho} + V_{\text{eff}}(\mathbf{r}) = \mu
 \end{aligned} \tag{2.33}$$

where μ is a Lagrangian multiplier associated with the requirement on the total density in Eq. (2.26). This introduction of the potential V_{eff} means that the system of non-interacting particles can be considered as moving in an effective potential, in which the minimization yields the true energy functional. By this, it is in principle possible to obtain the exact density and total energy for a system of interacting, correlated electrons, by considering systems of non-interacting particles. Of course, this hinges on the use of the exact exchange-correlation functional $E_{\text{xc}}[\rho]$, which unfortunately remains unknown, save at a great cost for small systems.¹⁰⁰

Solving this new system becomes a matter of solving N single-particle Schrödinger equations of the form

$$\left(-\frac{1}{2} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \right) \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}), \tag{2.34}$$

with the total wave function of the system given by populating the N lowest solution of this single-particle equation, with the density calculated as

$$\rho(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r})|^2. \tag{2.35}$$

With this, we now have tractable means of calculating the electron density (save for the details of the exchange-correlation functional).^{vii} Before moving to a discussion on DFT functionals, it is to be noted that the effective potential requires knowledge of the electron density, which in turn depends on the effective potential. As such, the solution of this problem requires the initiation using some physically realistic starting guess, following which the solution and refinement of the effective potential can be formed iteratively, up to some desired threshold.

Furthermore, it is to be noted that for relativistic DFT it becomes necessary to consider also the dependence on the current, constructing current density functional theory (CDFT).⁷⁰ However, there are currently no wide selection of CDFT functionals of sufficiently good quality, such that most studies are conducted with the non-relativistic DFT functionals instead.

2.2.2 Approximate exchange-correlation functionals

A major problem of DFT is the lack of knowledge on the exact form of the exchange-correlation functional $E_{\text{xc}}[\rho]$. Up to this point the formulation of DFT

^{vii}This is thus the basics of Kohn–Sham DFT, or KS-DFT. Note that the terms KS-DFT and DFT are often used more or less interchangeably, but in the strict sense KS-DFT is but a special formalism of the more general field of DFT.

has been exact, but the lack of an exact exchange-correlation functional necessitates the introduction of approximate functionals. This is at present the greatest disadvantage of DFT, and a plethora of different functionals have been developed, typically parameterized either from theoretical considerations or in order to fit experimental measurements of high-level *ab initio* calculations. Choosing between these two schools of thought is largely a matter of taste, as both have the same problem of predictability — using any functional for a new physical situation is always wrought with uncertainties, and it is not always clear that any ability to accurately reproduce experimental measurements is a coincidence or not. In general, fitting to experiments or high-level calculations typically yield higher accuracy to those systems fitted to (often by factor 2), but greater inaccuracies far away.⁹⁰ As such, there is no absolute hierarchy in terms of the accuracy of different functional, but Perdew introduced Jacob’s ladder to describe the approximate hierarchy of different families of functionals.¹⁰¹ In this ladder, the computational complexity and, ideally, reliability of a set of functionals are increased when climbing up the ladder, and we will here briefly describe the first four rungs.

Local density approximation

The simplest exchange-correlation functional, the local density approximation (LDA), was formulated by Kohn and Sham,⁹⁹ who proposed that the exchange-correlation energy can be approximated as that of an electron gas with the same density as the system in consideration. This proposal was made with mainly systems of slowly varying electron densities, *e.g.* crystals, in mind, and gives a exchange-correlation functional of the form

$$E_{xc}^{LDA} = \int \rho(\mathbf{r}) \varepsilon_{xc}[\rho(\mathbf{r})] d\mathbf{r}, \quad (2.36)$$

with the exchange-correlation energy per electron in the uniform gas amounting to $\varepsilon_{xc}[\rho(\mathbf{r})]$. Splitting this energy into a linear combination of a correlation energy and an exchange energy, the latter is given as

$$\varepsilon_x^{LDA} = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{\frac{1}{3}} \rho^{\frac{1}{3}}. \quad (2.37)$$

By comparison, the exact form of the correlation energy is unknown, save for high- and low-density limits, and thus needs to be constructed and parameterized from experiments and/or theoretical considerations. As LDA is developed for slowly varying electron densities, it is generally not suitable for molecular systems and more advanced functionals should be used in such cases.

It is to be noted that the appearance of such fractional powers of the density hinders an analytical calculation of the DFT integrals. As such, numerical methods are used, and it is then important to ensure that the underlying grid is of sufficiently good quality.

Example: The VWN LDA-functional

The VWN correlation-functional of Vosko, Wilk, and Nusair,¹⁰² was fitted to quantum Monte Carlo calculations, and takes the general form⁷¹

$$\begin{aligned}\varepsilon_c^{\text{VWN}}(r_s, \zeta) &= \varepsilon_c(r_s, 0) + \varepsilon_a(r_s) \left[\frac{f_2(\zeta)}{f_2''(0)} \right] (1 - \zeta)^4 \\ &\quad + [\varepsilon_c(r_s, 1) - \varepsilon_c(r_s, 0)] f_2(\zeta) \zeta^4, \\ f_2(\zeta) &= \frac{f_1(\zeta) - 2}{2^{1/3} - 1}.\end{aligned}$$

The expressions for ε_c , ε_a , and f_1 are too cumbersome to be given here, but we note that even the most approximate functionals have a rather complicated analytical form, as well as a number of parameters which have been set by some means.

Generalized gradient approximation

In order to better account for varying electron density, the exchange-correlation functional should depend not only on the electron density, but also on its gradient,

$$E_{\text{xc}}^{\text{GGA}} = \int \rho(\mathbf{r}) \varepsilon_{\text{xc}}[\rho(\mathbf{r}), \nabla \rho(\mathbf{r})] d\mathbf{r}. \quad (2.38)$$

This is known as the generalized gradient approximation (GGA), and corrections to both the exchange and correlation functionals are available.

Example: The BLYP GGA-functional

The BLYP functional¹⁰³ combines the gradient-corrected exchange functional of Becke,¹⁰⁴ with the gradient-corrected functional of Lee, Wang, and Parr¹⁰⁵

$$\varepsilon_{\text{xc}}^{\text{BLYP}} = \varepsilon_{\text{x}}^{\text{B88}} + \varepsilon_{\text{c}}^{\text{LYP}},$$

with

$$\varepsilon_{\text{x}}^{\text{B88}} = \varepsilon_{\text{x}}^{\text{LDA}} - \beta \rho^{1/3} \frac{x^2}{1 + 6 \sinh^{-1} x}, \quad \text{where} \quad x = \frac{|\nabla \rho|}{\rho^{4/3}}.$$

This exchange-functional contains only a single parameter, obtained by fitting to exchange energies for noble gases.

The form of the gradient-corrected functional is too cumbersome to be repeated here, but we note that it contains four fitting parameters, determined for the helium atom.

Hybrid functionals

The functionals discussed so far have all been local, meaning that the exchange-correlation energy contribution depends only on the electron density at a specific point in space. In order to address additional effects, the most common approach is to adopt a hybrid approach, in which Hartree–Fock exchange energy, calculated for Kohn–Sham orbitals $\phi(\vec{r})$, contribute to varying degrees.

$$E_{xc}^{\text{hybrid}} = \int \rho(\mathbf{r}) \varepsilon_{xc}[\rho(\mathbf{r}), \nabla \rho(\mathbf{r})] d\mathbf{r} + \zeta E_x^{\text{exact}}. \quad (2.39)$$

This category contains the most frequently used functionals to date, of which the B3LYP functional^{106,107} is worth special mentioning due to its significant contributions to the field of theoretical chemistry. As stated in the beginning of our discussion on DFT, it is the go-to exchange-correlation functional, used for a multitude of different chemical questions.^{viii}

Example: The B3LYP hybrid functional

The B3LYP parameter is so named as it utilize three parameters fitted to replicate atomic properties, taking the form of

$$E_{xc}^{\text{B3LYP}} = E_x^{\text{VWN}} + a(E_x^{\text{HF}} - E_x^{\text{VWN}}) + b(E_x^{\text{B88}} - E_x^{\text{VWN}}) \\ + E_c^{\text{LDA}} + c(E_c^{\text{LYP}} - E_c^{\text{LDA}}),$$

with $a = 0.20$, $b = 0.72$, and $c = 0.81$.

Range-corrected functionals

While hybrid functionals are an improvement for the description of short-range electron-electron interactions, they typically exhibit difficulties in describing long-range interactions. This is notably the case for the calculation of transitions to Rydberg states, as well as charge-transfer transitions, and can be explained by the lack of long-range exchange interactions. In order to achieve this inclusion, more long-range exact exchange is required — however, if a global exact exchange parameter is corrected, short-range interactions will suffer instead. The solution to this conundrum is met by the use of Coulomb-attenuated, or range-separated, functionals, for which the amount of exact exchange depends on the interelectronic distance.

^{viii}However, it is typically not much of a problem to find individual functionals which performs better for some specific applications, but it can still be argued that it may be of benefit to use a well-known functional, as the performance of it is well investigated.

Example: The CAM-B3LYP range-corrected functional

For the CAM-B3LYP functional,¹⁰⁸ Yanai, Tew, and Handy proposed a partitioning of the electron-electron repulsion operator into short- and long-range components

$$\frac{1}{r_{12}} = \text{LR} + \text{SR} = \frac{[\alpha + \beta \text{erf}(\mu r_{12})]}{r_{12}} + \frac{1 - [\alpha + \beta \text{erf}(\mu r_{12})]}{r_{12}},$$

where $\text{erf}(\mu r_{12})$ is an error function with μ controlling the rate of attenuation. The parameters were fitted to charge transfer excitations and atomization energies, and amounts to $\alpha = 0.19$, $\beta = 0.46$, and $\mu = 0.33$ — in other words, the amount of short-range exact exchange is 19%, and in the asymptotic limit it becomes 65%.

Other families of functionals

In line with the improvement of the LDA functionals by including gradients, it is natural to further include higher-order derivatives of the electron density, or consider the kinetic energy density, thus formulating so-called meta-GGA:s. However, in many cases the main deficiency of exchange-correlation functionals are rather associated to difficulties in reliable emulating dispersion effects, as due to the lack of correct r^{-6} long-range limiting behaviour. The most common procedure to include such effects is by adding correction terms to the exchange-correlation energy,¹⁰⁹ which is then typically parameterized for every pair of atoms.

2.2.3 The self-interaction error in density functional theory

While there is no principal differences in considering either the valence or core densities in DFT, the use of approximate functionals introduce an error that is more important to account for when core electrons are addressed: the self-interaction error (SIE). This error is a result of spurious self-interactions for all electrons, but the larger density of the core orbitals makes it more influential for such a considerations — localized densities have larger self-repulsion than delocalized densities. For a single-electron systems the following equality should hold for the two-electron terms

$$J[\rho] + E_{\text{xc}}[\rho] = 0. \quad (2.40)$$

This cancellation is achieved for, *e.g.* Hartree–Fock theory, but for any approximate functionals in DFT it will instead result in an erroneous contribution to the energy. As the erroneous self-interaction occurs in terms of self-repulsion, this will lead to an increase in the energy of the orbital in question (*i.e.* the absolute value will decrease). The simplest correction to this error was proposed by Perdew and Zunger,¹¹⁰ by correcting the total exchange-correlation energy by a term

$$E^{\text{PZ}} = E^{\text{DFT}} - \sum_i (J[\rho_i] + E_{\text{xc}}[\rho_i]), \quad (2.41)$$

summed over all singly occupied orbitals. This correction improves the potential energy surfaces, but gives minor improvements for orbital energies. Several schemes of correcting the SIE also exist for correcting orbital energies,^{111–113} but none have been utilized in this thesis — we argue instead that the relative energies are most important and thus, in most cases, treat the SIE as a scalar element-dependent error to be accounted for. The SIE will be more thoroughly discussed in Section 5.2, but we here want to reiterate that the self-interaction depends strongly on the density of the orbital, and is thus most significant for core electrons of heavy elements.

2.3 Coupled cluster theory

In order to account for the dynamical correlation of the molecular system in a reliable, hierarchical way, one is well advised to turn to the realm of coupled cluster (CC) theory. This methodology contains some of the most accurate electronic structure computational schemes available to date, and address correlation effects by means of virtual excitations from a reference wave function, yielding a set of models by which the exact wave function can be approached. This section will briefly discuss the basic principles of CC theory, as well as manners by which approximate CC methods, developed with response calculations in mind, can be constructed — for more details on the theory, see *e.g.* Refs. [68, 70, 71].

2.3.1 The exponential *ansatz*

The whole is more than the sum of its parts.

Aristotle¹¹⁴

In the CC approach dynamic correlation effects are accounted for by means of excitations to unoccupied (virtual) orbitals, using an excitation operator

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_N, \quad (2.42)$$

for a system of N electrons. The separate $\hat{T}_i$ designates excitation operators that simultaneously excite i electrons from occupied to unoccupied orbitals. For example, the effects of the single and double excitation operators are given as

$$\hat{T}_1 |\Psi_0\rangle = \sum_i^{\text{occ}} \sum_a^{\text{virt}} t_i^a \hat{\tau}_i^a |\Psi_0\rangle = \sum_i^{\text{occ}} \sum_a^{\text{virt}} t_i^a |\Psi_i^a\rangle, \quad (2.43)$$

$$\hat{T}_2 |\Psi_0\rangle = \sum_{i>j}^{\text{occ}} \sum_{a>b}^{\text{virt}} t_{ij}^{ab} \hat{\tau}_{ij}^{ab} |\Psi_0\rangle = \sum_{i>j}^{\text{occ}} \sum_{a>b}^{\text{virt}} t_{ij}^{ab} |\Psi_{ij}^{ab}\rangle, \quad (2.44)$$

where t_i^a and t_{ij}^{ab} are the expansion coefficients, known also as coupled cluster amplitudes, and $\hat{\tau}_i^a$ and $\hat{\tau}_{ij}^{ab}$ are the explicit excitation operators, most succinctly expressed using second quantization. To avoid double-counting we impose the conditions of $i > j$ (occupied orbitals) and $a > b$ (unoccupied orbitals) in Eq. (2.44).

Using the excitation operator, the CC wave function is constructed by the use of the exponential *ansatz*, where an exponential operator is allowed to operate on a reference wave function

$$|\text{CC}\rangle = e^{\hat{T}} |\Psi_0\rangle = e^{\hat{T}} |0\rangle. \quad (2.45)$$

The reference wave function is usually in the form of a single Slater determinant, corresponding to the HF wave function for the system.^{ix} In this case the reference state is static and the system considered is more accurately described if it is dominated by a single electronic configuration (*i.e.* weak static correlation).¹¹⁵

So far, this approach can be considered as a non-linear alternative to the configuration interaction (CI) approach, the latter in which a sum of excitation operators of different orders is used. In fact, if the full excitation space is spanned, as is done in Eq. (2.42), both CI and CC will give the same result — the full CI wave function — which corresponds to the highest level of theory on the N -particle axis of Fig. 2.1. Unfortunately, as previously discussed, this is computationally feasible only for very small systems and a truncation is thus employed in most applications, giving a hierarchical approach towards the exact solution. The level of this truncation determines the model in the hierarchy of CC methods: including only single excitations yields coupled cluster singles (CCS), including both single and double excitations yields coupled cluster singles and doubles (CCSD),¹¹⁶ and so on. For practical purposes the inclusion of triple excitations are generally too demanding, and such effects can instead be introduced in an approximate manner by perturbation theory.^{68, 71}

Expanding the exponential operator yields

$$\begin{aligned} e^{\hat{T}} &= 1 + \hat{T} + \frac{1}{2}\hat{T}^2 + \dots \\ &= 1 + \hat{T}_1 + \left(\hat{T}_2 + \frac{1}{2}\hat{T}_1^2\right) + \left(\hat{T}_3 + \hat{T}_2\hat{T}_1 + \frac{1}{6}\hat{T}_1^3\right) + \dots \end{aligned} \quad (2.46)$$

reordered such that the first term gives the reference state, the second all singly excited states, the third all doubly excited states, and so on.

With this reordering, it is clear that the excited states of a higher order includes simultaneous excitations of lower order. As an example, the doubly excited states includes not only the connected double excitations $\hat{T}_2$, but also the disconnected simultaneous single excitations $\hat{T}_1^2$. This results in coupled cluster being size-extensive, *i.e.*, it yields consistent results for arbitrary numbers of non-interacting molecules. By comparison, the expansion of CI, while being less complicated, does not give the same result for two molecules in isolation as when separated in space by a large distance. Further, disconnected excitations may be most important for higher-order excitations, with, *e.g.*, the $\hat{T}_2^2$ terms being more important for quadruple excitations than $\hat{T}_4$, so the system can be well described when truncated to only a few terms.^{116, 117}

^{ix}Other reference wave functions, including using several determinants, are possible, but we will here focus on the case of a HF reference.

The coupled cluster ground state can in principle be solved by using the variational principle, *i.e.*

$$E_{\text{CC}} = \frac{\langle \text{CC} | \hat{H} | \text{CC} \rangle}{\langle \text{CC} | \text{CC} \rangle} = \frac{\langle \Psi_0 | [e^{\hat{T}}]^\dagger \hat{H} e^{\hat{T}} | \Psi_0 \rangle}{\langle \Psi_0 | [e^{\hat{T}}]^\dagger e^{\hat{T}} | \Psi_0 \rangle}. \quad (2.47)$$

However, this is only feasible for small systems due to the non-linear nature of the CC ansatz — the computational cost of solving this variational problem is of the same order regardless of the level of truncation, thus making it as expensive as full CI.⁷⁰ The procedure by which CC is more commonly considered is by projecting the Schrödinger equation onto a HF state $|0\rangle$ and a manifold of excited states

$$\hat{\tau}_n |0\rangle = |n\rangle. \quad (2.48)$$

This manifold consists of all single excited states for CCS, all single and double excited states for CCSD and so on.

For convenience, we choose to multiply the time-independent Schrödinger equation by the exponential operator $e^{-\hat{T}}$ from the left, resulting in what can be regarded as an effective, non-Hermitian Hamiltonian

$$\hat{H}_T = e^{-\hat{T}} \hat{H} e^{\hat{T}}, \quad (2.49)$$

called the similarity-transformed Hamiltonian. The Schrödinger equation becomes

$$\hat{H}_T |0\rangle = E |0\rangle. \quad (2.50)$$

By projection onto the HF state and the manifold of excited states this yields

$$\langle 0 | \hat{H}_T | 0 \rangle = E, \quad (2.51)$$

$$\langle n | \hat{H}_T | 0 \rangle = 0, \quad (2.52)$$

which corresponds to the CC equations and can be solved for the CC ground state energy and amplitudes. Further, from Eq. (2.51) it can be shown that

$$\langle 0 | e^{-\hat{T}} = \langle 0 |, \quad (2.53)$$

as all excitation operators here attempts to de-excite a reference ground state and thus do not contribute. If the reference state used is an optimized HF state, it can be shown that one-particle excitation operators do not contribute to the electronic energy in a connected manner, by virtue of Brillouin's theorem⁶⁸

$$\langle 0 | \hat{H} \hat{T}_1 | 0 \rangle = 0. \quad (2.54)$$

Using Eqs. (2.46), (2.51), (2.53), and (2.54), and the fact that the Hamiltonian is a two-particle operator, the CC energy expression is thus simplified as

$$\begin{aligned} E &= \langle 0 | \hat{H} \left(1 + \hat{T} + \frac{1}{2} \hat{T}^2 + \dots \right) | 0 \rangle \\ &= \langle 0 | \hat{H} \left(1 + \hat{T}_2 + \frac{1}{2} \hat{T}_1^2 \right) | 0 \rangle, \end{aligned} \quad (2.55)$$

as the higher-order excitation operators yields states that are orthogonal to the reference state. The energy of a CC method thus depends explicitly on only the single and double excitations, while higher-order excitations contribute indirectly in the coupling of amplitudes, as given by Eq. (2.52).

2.3.2 Approximate coupled cluster methods

As discussed in connection to Eq. (2.42), considering all possible excitations is computationally unviable for most systems, and some way of decreasing the size of the excitation manifold needs to be employed. The most direct way of doing this has already been discussed, *i.e.*, truncating the excitation operator to certain order, but for the inclusion of higher-order excitation this may still be too demanding, with *e.g.* CCSDT scaling as m^8 (m being the number of basis functions). A major topic in CC theory is thus the development of methods by which approximate higher-order excitations can be included at a lower computational cost, and the work presented in this thesis has utilized two such methods: the approximate methods for inclusion of double excitations CC2¹¹⁸ and triple excitations CCSDR(3),¹¹⁹ both developed for the calculation of molecular properties.

The CC2 method utilizes perturbation theory to determine the order of contribution from the different excitations. For the CCSD ground state energy, the excited state manifold can be separated into a single excited and a double excited manifold, resulting in

$$0 = \langle n_1 | \hat{H}_T + [\hat{H}_T, \hat{T}_2] | 0 \rangle, \quad (2.56)$$

$$0 = \langle n_2 | \hat{H}_T + [\hat{H}_T, \hat{T}_2] + \frac{1}{2} [[\hat{H}_T, \hat{T}_2], \hat{T}_2] | 0 \rangle. \quad (2.57)$$

where the Baker–Campbell–Hausdorff expansion has been employed.⁶⁸ For CC2, the double excitation manifold is restricted to include only contributions of non-vanishing order, resulting in amplitude equations

$$0 = \langle n_1 | \hat{H}_T + [\hat{H}_T, \hat{T}_2] | 0 \rangle, \quad (2.58)$$

$$0 = \langle n_2 | \hat{H}_T + [\hat{H}_T, \hat{T}_2] | 0 \rangle. \quad (2.59)$$

What is obtained is a subset of the CCSD equations, solved iteratively with a scaling of m^5 . An analogous approach can be used for CCSDT, yielding the CC3 method,¹²⁰ which instead scale as m^7 and thus remains highly computationally demanding. Instead, it is possible to define a perturbative correction to the CCSD excitation energies that is of same order of accuracy as CC3, but at a lower computational cost. This is done by the CCSDR(3) method, which is a non-iterative correction to CCSD eigenvectors that incorporates lowest order triple corrections.

With a perturbative theoretical treatment it is possible to determine the order to which these approaches are correct for, *e.g.*, ground state and property calculations.¹²¹ Such order analysis is given in Table 2.1 for the ground state and some excitation energies along with the full scaling of the different methods, save for CCSDR(3). In terms of relative performance, benchmark studies on valence

excitations have shown that CCSDR(3) gives results close to those obtained by CC3,¹²² and is thus a cost-efficient alternative. Further, basis set effects on CC2 and CCSDR(3) seem to be similar,¹²³ and CC2 may perform better than CCSD for certain systems.¹²⁴

Table 2.1. Perturbative theoretical analysis of the order to which a selection of coupled cluster methods are correct for calculation of ground state energies (E_0), single and double electron excitation energies (S and D, respectively), as well as the scaling of the methods.

Method	E_0	E_s	E_D	Scaling
CCS	1	1	-	m^4
CC2	2	2	0	m^5
CCSD	3	2	1	m^6
CC3	4	3	2	m^7
CCSDT	4	4	2	m^8

2.4 Illustrations of concepts

We expect that the MP2/aug-cc-pVTZ results are not far from being close to the CBS limit.

S. Osuna *et al.*, 2009¹²⁵

We will now illustrate the concepts discussed in this chapter by explicitly studying valence excitations, core excitations, orbital energies, and relativistic effects. Special focus will be dedicated to the three-dimensional model presented in Fig. 2.1, and hopefully we will be able to see how we reach conclusions more definitive than the above subjective “not far from being close to”. Some of the results presented here utilize response theory, as will be described in the next chapter.

2.4.1 Approaching the correct transition energies of ethene

In reference to the three-dimensional illustration of theoretical models in Fig. 2.1, we consider the $\pi \rightarrow \pi^*$ and $1s \rightarrow \pi^*$ transition energies of ethene, as obtained using a number of different electronic structure methods, basis sets, and Hamiltonians. These properties are considered using the equilibrium structure,^x *i.e.* considering vertical transition energies, as all other results presented in this thesis. Reference $\pi \rightarrow \pi^*$ vertical transition energy has been reported at 8.0 eV, even while the maximum of the band is situated at 7.66 eV,^{127,128} and the $\pi \rightarrow \pi^*$ excitation energies are compared to experimental $\lambda_{\max}$.¹²⁹

^xAs calculated at a B3LYP/cc-pVTZ level of theory using the Gaussian¹²⁶ program. All molecular structures used in this thesis have been obtained in this manner, unless otherwise stated.

$\pi \rightarrow \pi^*$ [eV]

Ref. 8.0 eV

$1s \rightarrow \pi^*$ [eV]

Ref. 284.7 eV

Figure 2.3. Excitation energies of ethene, as obtained using a plethora of electronic structure methods, basis sets, and Hamiltonians. Color coded according to accuracy to reference values, as obtained from computational studies for $\pi \rightarrow \pi^*$,^{127, 128} and from experiment for $1s \rightarrow \pi^*$.¹²⁹ Basis set designation indicates set for carbon, while hydrogen is given the basic basis set at the corresponding level (*i.e.* cc-pVDZ or cc-pVTZ). TDHF, TDDFT, and valence CC transition energies obtained using standard linear response theory, with the SCF core excitation results obtained with restrictions in the excitations channels. CC core excitation results obtained using the Lanczos method, at a chain length of $J = 5000$ and 2000 for the double- and triple- ζ results, respectively.

For the one-particle description, Dunning’s basis sets¹³⁰ at a double- and triple- ζ level have been utilized, as augmented with additional sets of diffuse functions in order to improve the description of delocalized states,⁷⁶ as well as core-polarizing functions to improve the description of the core.¹³¹ The N -particle description has been evaluated by expanding the coupled cluster manifold, as well as by choosing more sophisticated exchange-correlation functionals on Jacob’s ladder to improve the electron density. For the time-dependent Hartree–Fock (TDHF) and time-dependent density functional theory (TDDFT) calculations results have been obtained using a non-relativistic,¹³² scalar relativistic,¹³³ and fully relativistic^{xi} Hamiltonian, as available in the Dirac program.¹³⁴ The CC results have been obtained using the Dalton program,¹³⁵ in which non-relativistic and scalar relativistic^{136,137} Hamiltonians are available.

The transition energies are illustrated in Fig. 2.3, color coded for easy of interpretation. It is immediately noted that the accuracy of the theoretical valence transition energies are far better than those of the core transitions, especially for TDHF and TDDFT. This is related to difficulties due to lack of relaxation and self-interaction errors, as will be discussed in later sections. Considering the $\pi \rightarrow \pi^*$ excitations, TDHF yields excellent agreement in energy for the smallest basis set, but the result deteriorates when the basis set is expanded. Similar effects are also seen for TDDFT, where especially the results using the LDA exchange-correlation functional (VWN), is reasonable for the smallest double- ζ level but then quickly becomes significantly worse. The assignment of spectral features for this functional is difficult, as will be seen later, and it should clearly be avoided for these properties. This is not particularly surprising, seeing that it is built on the assumption of an electron gas, which is a bad approximation for a molecular system. The remaining TDDFT results are of similar quality, with the pure hybrid performing slightly worse. In contrast, the coupled cluster results improve with each expansion of the basis set, clearly illustrating the need of a more flexible basis set for this approach. The final CC3 results are in excellent agreement to the reference value, underestimating the transition energy by 0.01 eV. Relativistic effect are observed to be negligible for this property, as the π electrons are very weakly affected by relativity.

For the core excitations, the discrepancies are quite significant, with TDHF overestimating the excitation energy by approximately 10 eV — this is related not only to the lack of electron correlation, but more importantly due to a lack of relaxation, as will be discussed in Section 4.1. Introducing virtual excitations, the CC method improve greatly the transition energies, converging to within 1.5 eV of experimental measurements. For these results, basis set effects are once again significant, and the relativistic effects experienced by the core electrons gives energy corrections of approximately 0.1 eV, as captured already using scalar relativistic Hamiltonians. Here it is also interesting to note that the final improvement of the

^{xi}We remind the reader that the Dirac–Coulomb Hamiltonian, as is used here, is in principle not fully relativistic, as it is not Lorentz-invariant. Further, in order to decrease computational costs, (SS|SS) integrals are here replaced by parameterized energy corrections.⁸⁴ However, these two approximations should have negligible influence, and we will continue describing these calculations as “fully relativistic”, for simplicity.

basis set for CCSD yields results in worse agreement to experiments than the level below. This merely implies that the daug-cc-pVTZ basis set is not yet near saturation. As for TDDFT, energetics are far underestimated, amounting to ~ 50 eV for the LDA and 10–15 eV for the more advanced functionals. This is due to the self-interaction error discussed in Section 2.2.3 — however, we will later argue that the *relative* energies are more important than the *absolute* energies, and we thus deem it to be appropriate to use well tested functionals, even if the absolute error is significant.

In conclusion, we see that coupled cluster gives good results for all both properties investigated here, but large basis sets are typically required. Using a more approximate electronic structure method — *i.e.* TDHF or TDDFT with approximate exchange-correlation functionals — the obtained results are more erratic, illustrating the need for benchmarking DFT methods with experimental or *ab initio* wave function results (as has been done in Papers [III-IV]). In accordance with the three-dimensional model of quantum chemical methods, the basis set requirements of these less accurate methods are less demanding. For the properties investigated here, relativistic effects are not very significant, amounting to a correction of 0.02–0.03% in relative energetics, well accounted for using a scalar relativistic Hamiltonian.

2.4.2 Relativistic effects on orbital energies

Considering instead the orbital energies of neon, the effects of inclusions of relativity can be studied for the different orbitals. Additionally, results can be compared to exact analytical calculations on hydrogen-like systems, which will later be used as a simple tool for analysis.

The HF orbital energies (which approximate the electron binding energies in accordance to Koopmans’ theorem) are reported in Fig. 2.4. For 1s the relativistic effects leads to a contraction of the orbital, decreasing the energy by 1.23 eV. This effect is well accounted for using the scalar relativistic Hamiltonian, for which the resulting energy agrees with that of the relativistic calculation to within 0.001 eV. This relativistic contraction can most easily be conceptualized as arising due to the increase in relativistic mass^{xii}

$$m = m_0 \left(\sqrt{1 - \frac{v^2}{c^2}} \right)^{-1}, \quad (2.60)$$

which yields $m/m_0 = 1.002$ for the fully relativistic 1s orbital energy, as can be compared to $E_{1s,REL}/E_{1s,NR} = 1.001$. These results can further be compared to the relativistic correction (term three) in the energy expression for a hydrogenic system in Eq. (2.63), which amounts to 0.07 eV — it is clear that the approximation of a hydrogenic system is insufficient, as could be expected, with a binding energy

^{xii}The concept of relativistic mass has in some cases been criticized, with some authors avoiding it all together, preferring instead to discuss relativistic momentum. For the purposes of this thesis this distinction is largely a matter of semantics, and we will use the term relativistic mass, for simplicity.

of 1362 eV, as compared to the 893 eV for the relativistic HF calculation. Also the 2s orbital is contracted, although to a smaller degree, with an increase in energy of 0.15 eV.

Example: Hydrogenic atoms

For a hydrogenic system, *i.e.* an atom with a single electron, the Schrödinger equation can be solved exactly, with the resulting (non-relativistic) wave function given in Eq. (2.8). For a 1s electron, the radial part of this equation becomes

$$\Psi_r(r) = 2Z^{3/2}e^{-Zr}. \quad (2.61)$$

Focusing on the energy, the relativistic expression is given as⁷⁰

$$E = \frac{mc^2}{\sqrt{1 + \left(\frac{Z/c}{n-j-1/2 + \sqrt{(j+1/2)^2 - Z^2/c^2}} \right)^2}}, \quad (2.62)$$

for an orbital with principal quantum number n and total angular momentum quantum number $j = |l \pm s|$. This is a somewhat cumbersome expression, but by expanding in terms of Z/c

$$E = mc^2 - \frac{Z^2}{2n^2} + \frac{Z^4}{2n^4c^2} \left(\frac{3}{4} - \frac{n}{j+1/2} \right) + \mathcal{O}\left(\frac{Z^6}{c^4}\right), \quad (2.63)$$

we can identify the first term as the rest mass of the electron, and the second term is the standard non-relativistic binding energy. Higher-order terms give the relativistic corrections for the binding energy.

In a relativistic setting the spin-orbit coupling ensures that l and s no longer are good quantum numbers. Instead, the total angular momentum is given as

$$j = |l \pm s|, \quad (2.64)$$

which is projected according to

$$m_j = -j, (-j+1), \dots, (j-1), +j. \quad (2.65)$$

For the 2p orbitals this leads to $2p_{1/2}$ and $2p_{3/2}$, with corresponding projected total angular momentum

$$2p_{1/2} : \quad m_j = -1/2, 1/2, \quad (2.66)$$

$$2p_{3/2} : \quad m_j = -3/2, -1/2, 1/2, 3/2. \quad (2.67)$$

As such, the $2p_{1/2}$ orbitals are populated by two electrons and $2p_{3/2}$ by four electrons, and the degeneracy of the non-relativistic 2p orbital is now broken. As such, scalar relativistic effects only change the energies of the degenerate states, and for neon they are increased by 0.02 eV due to an increased screening from the more compact 1s and 2s orbitals. However, using a relativistic Hamiltonian which

Figure 2.4. Orbital energies of neon, as obtained at a Hartree–Fock/decontracted cc-pVQZ level of theory, using non-relativistic (NR), scalar relativistic (SR), and relativistic (REL) Hamiltonians.

includes spin-orbit effects, the degeneracy is lifted, with $2p_{1/2}$ lower in energy due to the stabilization from the anti-alignment of the (classical) angular momentum and spin momentum.

2.4.3 Relativistic effects on valence properties

Finally, we consider the effects of relativity on valence properties of metal-substituted porphyrins. This is discussed in more details in Paper [IV], and we will here briefly present the main findings. Importantly, relativity has two main distinct effects, both of which have been touched upon: the scalar relativistic effects affecting the stability of orbitals, and spin-orbit effects. The latter has been discussed in terms of the broken degeneracy of the $2p$ orbitals, and now the different electronic decay channels will be added to the discussion.

When an electron is excited it typically keep the spin from the original spin-orbital and the molecule thus retains the spin-state it originally has — in a non-relativistic setting any changes in spin-state are forbidden, unless some *ad hoc*-like correction is imposed. As this excited singlet state relax, it can decay back to the original state by photoemission, yielding fluorescence. These events are typically very fast, and can be used for, for example, black-lights. Through spin-orbit

interactions it is possible for the excited electron to either change the spin, the molecule thus being excited to a triplet state, or decay back through such a triplet states. If the latter case results in photoemission, phosphorescence is the result, which is typically a relatively slow process, owing to the weak^{xiii} coupling between the singlet and triplet states. This can be used, for instance, on clock dials for a wrist-watch.^{xiv}

In order to study the strength of the singlet-triplet coupling, or the lifetime of the triplet excited states, it is possible to either use linear response theory with magnetic interactions included in the zeroth-order Hamiltonian, or use cubic response theory. In Paper [IV] we advocate the former, and obtained transition energies and lifetimes reported in Table 2.2. For a discussion on the phosphorescence parameters we refer to the paper, but we note here that the addition of heavy elements decrease the phosphorescence lifetimes by several orders of magnitude, as expected.

Table 2.2. Phosphorescence energies and lifetimes of free-base and metal-substituted porphyrins.

Molecule	Method	Energy [eV]	Lifetime [s]
H ₂ P	PBE0/6-31G	1.30	262.8
	B3LYP/6-31G	1.44	167.2
	B3LYP/aug-cc-pVDZ	1.47	968.7
	B3LYP/aug-cc-pVTZ	1.46	459.9
	Expt ¹³⁸	1.56	130
	Expt ¹³⁹		>70
	Expt ¹⁴⁰		<i>circa</i> 500
ZnP	PBE0/6-31G	1.35	14.8
	B3LYP/6-31G	1.45	8.31
	B3LYP/aug-cc-pVDZ	1.50	13.8
	Expt ^{141, 142}	1.82	< 10
CdP	PBE0/6-31G	1.23	8.25
	B3LYP/6-31G	1.34	5.17
	B3LYP/aug-cc-pVDZ	1.38	11.2
HgP	PBE0/6-31G	0.80	0.0380
	B3LYP/6-31G	0.80	0.0294
	B3LYP/aug-cc-pVDZ	0.89	0.0155

In terms of UV/vis absorption, Fig. 2.5 report the theoretical spectra for H₂P, ZnP, CdP, and HgP, with comparison to experimental measurements on H₂P. The main difference in spectral features occur when substituting with a metal, with minor changes in spectral features between the different substitution. Now, focusing on the density of states, the coloured circles on the bottom of the spectra indicates one or more possible transition(s), and we see that this density of states is relatively high for the systems in consideration. For HgP, it has been demonstrated that totally 43 states need to be resolved before the intense so-called Soret band

^{xiii}In non-relativistic theory non-existent.

^{xiv}Which does seem like a superiour alternative to the old technique of painting the dials with radioactive material.

can be addressed, and for larger molecular system this will be problematic to resolve using bottom-up approaches. This number can be reduced to 33 if only dipole-allowed transitions are considered, or all the way down to 4 if only singlet transitions are allowed. In other words, if non-relativistic spectra are sought, a bottom-up approach will work very well indeed, but if spin-orbit effects are to be accounted for there will be problems in considering large molecular systems. By comparison, damped linear response theory can address any frequency region of interest, and a high density of states affects mainly the convergence rate.

Figure 2.5. UV/vis spectra of free-base porphyrin, Zn-porphyrin, Cd-porphyrin, and Hg-porphyrin, as obtained using a relativistic Dirac–Coulomb Hamiltonian with (SS|SS) integrals neglected and replaced by interatomic SS energy corrections,⁸⁴ and compared against experiment.¹⁴³ Coloured circles indicate the position of resonances, separating the dipole symmetry-allowed (black) and dipole symmetry-disallowed (red) states. Vertical line in the panel with experimental measurement indicates the visible region (400–700 nm).

CHAPTER 3

Molecular response theory

Because the theory of quantum mechanics could explain all of chemistry and the various properties of substances, it was a tremendous success. But still there was the problem of the interaction of light and matter.

R.P. Feynman, 1985¹⁴⁴

In the field of theoretical spectroscopy, response theory offers a framework general enough to be used for a plethora of different spectroscopies, seemingly too different in nature to be treated on common grounds. In this approach, the molecular properties, which describe the interaction of the molecule with an internal or external perturbation, are determined as the response of the electronic wave function (or electron density), using time-dependent perturbation theory. For the purposes of this thesis, the perturbation will from this point on be assumed to be external.

In this chapter, we will discuss the fundamentals of response theory for exact states and determine the linear response function that is the key property needed for the calculation of X-ray absorption and non-resonant X-ray emission spectra. We then continue with the derivation of the time-dependent DFT and damped coupled cluster linear response functions, and discuss the solution of these functions using three different computational schemes. Finally, the limits of response theory in which the approach breaks down are discussed.

A general discussion on response theory can be found in the book of Norman, Saue, and Ruud,¹⁴⁵ and for a thorough investigation on the current status on (wave function-based) response theory, the comprehensive work of Helgaker *et al.*¹⁴⁶ is recommended, in which an extensive reference list can guide the Reader to details concerning any molecular properties of interest. The historical perspective can be found elsewhere,¹⁴⁷ but it can be pointed out that the modern formulation of response theory owes much to the seminal works of Olsen and Jørgensen,¹⁴⁸ who applied the Ehrenfest theorem on Hartree–Fock and multi-

configurational self-consistent field wave functions and achieved response functions free from secular divergences.

3.1 Exact state response theory

First, consider the case of exact state response theory, where the exact eigenstates of the Hamiltonian of the unperturbed system is known. For this case, we discuss the general determination of molecular properties and the damped formulation of response theory using which it is possible to address external perturbations exciting the molecular system to some excited state.

3.1.1 General response theory

Mathematics is the cheapest science. Unlike physics or chemistry, it does not require any expensive equipment. All one needs for mathematics is a pencil and paper.

G. Pólya¹⁴⁹

When an external field is applied to a molecular system the system interacts with this field and responds to the applied perturbation. If such field is of sufficiently small field strength, *i.e.* sufficiently small intensity, we can address the response using perturbation theory with the perturbed Hamiltonianⁱ

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t), \quad (3.1)$$

where $\hat{H}_0$ is the unperturbed Hamiltonian and $\hat{V}(t)$ is a homogeneous, external field.¹⁵⁰ⁱⁱ The requirement of a weak perturbation is met for most externally applied fields — for example, a conventional laser with an intensity of 0.3 GW/cm³ corresponds to an electric field amplitude of $\sim 5 \times 10^{-5}$ a.u., which indeed has a small influence on a molecular system.¹⁴⁵

If the perturbing field is taken as a static field, *i.e.* $\hat{V}(t) = \hat{V}_\alpha F_\alpha$ for a field direction α , the problem is reduced to the time-independent case. The time-independent Schrödinger equation can then be utilized in order to obtain ground and excited state energies that are well-defined. The energy of the static case can be considered with a Taylor expansion at zero perturbing field strength

$$E = E_0 + \left. \frac{\partial E}{\partial F_\alpha} \right|_{F_\alpha=0} F_\alpha + \frac{1}{2} \left. \frac{\partial^2 E}{\partial F_\alpha \partial F_\beta} \right|_{F_\alpha=F_\beta=0} F_\alpha F_\beta + \dots, \quad (3.2)$$

with implied summation over indices. Molecular properties are now identified as field derivatives of different orders and different perturbing fields, as the observables associated with the properties changes according to these derivatives. For example, the polarizability may be obtained through the second derivative of the

ⁱNote that the approach described here is semi-classical, with a quantum description of the molecular system but a classical description of the perturbing field. Any more accurate descriptions lies in the field of quantum field theory, which is beyond the scope of this Thesis.

ⁱⁱInhomogeneous external fields will be discussed in Section 3.5.3.

energy with respect to a perturbing electric field, while the first derivative corresponds to the permanent dipole moment, both at zero field strength.

Unfortunately, this approach is not viable for time-dependent perturbations, *e.g.* probing with radiation, as the interaction between the field and the molecular system yields ill-defined energies due to exchange of energy between the field and the molecule. Here we move instead to a slightly different approach, remembering the identification of molecular properties as field derivatives, starting by choosing a perturbation operator as

$$\hat{V}(t) = \sum_{\omega} \hat{V}_{\alpha}^{\omega} F_{\alpha}^{\omega} e^{-i\omega t} e^{\varepsilon t}, \quad (3.3)$$

where F_{α}^{ω} is the Fourier amplitude of the field along a molecular axis α , we adopt implied summation over this index. A small, positive ε gives the adiabatical switch-on as $t \rightarrow -\infty$, while ensuring that the last term differs negligible from unity at times close to $t = 0$ (*i.e.* present time). This condition is imposed to ensure that the system resided in the ground state at a time long past, sufficiently long ago so that all memory of the switch-on process is lost. The summation is understood to be over both positive and negative frequencies, and due to the real nature of the perturbation we have $F_{\alpha}^{-\omega} = [F_{\alpha}^{\omega}]^*$ and $\hat{V}_{\alpha}^{-\omega} = [\hat{V}_{\alpha}^{\omega}]^{\dagger} = \hat{V}_{\alpha}^{\omega}$.

The time-dependent molecular properties can now be defined through the time-dependent expectation value of an observable, associated with an operator $\hat{\Omega}$. We first expand the wave function in orders of the perturbation

$$|\psi(t)\rangle = |\psi^{(0)}\rangle + |\psi^{(1)}\rangle + |\psi^{(2)}\rangle + \dots, \quad (3.4)$$

noting that this wave function is to be normalized at all times. Now, the expectation value of the operator is expanded as

$$\begin{aligned} \langle \psi(t) | \hat{\Omega} | \psi(t) \rangle &= \langle \psi^{(0)} | \hat{\Omega} | \psi^{(0)} \rangle \\ &+ \langle \psi^{(1)} | \hat{\Omega} | \psi^{(0)} \rangle + \langle \psi^{(0)} | \hat{\Omega} | \psi^{(1)} \rangle \\ &+ \langle \psi^{(2)} | \hat{\Omega} | \psi^{(0)} \rangle + \langle \psi^{(1)} | \hat{\Omega} | \psi^{(1)} \rangle + \langle \psi^{(0)} | \hat{\Omega} | \psi^{(2)} \rangle \\ &+ \dots, \end{aligned} \quad (3.5)$$

rewritten for simplicity as

$$\langle \psi(t) | \hat{\Omega} | \psi(t) \rangle = \langle \hat{\Omega}^{(0)} \rangle + \langle \hat{\Omega}^{(1)} \rangle + \langle \hat{\Omega}^{(2)} \rangle + \dots, \quad (3.6)$$

where the different terms at the right-hand-side are again understood as the correction of the expectation value of a given order. By use of the perturbation operator

in Eq. (3.3), the expansion is written asⁱⁱⁱ

$$\begin{aligned}
 \langle \psi(t) | \hat{\Omega} | \psi(t) \rangle &= \langle 0 | \hat{\Omega} | 0 \rangle \\
 &+ \sum_{\omega_1} \langle \langle \hat{\Omega}; \hat{V}_{\beta}^{\omega_1} \rangle \rangle F_{\beta}^{\omega_1} e^{-i\omega_1 t} e^{\varepsilon t} \\
 &+ \frac{1}{2} \sum_{\omega_1 \omega_2} \langle \langle \hat{\Omega}; \hat{V}_{\beta}^{\omega_1}, \hat{V}_{\gamma}^{\omega_2} \rangle \rangle F_{\beta}^{\omega_1} F_{\gamma}^{\omega_2} e^{-i(\omega_1 + \omega_2)t} e^{2\varepsilon t} \\
 &+ \dots,
 \end{aligned} \tag{3.7}$$

explicitly giving the expressions for the first-, second- and third-order properties. The term $\langle \langle \hat{\Omega}; \hat{V}_{\beta}^{\omega_1} \rangle \rangle$ in the second-order property is referred to the linear response function, collecting all expectation values that are linear in order of the perturbation. In an analogous manner, $\langle \langle \hat{\Omega}; \hat{V}_{\beta}^{\omega_1}, \hat{V}_{\gamma}^{\omega_2} \rangle \rangle$ collects all first-order non-linear terms and are thus designated as the first-order non-linear response function (but second-order response function), and so on for higher-order terms.

3.1.2 Damped linear response theory

Determining the explicit expressions for the linear and non-linear response functions can be done in several different manners, the most common being using either the Ehrenfest expectation value of the quasi-energy derivative formulation — in the former the corrections of the wave function at different orders in the perturbation are collected and used to identify different orders of molecular properties, and the latter is used to identify properties as derivatives of the quasi-energy.^{151, 152} Here, we will instead focus on an approach employing the Liouville equation, but some aspects of the quasi-energy formalism will be considered in Section 3.2 in order to facilitate our discussion of coupled cluster response theory.

Before moving to the derivation of the linear response function, there is a yet unaddressed issue of resonance frequencies in the external, perturbing field. As will be demonstrated in this section, the standard formulation of response theory suffers from divergences at resonance frequencies, due to singularities in the response equations. In order to obtain resonance-convergent expressions, we instead move to a damped formulation of response theory, by which the divergences can be accounted for, if we first consider the ways by which the molecular system relaxes and experience de-excitations.

In the absence of any external interactions (external fields, other molecules, *etc.*) an excited state will eventually relax into the ground state — the excited state has a finite lifetime and experiences spontaneous relaxation. If the system is allowed to interact with other molecules, *e.g.* by collisions, the lifetime may be lowered as the system can be relaxed through radiative and non-radiative relaxation channels. A (weak) perturbing field affecting a ground state, on the other hand, can both influence the population of the different states of the system by absorption and stimulated emission. Accounting for all these effects, the decay rates of the excited states will be such that the population of the excited states remains

ⁱⁱⁱAgain, note that we use implied summation, for brevity.

small and is thus possible to apply perturbation theory on the system. However, incorporating these relaxation effects directly into the Schrödinger equation is not easily done, and the effects will instead be incorporated in a phenomenological manner.

A formalism suitable for this task is the density matrix formalism. Introducing the density operator

$$\hat{\rho} = \sum_s p(s) |\psi_s(t)\rangle \langle \psi_s(t)|, \quad (3.8)$$

for the statistical ensemble of system configurations s with corresponding probabilities $p(s)$. For simplicity, let us consider ensembles that can be described by a single wave function, *i.e.* pure states, and a wave function expansion in form of projections:

$$|\psi_s(t)\rangle = \sum_n c_n^s(t) |n\rangle, \quad (3.9)$$

for which the matrix elements of the density operator are expressed as

$$\rho_{mn} = \sum_s p(s) c_m^s c_n^{s*}. \quad (3.10)$$

With the Schrödinger equation (2.1) for bra- and ket-vectors, it is easy to show that the equation of motion for the density operator can be written as

$$\frac{\partial}{\partial t} \hat{\rho} = \frac{1}{i\hbar} [\hat{H}, \hat{\rho}]. \quad (3.11)$$

This equation is known as the Liouville equation. It can easily be modified to, phenomenologically, include relaxations of the system. For a matrix element of the density operator, this modification is made such that the Liouville equation becomes the damped counterpart

$$\frac{\partial}{\partial t} \rho_{mn} = \frac{1}{i\hbar} [\hat{H}, \hat{\rho}]_{mn} - \gamma_{mn} (\rho_{mn} - \rho_{mn}^{\text{eq}}), \quad (3.12)$$

where the damping term γ_{mn} corresponds to the rate of ρ_{mn} decaying into the equilibrium value ρ_{mn}^{eq} . We further assume that electronic excitations by thermal or other effects are negligible, and the equilibrium value is thus the ground state with matrix elements $\delta_{n0}\delta_{m0}$.

As the diagonal elements of the density operator can, for a pure state, be regarded as the population of the different states, the diagonal elements of the damping matrix can be understood as the inverse of the average lifetime. With this in mind, we now have a way by which the lifetimes, obtained by experiment or other means, can be phenomenologically addressed for the system.

In order to get the linear response function, the expansion of an expectation value as given in Eq. (3.5) may be considered. In the density matrix formalism expectation values are given as the trace

$$\langle \hat{\Omega} \rangle = \text{Tr}(\hat{\rho} \hat{\Omega}) = \text{Tr}(\hat{\Omega} \hat{\rho}), \quad (3.13)$$

and it is thus possible to calculate the molecular properties by using an expansion of the density operator

$$\rho_{mn}(t) = \rho_{mn}^{(0)} + \rho_{mn}^{(1)} + \rho_{mn}^{(2)} + \dots, \quad (3.14)$$

with a zeroth-order value given by the ground state, *i.e.* of the unperturbed system

$$\rho_{mn}^{(0)} = \delta_{n0}\delta_{m0}. \quad (3.15)$$

With the total Hamiltonian from Eq. (3.1), the unperturbed part yields, for the equation-of-motion

$$[\hat{H}_0, \hat{\rho}]_{mn} = \hbar\omega_{mn}\rho_{mn}, \quad (3.16)$$

and the damped Liouville equation (3.12) is solved in order N by time integration

$$\rho_{mn}^{(N)} = e^{-(i\omega_{mn} + \gamma_{mn})t} \int_{-\infty}^t \frac{1}{i\hbar} [\hat{V}, \hat{\rho}^{(N-1)}]_{mn} e^{(i\omega + \gamma_{mn}t')} dt'. \quad (3.17)$$

The perturbation operator $\hat{V}$ is given in Eq. (3.3), and we obtain the first-order response as

$$\begin{aligned} \rho_{mn}^{(1)} &= \frac{1}{i\hbar} \sum_{\omega} \frac{[\hat{V}_{\beta}^{\omega}, \rho^{(0)}]_{mn} F_{\beta}^{\omega}}{i\omega_{mn} - i\omega + \gamma_{mn} + \varepsilon} e^{-i\omega t} e^{\varepsilon t} \\ &= \frac{1}{i\hbar} \sum_{\omega} \left[\frac{\langle m | \hat{V}_{\beta}^{\omega} | 0 \rangle \delta_{n0}}{i\omega_{m0} - i\omega + \gamma_{m0} + \varepsilon} - \frac{\langle 0 | \hat{V}_{\beta}^{\omega} | n \rangle \delta_{m0}}{-i\omega_{n0} - i\omega + \gamma_{n0} + \varepsilon} \right] F_{\beta}^{\omega} e^{-i\omega t} e^{\varepsilon t}. \end{aligned} \quad (3.18)$$

Note that the frequency ω runs over both positive and negative values. The first-order correction of the expectation value of an operator can now be identified as

$$\begin{aligned} \langle \hat{\Omega}^{(1)} \rangle &= \text{Tr}(\hat{\rho}^{(1)} \hat{\Omega}) = \sum_{mn} \rho_{mn}^{(1)} \Omega_{mn} \\ &= -\frac{1}{\hbar} \sum_{\omega} \left[\frac{\langle 0 | \hat{\Omega} | n \rangle \langle n | \hat{V}_{\beta}^{\omega} | 0 \rangle}{\omega_{n0} - \omega - i\gamma_{n0} - i\varepsilon} + \frac{\langle 0 | \hat{V}_{\beta}^{\omega} | n \rangle \langle n | \hat{\Omega} | 0 \rangle}{\omega_{n0} + \omega + i\gamma_{n0} + i\varepsilon} \right] F_{\beta}^{\omega} e^{-i\omega t} e^{\varepsilon t}. \end{aligned} \quad (3.19)$$

This expression still contains the small, positive ε , adapted for an adiabatic switching on of the field, so for simplicity we set $\varepsilon = 0$. This is possible for a reasonable laser detuning. Further, we adopt a global lifetime $\gamma_{nm} = \gamma$, thus associating this damping parameter with the external frequency ω , rather than the transition specific frequencies ω_{n0} . With the interpretation of the damping parameter as discussed above, a global parameter would imply that the average lifetime of all excited states of the molecular system is identical. While this is strictly not correct, we will show that it results not only in more tractable expressions, but it also carries with it potentially large computational savings (especially for the approach described in Section 3.4.3).

By comparing the above expression to Eq. (3.7), the linear response function is found to be equal to

$$\langle\langle\hat{\Omega};\hat{V}_\beta^\omega\rangle\rangle_\omega = -\frac{1}{\hbar} \sum_n \left[\frac{\langle 0|\hat{\Omega}|n\rangle\langle n|\hat{V}_\beta^\omega|0\rangle}{\omega_{n0} - \omega - i\gamma} + \frac{\langle 0|\hat{V}_\beta^\omega|n\rangle\langle n|\hat{\Omega}|0\rangle}{\omega_{n0} + \omega + i\gamma} \right]. \quad (3.20)$$

Returning to our discussion of the resonance-divergent nature of (standard) response theory lacking phenomenological damping, or relaxation, described here, it is possible to arrive to an equivalent expression for the linear response function. This expression differs only in that the damping term $\gamma = 0$ (which would correspond to an infinite lifetime, *i.e.* no relaxation back to the ground state), and the response function as a whole is thus real. As can be seen in the denominators, we thus have singularities at resonance. In other words, by letting the frequency $\omega \rightarrow \omega + i\gamma$, we obtain a complex response function which allows for calculations including resonance frequencies.

With this damped linear response function, the polarizability is given by the case where an electric dipole moment operator is the operator corresponding to the perturbing field and the observable. Then Eq. (3.20) corresponds to the complex polarization propagator (CPP) and the complex polarizability is given as

$$\alpha_{\alpha\beta}(-\omega;\omega) = \alpha_{\alpha\beta}^I(-\omega;\omega) + i\alpha_{\alpha\beta}^R(-\omega;\omega) = -\langle\langle\hat{\mu}_\alpha;\hat{\mu}_\beta\rangle\rangle_\omega. \quad (3.21)$$

In Fig. 3.1 the behaviour of the real and imaginary part of this complex polarizability, as obtained for a single excited state in Eq. (3.20), is illustrated at and in the vicinity of resonance.

Figure 3.1. The real and imaginary part of the complex polarizability at and in the vicinity of resonance.

The imaginary part of the polarizability is seen to be equal to

$$\alpha_{\alpha\beta}^I = \frac{\gamma}{\hbar} \sum_n \left[\frac{\langle 0|\hat{\mu}_\alpha|n\rangle\langle n|\hat{\mu}_\beta|0\rangle}{(\omega_{0n} - \omega)^2 + \gamma^2} - \frac{\langle 0|\hat{\mu}_\beta|n\rangle\langle n|\hat{\mu}_\alpha|0\rangle}{(\omega_{0n} + \omega)^2 + \gamma^2} \right], \quad (3.22)$$

where, at resonance, the leading term is

$$f(\omega; \omega_{n0}, \gamma) = \frac{A_{n0}}{\pi} \frac{\gamma}{(\omega_{0n} - \omega)^2 + \gamma^2}, \quad \text{with} \quad A_{n0} = \pi \frac{\langle 0|\hat{\mu}_\alpha|n\rangle\langle n|\hat{\mu}_\beta|0\rangle}{\hbar}, \quad (3.23)$$

corresponding to a Lorentzian function with amplitude $A_{n0}/(\pi\gamma)$ and a half-width at half-maximum of γ . This imaginary component is related to the energy loss in the material, *i.e.* the absorption of radiation, while the real part can be associated with scattering. The absorption cross section is then given as ^{iv}

$$\sigma(\omega) = \frac{\omega}{3c\varepsilon_0} \sum_{\alpha=x,y,z} \alpha_{\alpha\alpha}^I(-\omega; \omega), \quad (3.24)$$

for all Cartesian component β of the electric dipole moment operator and c is the speed of light.

By comparison, non-resonant linear response approaches typically performs a residue analysis to identify poles in the linear response function, *i.e.* excitation energies, and transition moments are given as corresponding residues

$$\lim_{\omega \rightarrow \omega_{0n}} (\omega_{n0} - \omega) \alpha_{\alpha\beta}(-\omega; \omega) = \langle 0|\hat{\mu}_\alpha|n\rangle\langle n|\hat{\mu}_\beta|0\rangle, \quad (3.25)$$

from which oscillator strengths are calculated as

$$f^{0 \rightarrow n} = \frac{2\omega_{n0}}{3} \sum_{\alpha=x,y,z} |\langle 0|\hat{\mu}_\alpha|n\rangle|^2. \quad (3.26)$$

With the oscillator strengths $f^{0 \rightarrow n}$ substituting A_{n0} in Eq. (3.23), rescaling a Lorentzian broadened spectrum from such an approach in order to obtain a cross section scale in a.u. then becomes

$$\sigma(\omega) = \frac{\pi}{2c\varepsilon_0} \sum_n f(\omega; \omega_{n0}, \gamma), \quad (3.27)$$

with all entities expressed in a.u.

For any measurement, the excitation peaks are broadened by a number of processes, including already considered spontaneous and stimulated emission, molecular vibrations and the finite resolution of the experimental equipment (resulting in an asymmetric and Gaussian broadening, respectively¹¹), as well as through Doppler shift due to the relative movements and thermal vibrations of the molecules.¹⁵³ As a result, the theoretical Lorentzian broadening will not correspond exactly to the broadening of experimental spectra—the other effects will in most cases dominate over lifetime broadening, especially for significant temperatures. Nonetheless, the spectral features will be close to that of experiment and additional effects can be addressed if desired, *e.g.* by performing response calculations on snapshots from dynamics or addressing vibronic effects.

^{iv}Note that the pre-factor is sometimes given as $\frac{4\pi\omega}{3c}$, which is numerically equivalent to Eq. (3.24) when atomic units are used.

3.2 Coupled cluster response theory

In this section we will focus on the derivation of the resonance-divergent CC linear response function, for which the complex counterpart is found by the substitution $\omega \rightarrow \omega + i\gamma$. This derivation starts with the quasi-energy formalism and then utilize Lagrangian multipliers to ensure that the wave function is normalized.

3.2.1 Quasi-energy formalism

As was explained in the beginning of this chapter, identifying molecular properties with energy derivatives is a valid approach for static perturbations, but this approach is not possible for time-dependent perturbations owing to the ill-defined energies of such interactions. There exists, however, a similar property we can expand in orders of the perturbation instead, namely the quasi-energy.

First, let us reformulate the wave function as a product of two time-dependent functions

$$|\psi(t)\rangle = e^{-i\phi(t)} |\bar{\psi}(t)\rangle. \quad (3.28)$$

The choice of these functions are made unique by requiring $\phi(t)$ to be a real function and the phase of the projection of $\bar{\psi}(t)$ onto ground state ψ_0 to be zero. This can be compared to the time-evolution of the unperturbed (static) system, which is given by variable separation in the Schrödinger equation 2.1 as

$$|\psi(t)\rangle = e^{-iE_0 t/\hbar} |0\rangle, \quad (3.29)$$

with $|0\rangle$ as the ground state wave function. Inserting Eq. (3.28) in the Schrödinger equation yields

$$\left(\hat{H} - i\hbar \frac{\partial}{\partial t} \right) |\bar{\psi}(t)\rangle = Q(t) |\bar{\psi}(t)\rangle = \hbar \dot{\phi}(t) |\bar{\psi}(t)\rangle, \quad (3.30)$$

where $Q(t)$ is the time-dependent quasi-energy. This property can in principle be calculated by the projection

$$Q(t) = \langle \bar{\psi}(t) | \left(\hat{H} - i\hbar \frac{\partial}{\partial t} \right) | \bar{\psi}(t) \rangle, \quad (3.31)$$

and thus refers to expectation value of the difference between the time and Hamiltonian operators.

The requirements of Eq. (3.28) and the definition of $Q(t)$ in Eq. (3.30) results in the following expression in the absence of perturbing fields:

$$|\bar{\psi}(t)\rangle = |\psi_0\rangle, \quad (3.32)$$

$$\phi(t) = E_0 t/\hbar, \quad (3.33)$$

$$Q(t) = E_0. \quad (3.34)$$

For the phase-isolated wave function, phase function and quasi-energy, respectively. We also define the time-averaged quasi-energy as

$$Q_T = \frac{1}{T} \int_t^{t+T} Q(t') dt', \quad (3.35)$$

where T is the period time.

If we consider times when only the fundamental frequencies remains to be accounted for, the time-averaged quasi-energy will have no dependencies on time. In a manner analogously to Eqs. (3.2) and (3.7), the time-averaged quasi-energy is expanded in orders of the external perturbation as

$$\begin{aligned}
 Q_T(F^\omega) &= E_0 \\
 &+ \sum_{\omega_1} \frac{dQ_T}{dF_\alpha^{\omega_1}} \bigg|_{F^\omega=0} F_\alpha^{\omega_1} \\
 &+ \frac{1}{2!} \sum_{\omega_1 \omega_2} \frac{d^2 Q_T}{dF_\alpha^{\omega_1} dF_\beta^{\omega_2}} \bigg|_{F^\omega=0} F_\alpha^{\omega_1} F_\beta^{\omega_2} \\
 &+ \frac{1}{3!} \sum_{\omega_1 \omega_2 \omega_3} \frac{d^3 Q_T}{dF_\alpha^{\omega_1} dF_\beta^{\omega_2} dF_\gamma^{\omega_3}} \bigg|_{F^\omega=0} F_\alpha^{\omega_1} F_\beta^{\omega_2} F_\gamma^{\omega_3} \\
 &+ \dots
 \end{aligned} \tag{3.36}$$

From these derivatives we can thus identify the different molecular properties. As an example, the first-order correction is calculated as

$$\frac{dQ_T}{dF_\alpha^\omega} = \frac{1}{T} \int_t^{t+T} \langle \bar{\psi}(t') | \frac{\partial \hat{H}}{\partial F_\alpha^\omega} | \bar{\psi}(t') \rangle dt' = \frac{1}{T} \int_t^{t+T} \langle \bar{\psi}(t') | \hat{V}_\alpha^\omega | \bar{\psi}(t') \rangle e^{-i\omega t'} e^{i\omega t'} dt', \tag{3.37}$$

which is the Hellmann–Feynman theorem for time-independent quasi-energy.

3.2.2 The coupled cluster linear response function

As previously discussed, explicit response expressions for exact states can be formulated using both the Ehrenfest and quasi-energy formulations. However, for non-variational electronic structure methods such as coupled cluster, the Ehrenfest formalism can no longer be used.¹⁵¹ We will thus discuss the derivation of linear response equations in coupled cluster using quasi-energy,^{151,154} for which Eq. (3.30) becomes

$$\left(\hat{H} - i\hbar \frac{\partial}{\partial t} \right) e^{\hat{T}(t)} |0\rangle = Q(t) e^{\hat{T}(t)} |0\rangle. \tag{3.38}$$

With the time-derivative of the phase-isolated coupled cluster state being orthogonal to the reference HF state, the quasi-energy can be isolated as

$$Q(t) = \langle 0 | \left(\hat{H} - i\hbar \frac{\partial}{\partial t} \right) e^{\hat{T}(t)} |0\rangle = \langle 0 | \hat{H} e^{\hat{T}(t)} |0\rangle. \tag{3.39}$$

This expression can be regarded as the quasi-energy analogue of the coupled cluster energy equation (2.51). Likewise, projecting Eq. (3.38) onto the excitation manifold analogous to Eq. (2.52) yields the time-dependent amplitudes as

$$0 = \langle n | e^{-\hat{T}(t)} \left(\hat{H} - i\hbar \frac{\partial}{\partial t} \right) e^{\hat{T}(t)} |0\rangle. \tag{3.40}$$

It should be noted that the quasi-energy isolated above is no longer guaranteed to be real, as this projection is not fully analogous with the expectation value expressed in Eq. (3.31). Care must be taken to ensure that the response equations derived from this property are well defined.

The coupled cluster response functions are now sought using the quasi-energy in Eq. (3.39), with the constraints imposed by Eq. (3.40). The constraints can be incorporated by means of a variational Lagrangian technique, where equations of motion must fulfill the variational conditions

$$\delta L_T = 0, \quad (3.41)$$

for the time-averaged Lagrangian. This time-averaged Lagrangian can be formed from the coupled cluster Lagrangian in the same manner as the time-averaged quasi-energy of Eq. (3.35), with a time-dependent Lagrangian equal to

$$L(t) = Q(t) + \sum_n \lambda_n(t) \langle n | e^{-\hat{T}(t)} \left(\hat{H} - i\hbar \frac{\partial}{\partial t} \right) e^{\hat{T}(t)} | 0 \rangle. \quad (3.42)$$

The time-dependent Lagrangian multipliers λ_n are here associated with the constraints given by a specific excited determinant n .

We now seek the derivatives of L_T in order to determine molecular property, as can be compared to the expansion of the time-averaged quasi-energy in Eq. (3.36), and we first consider the zeroth-order response function

$$\langle \hat{V}_\alpha^{\omega_1} \rangle = \left. \frac{dL_T}{dF_\alpha^{\omega_1}} \right|_{F^\omega=0}. \quad (3.43)$$

In order to evaluate this field derivative, the derivative of the time-averaged Lagrangian with respect to the Lagrangian multipliers and the amplitudes are first required. With the variational condition 3.41 the derivatives with respect to the multipliers are equal to zero, *i.e.*

$$\left. \frac{\partial L_T}{\partial \lambda_n^{(0)}} \right|_{F^\omega=0} = \langle n | e^{-\hat{T}^{(0)}} \hat{H}_0 e^{\hat{T}^{(0)}} | 0 \rangle = 0, \quad (3.44)$$

determining the amplitudes of the CC reference state in a manner similar to Eq. (3.40). Superscripts designate the N :th order correction with respect to the perturbation.

For the amplitude derivatives the variational condition instead gives

$$\left. \frac{\partial L_T}{\partial t_n^{(0)}} \right|_{F^\omega=0} = \langle 0 | \hat{H}_0 \hat{\tau}_n^\dagger | \text{CC} \rangle + \sum_k \lambda_k^{(0)} \langle k | e^{-\hat{T}^{(0)}} [\hat{H}_0, \hat{\tau}_n^\dagger] e^{\hat{T}^{(0)}} | 0 \rangle = 0, \quad (3.45)$$

where $\hat{\tau}_n^\dagger$ is the excitation operator corresponding to amplitude t_n , which is given as

$$t_n(0) = t_n^{(0)} + \sum_{\omega_1} t_n^{(1)} e^{-i\omega_1 t} + \dots \quad (3.46)$$

In order to obtain the zeroth-order multipliers, we see that we can rearrange and then rewrite Eq. (3.45) in matrix form, such that the multipliers in vector form is given as

$$\lambda^{(0)} = -\bar{\kappa} \mathbf{A}^{-1}, \quad (3.47)$$

with

$$\bar{\kappa}_n^{[1]} = \langle 0 | \hat{H}_0 \hat{\tau}_n^\dagger e^{\hat{T}} | 0 \rangle \quad \text{and} \quad A_{kn} = \langle k | e^{-\hat{T}^{(0)}} [\hat{H}_0, \hat{\tau}_n^\dagger] e^{\hat{T}} | 0 \rangle, \quad (3.48)$$

the matrix $\mathbf{A}$ here is the non-symmetric coupled cluster Jacobian.

The zeroth-order response functions are now calculated via Eq. (3.43), for which the field derivatives are found to be

$$\begin{aligned} \left. \frac{dL_T}{dF_\alpha^{\omega_1}} \right|_{F^\omega=0} &= \left. \frac{\partial L_T}{\partial F_\alpha^{\omega_1}} \right|_{F^\omega=0} + \sum_n \left[\frac{\partial L_T}{\partial t_n^{(1)}} \frac{\partial t_n^{(1)}}{\partial F_\alpha^{\omega_1}} + \frac{\partial L_T}{\partial \lambda_n^{(1)}} \frac{\partial \lambda_n^{(1)}}{\partial F_\alpha^{\omega_1}} \right] \Big|_{F^\omega=0} \\ &= \left. \frac{\partial L_T}{\partial F_\alpha^{\omega_1}} \right|_{F^\omega=0} + \left[\langle 0 | \hat{V}_\alpha^{\omega_1} e^{\hat{T}^{(0)}} | 0 \rangle + \sum_n \lambda_n^{(0)} \langle n | e^{-\hat{T}^{(0)}} \hat{V}_\alpha^{\omega_1} e^{\hat{T}^{(0)}} | 0 \rangle \right] \delta_{\omega_1}, \end{aligned} \quad (3.49)$$

where the evaluation is made at zero field strength and the variational condition ensures that derivatives with respect to amplitudes and multipliers in the first row vanish.

With the zeroth-order response function derived, and the zeroth-order multipliers given by Eq. (3.47), we continue with the linear response function, obtained from the field derivative

$$\langle \langle \hat{V}_\alpha^{\omega_1}; \hat{V}_\beta^{\omega_2} \rangle \rangle = \left. \frac{d^2 L_T}{dF_\alpha^{\omega_1} dF_\beta^{\omega_2}} \right|_{F^\omega=0}. \quad (3.50)$$

These functions are determined by further derivations of Eq. (3.49) with respect to the external field and to ensure that the expression is symmetric a permutation operator $P_{\alpha,\beta}$ is introduced (acting by permuting the field amplitudes $F_\alpha^{\omega_1}$ and $F_\beta^{\omega_2}$). By cancellation of terms and implicit summation over indices, the linear response function is found to be

$$\begin{aligned} \langle \langle \hat{V}_\alpha^{\omega_1}; \hat{V}_\beta^{\omega_2} \rangle \rangle &= \left. \frac{d^2 L_T}{dF_\alpha^{\omega_1} dF_\beta^{\omega_2}} \right|_{F^\omega=0} \\ &= \sum P_{\alpha,\beta} \left[\left. \frac{\partial^2 L_T}{\partial F_\alpha^{\omega_1} \partial t_n^{(1)}} \frac{\partial t_n^{(1)}}{\partial F_\beta^{\omega_2}} \right|_{F^\omega=0} + \frac{1}{2} \frac{\partial t_m^{(1)}}{\partial F_\alpha^{\omega_1}} \frac{\partial^2 L_T}{\partial t_m^{(1)} \partial t_n^{(1)}} \frac{\partial t_n^{(1)}}{\partial F_\beta^{\omega_2}} \right]_{F^\omega=0}. \end{aligned} \quad (3.51)$$

The time-averaged Lagrangian derivatives can be expressed as

$$\frac{\partial^2 L_T}{\partial F_\alpha^{\omega_1} \partial t_n^{(1)}(\omega_2)} = \left[\langle 0 | \hat{V}_\alpha^{\omega_1} \hat{\tau}_n^\dagger e^{\hat{T}} | 0 \rangle + \sum_k \lambda_k^{(0)} \langle k | e^{-\hat{T}^{(0)}} [\hat{V}_\alpha^{\omega_1}, \hat{\tau}_n^\dagger] e^{\hat{T}} | 0 \rangle \right] \delta_{\omega_1+\omega_2}, \quad (3.52)$$

$$\frac{\partial^2 L_T}{\partial t_m^{(1)}(\omega_1) \partial t_n^{(1)}(\omega_2)} = \left[\langle 0 | \hat{H}_0 \hat{\tau}^\dagger \hat{\tau}_n^\dagger e^{\hat{T}} | 0 \rangle + \sum_k \lambda_k^{(0)} \langle k | e^{-\hat{T}^{(0)}} [[\hat{H}_0, \hat{\tau}_m^\dagger], \hat{\tau}_n^\dagger] e^{\hat{T}} | 0 \rangle \right] \delta_{\omega_1+\omega_2}, \quad (3.53)$$

where $\delta_{\omega_1+\omega_2}$ ensures that the condition $\omega_1 = -\omega_2$ is met, *i.e.*

$$\delta_x = \begin{cases} 1 & \text{for } x = 0 \\ 0 & \text{for } x \neq 0 \end{cases}. \quad (3.54)$$

In order to evaluate the field derivative of the first-order amplitudes at zero field strength the variational condition 3.41 is used repeatedly, such that

$$\frac{d}{dF_\alpha^{\omega_1}} \left[\frac{\partial L_T}{\partial \lambda_m^{(1)}(\omega_2)} \right] = \frac{\partial^2 L_T}{\partial F_\alpha^{\omega_1} \partial \lambda_m^{(1)}} + \frac{\partial^2 L_T}{\partial \lambda_m^{(1)} \partial t_n^{(1)}} \frac{\partial t_n^{(1)}}{\partial F_\alpha^{\omega_1}}, \quad (3.55)$$

from which the amplitudes are calculated as the matrix-vector product

$$\left. \frac{\partial t^{(1)}(\omega_1)}{\partial F_\alpha^{\omega_1}} \right|_{F\omega=0} = - \left[\left. \frac{\partial^2 L_T}{\partial \lambda^{(1)} \partial t^{(1)}} \right|_{F\omega=0} \right]^{-1} \left. \frac{\partial^2 L_T}{\partial F_\alpha^{\omega_1} \partial \lambda^{(1)}} \right|_{F\omega=0} = 0. \quad (3.56)$$

The elements of the right-hand-side matrix and vector are expressed as

$$\left. \frac{\partial^2 L_T}{\partial \lambda^{(1)}(\omega_1) \partial t^{(1)}(\omega_2)} \right|_{F\omega=0} = [A_{mn} - \hbar\omega_2 \delta_{mn}] \delta_{\omega_1+\omega_2}, \quad (3.57)$$

$$\left. \frac{\partial^2 L_T}{\partial F_\alpha^{\omega_2} \partial \lambda_m^{(1)}(\omega_1)} \right|_{F\omega=0} = \langle m | e^{-\hat{T}^{(0)}} \hat{V}_\alpha^{\omega_1} e^{\hat{T}} | 0 \rangle \delta_{\omega_1+\omega_2} = \xi, \quad (3.58)$$

where the last identification is tailored for the following, simplified expression of Eq. (3.56)

$$(\mathbf{A} - \hbar\omega_2 \mathbf{1})t(\omega) = -\xi. \quad (3.59)$$

This is the linear response equation that needs to be solved in a efficient manner, with the Jacobian being of such size that the direct inversion of the matrix at the left size is unfeasible. Written in this form, we also notice that the singularities of the response function occurs when the matrix to the left is singular, meaning that the excitation energies can be determined by diagonalizing this Jacobian.

In order to avoid these singularities and get a resonance-convergent method, we incorporate relaxation in the response function in the manner discussed concerning Eq. (3.12), by letting $\omega \rightarrow \omega + i\gamma$. This results in the complex linear response equation

$$(\mathbf{A} - \hbar(\omega + i\gamma)\mathbf{1})t(\omega + i\gamma) = -\xi. \quad (3.60)$$

As the amplitude derivative vector t cannot be found by direct inversion due to the size of the coupled cluster Jacobian, we will now discuss different approaches by which the (damped) linear response function can be calculated.

Since the development of the damped linear response function in CC,^[I,II] it has been further developed to include environmental effects through polarizable embedding,¹⁵⁵ use a core-valence separation approach,¹⁵⁶ calculate the spectrum using a complex solver,¹⁵⁷ as well as used to calculate chemical shifts,^[III] consider the spectrum of water^[IV] and noble gases,¹⁵⁸ as well as modeling photoionization¹⁵⁹ and photodetachment¹⁶⁰ cross sections.

3.3 Time-dependent density functional theory

Terribly Difficult Darned Fine Theory

Alternative interpretation of the TDDFT abbreviation,
A. Bandrauk¹⁶¹

While Kohn–Sham-DFT has proven to be indispensable for ground state quantum chemistry, the development needed to treat time-dependent systems is in some sense not as fully matured — TDDFT inherits all problems with DFT and add a few more. The most important development for this field was the work of Runge and Gross in 1984,³⁰ where they presented the theorems underlying time-dependent DFT (TDDFT), the first of which is

1. For every single-particle potential $V(\bar{r}, t)$ which can be expanded in a Taylor series around t_0 there exists a map $G : V(\bar{r}, t) \rightarrow \rho(\bar{r}, t)$, invertible up to an additive time-dependent function in the potential. This mapping is defined by solving the time-dependent Schrödinger equation with a fixed initial state ϕ_0 and calculating the corresponding densities $\rho(\bar{r}, t)$.

In addition to this theorem, the authors presented three theorem which offers a theoretical basis for practical schemes, the most important for this work being Theorem 4

4. The exact time-dependent density can be expressed as a sum over states, analogous to Eq. (2.35)

$$\rho(\bar{r}, t) = \sum |\phi(\bar{r}, t)|^2. \quad (3.61)$$

These time-dependent orbitals can then be calculated from the time-dependent version of Eq. (3.62)

$$i \frac{\delta}{\delta t} \phi_i(\bar{r}, t) = \left(-\frac{1}{2} \nabla^2 + V_{\text{eff}}(\bar{r}, t) \right) \phi_i(\bar{r}, t). \quad (3.62)$$

The exact solution of this system of equations requires knowledge of the exact time-dependent exchange-correlation functional, which is not known. In fact, it is even less known than the ground-state correspondence, as it requires not only knowledge of the exact exchange-correlation, but also on how it evolves over time — in order to get more tractable expressions the most applications thus utilize the time-independent exchange-correlation functionals, *i.e.* employ the adiabatic approximation. With this the time-dependence of $E_{\text{xc}}[\rho, t]$ enters only through $\rho(\bar{r}, t)$, and it is a reasonable approximation for systems evolving slowly in time. In fact, the search for non-adiabatic functionals has been criticized as something as a futile quest, as knowledge of the exact exchange-correlation functional would require the time-dependent Schrödinger equation already to be solved.^{162–164}

For the calculation of linear response functions, we parameterize the time-dependent wave function as a single phase-isolated Slater determinant

$$|\bar{\Psi}(t)\rangle = e^{-i\bar{\kappa}(t)} |0\rangle, \quad (3.63)$$

with the time-dependent Hermitian operator

$$\bar{\kappa}(t) = \sum_s^{\text{unocc}} \sum_i^{\text{occ}} \left[\kappa_{si}(t) \hat{a}_s^\dagger \hat{a}_i + \kappa_{si}^*(t) \hat{a}_i^\dagger \hat{a}_s \right]. \quad (3.64)$$

We here emphasize the use of a single Slater determinant, as will be important later. The time-dependent expectation value is now given as

$$\langle \Psi(t) | \hat{\Omega} | \Psi(t) \rangle = \langle 0 | e^{i\bar{\kappa}(t)} \hat{\Omega} e^{-i\bar{\kappa}(t)} | 0 \rangle. \quad (3.65)$$

The derivation of the first-order response function can be found elsewhere,¹⁴⁵ and we here move immediately to the result

$$\langle \langle \hat{Q}; \hat{V}^\omega \rangle \rangle = -\bar{Q}^\dagger (\mathbf{E} - \hbar\omega\mathbf{S})^{-1} \bar{V}^\omega, \quad (3.66)$$

where $\mathbf{E}$ is the electronic Hessian, $\mathbf{S}$ is the overlap matrix, and $\bar{Q}$ and $\bar{V}^\omega$ are property gradients. This equation is referred to as the random phase approximation (RPA) equation, and the most computationally difficult operation is the calculation of the inverse, or the solution of

$$(\mathbf{E} - \hbar\omega\mathbf{S}) \bar{X}(\omega) = \bar{V}^\omega. \quad (3.67)$$

The structure of the components are found to be

$$\mathbf{E} = \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix}, \quad \mathbf{S} = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix}, \quad \bar{V}^\omega = \begin{pmatrix} \bar{g} \\ \bar{g}^* \end{pmatrix}. \quad (3.68)$$

The Hessian is a diagonal dominant matrix with diagonal elements referring to differences in canonical orbital energies, and an approximation of Eq. (3.66) is thus given by disregarding the $\mathbf{B}$ -block, yielding the Tamm–Dancoff approximation (TDA)¹⁶⁵

$$(\mathbf{A} - \hbar\omega\mathbf{1}) \bar{X}_{\text{TDA}}(\omega) = \bar{g}. \quad (3.69)$$

The damped counterpart of the RPA-equation is now found by the mere substitution $\omega \rightarrow z = \omega + i\gamma$.

Example: The Casida equation

The Reader well versed in TDDFT may have noticed that Eq. (3.66) is not of the form most usually given in the literature, as is due to the present need of accommodating damped linear response theory in the theory. The move to the more common expression is done by first decomposing the response vector as

$$\bar{X}(\omega) = \begin{pmatrix} \bar{P}(\omega) \\ \bar{P}^*(\omega) \end{pmatrix}, \quad (3.70)$$

and the property gradient is decomposed as in Eq. (3.69). Considering now non-resonant response theory, $\bar{P}(\omega)$ must be infinite for any resonant perturbation $\bar{g}$, with Eq. (3.66) taking the form¹⁶¹

$$(x)(+\infty) = 0, \quad (3.71)$$

where x must be zero, leading to the pseudo-eigenvalue problem

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \bar{X}' \\ \bar{Y}' \end{pmatrix} = \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} \bar{X}' \\ \bar{Y}' \end{pmatrix} \quad (3.72)$$

known as the Casida equation.³¹

In order to construct a damped RPA equation in the four-component regime, we adopt the methodology described in Ref. [166], as has been utilized in Papers [V] and [VI]. Here symmetries in terms of time-reversal and Hermiticity are used to decompose the response vector

$$\bar{X} = \bar{X}^{++} + \bar{X}^{-+} + \bar{X}^{+-} + \bar{X}^{--}, \quad (3.73)$$

where the signs corresponding to Hermiticity and time-reversal symmetry, respectively (explicit reference to the complex frequency is avoided, for brevity). We further convert the time-reversal antisymmetric elements into a symmetric form by extracting an imaginary phase according to

$$\mathbf{U}^{h,t} = i\bar{\mathbf{U}}^{-h,-t}, \quad (3.74)$$

reversing the sign of both Hermiticity and time-reversal symmetry. Applied to the solution vector, this decomposition yields

$$\bar{X} = \bar{X}^{++} + \bar{X}^{-+} + i(\tilde{\bar{X}}^{-+} + \tilde{\bar{X}}^{++}). \quad (3.75)$$

For the coupling to an external electric field, the property gradient is associated to a Hermitian ($h = +1$) and time-reversal symmetric ($t = +1$) operator, and is thus designated as $\mathbf{E}_B^{++}$. The components of the solution vectors are now expanded

in two sets of orthonormal vectors of different Hermiticities,

$$\begin{aligned}\bar{X}^+ &= \sum_{k=1}^p a_k^+ \bar{b}_k^+, & \tilde{\bar{X}}^+ &= \sum_{k=1}^p \tilde{a}_k^+ \bar{b}_k^+, \\ \bar{X}^- &= \sum_{k=1}^m a_k^- \bar{b}_k^-, & \tilde{\bar{X}}^- &= \sum_{k=1}^m \tilde{a}_k^- \bar{b}_k^-, \end{aligned}$$

where the reference to time-reversal symmetry is removed, as all properties are now time-reversal symmetric. The RPA linear response function in Eq. (3.66) is now solved in a reduced space, where the reduced equation takes the form

$$\begin{bmatrix} \tilde{\mathbf{E}}^{++} & -\omega \tilde{\mathbf{S}}^{+-} & \gamma \tilde{\mathbf{S}}^{+-} & \mathbf{0} \\ -\omega \tilde{\mathbf{S}}^{-+} & \tilde{\mathbf{E}}^{--} & \mathbf{0} & \gamma \tilde{\mathbf{S}}^{-+} \\ -\gamma \tilde{\mathbf{S}}^{-+} & \mathbf{0} & \tilde{\mathbf{E}}^{--} & -\omega \tilde{\mathbf{S}}^{-+} \\ \mathbf{0} & -\gamma \tilde{\mathbf{S}}^{+-} & \omega \tilde{\mathbf{S}}^{+-} & \tilde{\mathbf{E}}^{++} \end{bmatrix} \begin{bmatrix} \bar{a}^+ \\ \bar{a}^- \\ \tilde{\bar{a}}^- \\ \tilde{\bar{a}}^+ \end{bmatrix} = \begin{bmatrix} -\tilde{\mathbf{E}}_B^+ \\ \mathbf{0} \\ \mathbf{0} \\ \mathbf{0} \end{bmatrix}, \quad (3.76)$$

where $\tilde{\mathbf{E}}^{++}$ and $\tilde{\mathbf{E}}^{--}$ are square sub-matrices of dimension p and m , respectively, and $\tilde{\mathbf{S}}^{+-}$ and $\tilde{\mathbf{S}}^{-+}$ are rectangular sub-matrices of dimensions $(p \times m)$ and $(m \times p)$, respectively. It is to be noted that this reduced equation is real, such that no complex equations needs to be explicitly calculated. From this the linear response function can now be computed, and from the imaginary part of this function the absorption cross-section is then obtained.

It is important to note that the linear response formalism of TDDFT discussed above is not the only description of absorption processes in TDDFT, nor is TDDFT the only approach to using DFT for transitions. For the former there exists also the possibility of explicitly propagating the molecular system in time, as has been developed for use for core excitations^{33,167} and lately generalized to accommodate also relativistic effects by being applied in the four-component relativistic regime.^{34,168} For the latter, a direct way of approximating transition energies are given with the Δ SCF approach,^{169,170} in which the energetics of the ground state and explicit excited states are compared. Alternatively, it can be shown^{15,16} that the transition energy is correct to second order if half an electron is excited to explicitly relaxed excited states, forming the so-called Slater transition state method. However, both these methods suffers due to the state-specificity, as explicit excited states needs to be constructed an optimized — it is thus not viable to consider many excitations. As a simplification of the Slater transition state method, the transition potential DFT (TP-DFT) method has been developed,¹³ in which the excited half an electron is no longer placed in the explicit excited states, and the problem is thus reduced to an independent-particle problem in the potential of the partially occupied core-hole (available also for emission processes¹⁷¹). This method has been utilized in Paper [IV], in order to investigate the performance of TP-DFT for calculation of water spectra, as compared to TDDFT and coupled cluster. Other time-independent approaches includes the development of, *e.g.*, orthogonality constrained DFT, a method of variational formulation of excited state DFT showing promising results for core-excitations.¹⁷² Additional developments to be noted is the calculation of functional derivatives in TDDFT using automatic

differentiation, enabling the generation of arbitrary-order response functions in an efficient manner.¹⁷³ A plethora of benchmark¹⁷⁴ and review^{161,175} articles on TDDFT exists, with a fraction being dedicated to the use for core excitations.⁹

3.4 Computing the linear response function

It is nice to know that the computer understands the problem, but I would like to understand it too.

E. Wigner¹⁷⁶

In this section we will discuss, in some details, different approaches of solving the linear response function, with the most demanding step involving the solution of the general equation

$$(\mathbf{E} - z\mathbf{S})t(z) = -\xi, \quad (3.77)$$

with the electronic Hessian $\mathbf{E}$, the overlap matrix $\mathbf{S}$, and the gradient ξ . This is to be solved for $t(z)$, where z is in general a complex frequency.

We will discuss the state-addressing bottom-up Davidson algorithm and Lanczos-chain method, as well as a complex solver for which the response at an arbitrary frequency can be addressed. In this thesis, we advocate the use of a bottom-up Davidson approach if the density of states is low (*e.g.* small systems, symmetric systems, non-relativistic calculations) and the restriction imposed on the excitation manifold does not unphysically distort the results, or a direct complex solver if this is not the case. The Lanczos algorithm suffers from the lack of a clear convergence control, but it should be reliable for high-density features and is also a good control for the accuracy of a bottom-up approach, as well as identifying the frequency region of interest for a direct, complex solver.

3.4.1 Bottom-up calculation of eigenvalues

The most common approach to solving the linear response function is to treat the reell, resonant-divergent of it with a bottom-up approach, *e.g.* using some generalization of the Davidson algorithm.¹⁷⁷ Here we seek to calculate the transition energies as the poles in the linear response function in Eq. (3.51), with $\gamma = 0$, the oscillator strengths per the residue in Eq. (3.25). The absorption cross section is then obtained by convoluting the obtained oscillator strengths and transition energies with a Lorentzian, Eq. (3.23) function or similar — occasionally, a Gaussian broadening is used, and it is also possible to use a frequency-dependent broadening scheme.¹⁴

As this approach is most commonly used, we will consider it sufficient to discuss in general terms, and not delve into the explicit expressions. This is an iterative scheme which is typically initiated by selecting start vectors as occupied to unoccupied excitations. The algorithm is similar to that described in Section 3.4.3 — for a signal of this, consider the changes imposed by using Eq. (3.96) if the Casida equation from 3.72 is used. The procedure is, however, biased to converging the lowest eigenvalues, and thus converge to the lowest roots (even if the initialization is done with vectors corresponding to occupied core orbitals).

This approach has the advantage of giving access to the explicit excited states, which can then be analyzed. As for disadvantages, the approach can have difficulties if the density of states is high, leading to a large number of states to be resolved, or if the desired states occurs late in the spectrum. In principle, there is also an error associated with truncating the excited state manifold in Eq. (3.51), as is done whenever not all states are included, but this yields negligible errors if the states are not very close to the frequency window of interest. The problem with addressing embedded states, as is highly relevant for the purpose of this thesis, can be resolved by a number of computational techniques, including a restriction of the excitation channel,¹⁷⁸ a core-valence separation,,^{156,179} restricted excitation window techniques^{32,180} *etc.* Of course, it is necessary to ensure that these restrictions does not undermine the accuracy of the calculation too much. The errors due to restricting the excitation manifold for TDDFT have been reported to amount to, at the most, 0.01 eV in transition energy and 0.01 in oscillator strength for 1s excitations, or 0.07 eV and 0.02 for 2s excitations.¹⁸¹ The core-valence separation scheme in coupled cluster is reported to yield errors of less than 0.05 eV and modest changes in intensities.¹⁵⁶

3.4.2 The Lanczos-chain method

An established, iterative method of transforming a large matrix to a smaller, tri-diagonal form is the Lanczos-based algorithm (or the Lanczos-chain method), described in Ref. [182] and implemented in a symmetrical setting in Ref. [183]. With this, the entire spectral region is iteratively constructed, starting with the extremal, most intense transitions. This approach for the solution of the damped coupled cluster linear response function have been implemented and the performance evaluated in Papers I-III. Some aspects of this approach will now be discussed, largely following Paper II, but with some differences in notation.

Consider an asymmetric Hessian matrix $\mathbf{E}$ of dimension n . We seek a transformation of this matrix such that

$$\mathbf{T}^{(m)} = [\mathbf{P}^{(m)}]^T \mathbf{E} \mathbf{Q}^{(m)}, \quad (3.78)$$

where $\mathbf{T}^{(m)}$ is of dimension m ($\leq n$) and has an asymmetric tri-diagonal form such that

$$\mathbf{T}^{(m)} = \begin{pmatrix} \alpha_1 & \gamma_1 & 0 & & 0 \\ \beta_1 & \alpha_2 & & \ddots & \\ 0 & & \ddots & & 0 \\ & \ddots & & \alpha_{m-1} & \gamma_m \\ 0 & & 0 & \beta_m & \alpha_m \end{pmatrix}. \quad (3.79)$$

The transformation matrices $\mathbf{P}^{(m)}$ and $\mathbf{Q}^{(m)}$ are of dimension $n \times m$ and bi-orthonormal, *i.e.*

$$[\mathbf{P}^{(m)}]^T = [\mathbf{Q}^{(m)}]^{-1} \quad \Rightarrow \quad [\mathbf{P}^{(m)}]^T \mathbf{Q}^{(m)} = \mathbf{1}. \quad (3.80)$$

If the transformation is made in full dimension, *i.e.* $m = n$, the exact tri-diagonal representation is obtained, with properties such that

$$\mathbf{E}\mathbf{Q}^{(n)} = \mathbf{Q}^{(n)}\mathbf{T}^{(n)} \quad \text{and} \quad \mathbf{E}^T\mathbf{P}^{(n)} = \mathbf{P}^{(n)} \left[\mathbf{T}^{(n)} \right]^T. \quad (3.81)$$

By labeling the columns in $\mathbf{Q}^{(n)}$ as $\bar{q}_1, \bar{q}_2, \dots, \bar{q}_n$, and analogous for $\mathbf{P}^{(n)}$, the matrices and elements in $\mathbf{T}^{(n)}$ can be found to fulfill the relations

$$\mathbf{E}\bar{q}_i = \gamma_{i-1}\bar{q}_{i-1} + \alpha_i\bar{q}_i + \beta_i\bar{q}_{i+1}, \quad (3.82)$$

$$\mathbf{E}^T\bar{p}_i = \beta_{i-1}\bar{p}_{i-1} + \alpha_i\bar{p}_i + \gamma_i\bar{p}_{i+1}, \quad (3.83)$$

for all $i = 1, \dots, n-1$, with the requirement that $\gamma_0\bar{q}_0 = \beta_0\bar{p}_0 = 0$. It is thus possible to generate new vectors $\bar{q}_{i+1}$ and $\bar{p}_{i+1}$ recursively, by using the information obtained by previous iterations such that

$$\beta_i\bar{q}_{i+1} = r_i = (\mathbf{E} - \alpha_i\mathbf{1})\bar{q}_i - \gamma_i\bar{q}_{i-1}, \quad (3.84)$$

$$\gamma_i\bar{p}_{i+1} = s_i = (\mathbf{E}^T - \alpha_i\mathbf{1})\bar{p}_i - \beta_i\bar{p}_{i-1}. \quad (3.85)$$

The parameters α_i , β_i , and γ_i can be obtained from the bi-orthonormality condition 3.80, where α_i has a definite value and the remaining two parameters are related

$$\alpha_i = \bar{p}_i^T \mathbf{E} \bar{q}_i \quad \text{and} \quad \bar{p}_i^T \bar{q}_i = \left(\frac{s_i}{\gamma_i} \right) \left(\frac{r_i}{\beta_i} \right) = 1. \quad (3.86)$$

It is customary to enforce the latter condition (with δ_{ij} to the right) between all Lanczos vectors $\bar{q}_i$ and $\bar{p}_j$, as numerical noise would otherwise make the algorithm unstable for large dimensions.

If the calculation of the tri-diagonal matrix is halted at a dimension $m < n$, also designated as a chain length m , an error is introduced and $\mathbf{T}^{(m)}$ is only an approximation of the tri-diagonal matrix. In this case the first relation of Eq. (3.81) is now found to be

$$\mathbf{E}\mathbf{Q}^{(m)} = \mathbf{Q}^{(m)}\mathbf{T}^{(m)} + \beta_m\bar{q}_{m+1} \left[\bar{e}_m^{(m)} \right]^T, \quad (3.87)$$

where the last term is the truncation error, with $\bar{e}_m^{(m)}$ being a unit vector with 1 in element m .

Neglecting the truncation error, an approximate Hessian $\mathbf{E}^{(m)}$ is constructed as

$$\mathbf{E}^{(m)}\mathbf{Q}^{(m)} = \mathbf{Q}^{(m)}\mathbf{T}^{(m)}, \quad (3.88)$$

and the tri-diagonal matrix is diagonalized with left and right eigenvectors

$$\mathbf{T}^{(m)}\mathbf{R}^{(m)} = \mathbf{R}^{(m)}\mathbf{\Omega}^{(m)}, \quad (3.89)$$

$$\mathbf{L}^{(m)}\mathbf{T}^{(m)} = \mathbf{\Omega}^{(m)}\mathbf{L}^{(m)}, \quad (3.90)$$

where $\mathbf{\Omega}^{(m)}$ is a diagonal matrix with the m eigenvalues of $\mathbf{T}^{(m)}$. Using these eigenvectors the approximate eigenvectors of $\mathbf{E}$ are given as

$$\mathbf{X}_L^{(m)} = \mathbf{L}^{(m)} \mathbf{P}^{(m),T}, \quad (3.91)$$

$$\mathbf{X}_R^{(m)} = \mathbf{Q}^{(m)} \mathbf{R}^{(m)}. \quad (3.92)$$

For details on how the Lanczos algorithm is implemented in coupled cluster damped linear response theory, see Paper [II]. Included there are specifications on the choice of $\bar{q}_i$ and $\bar{p}_i$, including initial vectors, and the procedure of how Eq. (3.51) can be rewritten to the following form

$$\begin{aligned} \langle \langle \hat{\Omega}; \hat{V}_\beta^\omega \rangle \rangle_\omega = N_\eta N_\xi \sum_j & \left[\frac{L_{j1}^{(m)} R_{1j}^{(m)}}{\omega - \omega_j + i\gamma} - \frac{L_{j1}^{(m)} R_{1j}^{(m)}}{\omega + \omega_j + i\gamma} \right] \\ & + N_\xi^2 \sum_{jk} F_{kj} \frac{L_{j1}^{(m)} L_{k1}^{(m)}}{(\omega - \omega_j - i\gamma)(\omega - \omega_k + i\gamma)}. \end{aligned} \quad (3.93)$$

From this expression, we can thus directly address any spectrum region of interest, with broadening included. In addition to this, it is also possible to calculate the approximate coupled cluster eigenvectors in a manner analogously to Eqs. (3.91) and (3.92), and from these we get the explicit excited states with information concerning transition energies, oscillator strengths and the character of the excitations.

The main difficulty with the Lanczos algorithm is to ensure that the spectral region of interest is sufficiently well converged. If an insufficient chain length is chosen, it is possible that several less intense features are combined into one, incorrect, spectral feature, and care must be taken to ensure that this is not the case.

As an illustration of the convergence properties of the algorithm, we have calculated the spectrum of neon at the CCSD/taug-cc-pVTZ level of theory using different Lanczos chain lengths j , with the results shown in Fig. 3.2. The spectral features converge from the lowest and highest eigenvalues, with the features at the first 100 eV being very similar for $j = 200$ and $j = 800$. This is a property of the Lanczos algorithm and for the case of X-ray absorption spectroscopy it means that we need a large chain length to converge the core excited states (in this case at around 870 eV), as the valence states need to be converged first. In this context, we also note the difference in intensity between the low-energy states and those at around 870 eV (which are barely visible), this is due to the larger overlap of valence and excited state orbitals than of core and excited state orbitals. As the chain length is increased, the maximum of the peaks are observed to decrease, as the previously unconverged transitions are no longer summed into one larger one (of an intermediate energy).

As the Lanczos algorithm is a method by which the global spectrum is converged iteratively, it is possible to calculate the global integrated absorption cross-section I_S . For a variational method this value should be equal to the total number of electrons, as given by the Thomas–Reiche–Kuhn sum rule. For the results illustrated in Fig. 3.2, the I_S values are reported to be equal to 10.19, differing by most

0.0002 for the different chain lengths. This is in line with previous observations—the algorithm combine several low-intensity features into a stronger feature, conserving the total transition moment or integrated absorption cross-section. As an extreme example, a Lanczos CCSD calculation was carried out using a chain length $j = 1$, for which all the absorption cross-section is combined into one feature, resulting in a I_S value of 10.19. It is thus clear that the Lanczos CPP approach will give the converged I_S value using any chain length, and discrepancies in the values as compared to the Thomas–Reich–Kuhn sum rule is thus a result of the electronic structure and basis set used.

Figure 3.2. The global spectrum of neon, as calculated using CCSD damped linear response theory with different chain lengths j in the Lanczos algorithm. The spectral region is set as 0 – 1100 eV and the basis set is chosen as taug-cc-pVTZ.

3.4.3 Complex linear response equation solver

Finally, we will discuss the direct solution of Eq. (3.77) by means of direct inversion in a reduced space.^{157, 166, 184} In this scheme, an iterative subspace algorithm is used to construct a subspace in which arbitrary frequencies can be addressed and no restrictions of the excitation manifold are necessary.

First, we explicitly rewrite the solution vector and right-hand-side in the complex vectors, respectively

$$t = t^R + it^I, \quad \xi = \xi^R + i\xi^I. \quad (3.94)$$

Note that $\xi^I = 0$ for real operators, as is the case for the determination of complex polarizability. This yields the response equation

$$(\mathbf{E} - \hbar(\omega + i\gamma)\mathbf{1})(t^R + it^I) = -(\xi^R + i\xi^I), \quad (3.95)$$

written in real matrix form as

$$\begin{pmatrix} (\mathbf{E} - \hbar\omega\mathbf{1}) & \hbar\gamma\mathbf{1} \\ \hbar\gamma\mathbf{1} & -(\mathbf{E} - \hbar\omega\mathbf{1}) \end{pmatrix} \begin{pmatrix} t^R \\ t^I \end{pmatrix} = \begin{pmatrix} -\xi^R \\ \xi^I \end{pmatrix}. \quad (3.96)$$

We seek to solve Eq. (3.96) using an iterative subspace algorithm, for which, at k :th iteration, a subspace of trial vectors has been constructed such that

$$\begin{aligned} b^n &= \{b_1^R, b_1^I, \dots, b_{n/2}^R, b_{n/2}^I\} \\ &= \{b_1, b_2, \dots, b_{n-1}, b_n\}, \end{aligned} \quad (3.97)$$

where the vectors corresponding to the real and imaginary components are included in the same subspace, as this will give a larger subspace and faster convergence. In practice, it is most likely not the case that we have as many trial vectors that originate from real and imaginary trial vectors, due to orthonormalization procedures, and we also note that such operations ensures that the size of the subspace $n \leq k$.

For each trial vector, a corresponding linear transformed vector is formed, yielding the set

$$\sigma^n = \{\mathbf{E}b_1, \mathbf{E}b_2, \dots, \mathbf{E}b_{n-1}, \mathbf{E}b_n\}.$$

With this at hand, the reduced real matrix equation is constructed as

$$\begin{pmatrix} (\mathbf{E}_{\text{red}} - \hbar\omega\mathbf{1}_{\text{red}}) & \hbar\gamma\mathbf{1}_{\text{red}} \\ \hbar\gamma\mathbf{1}_{\text{red}} & -(\mathbf{E}_{\text{red}} - \hbar\omega\mathbf{1}_{\text{red}}) \end{pmatrix} \begin{pmatrix} t_{\text{red}}^R \\ t_{\text{red}}^I \end{pmatrix} = \begin{pmatrix} -\xi_{\text{red}}^R \\ \xi_{\text{red}}^I \end{pmatrix}, \quad (3.98)$$

with

$$[\xi_{\text{red}}^R]_i = b_i^T \xi^R, \quad [\xi_{\text{red}}^I]_i = b_i^T \xi^I, \quad [\mathbf{E}_{\text{red}}]_{ij} = b_i^T \mathbf{E}b_j = b_i^T \sigma_j. \quad (3.99)$$

The reduced matrix equation is solved by inversion, and by this the optimal solution vectors for iteration k are calculated as

$$t_{\text{opt}}^R = \sum_{i=1}^n [t_{\text{red}}^R]_i b_i \quad \text{and} \quad t_{\text{opt}}^I = \sum_{i=1}^n [t_{\text{red}}^I]_i b_i. \quad (3.100)$$

Using these solution vectors the residual is calculated as

$$\begin{pmatrix} R^R \\ R^I \end{pmatrix} = \begin{pmatrix} -\xi^R \\ \xi^I \end{pmatrix} - \begin{pmatrix} (\mathbf{E} - \hbar\omega\mathbf{1}) & \hbar\gamma\mathbf{1} \\ \hbar\gamma\mathbf{1} & -(\mathbf{E} - \hbar\omega\mathbf{1}) \end{pmatrix} \begin{pmatrix} t_{\text{opt}}^R \\ t_{\text{opt}}^I \end{pmatrix}. \quad (3.101)$$

The norm of this residual is then checked for convergence. Note that the full right-hand-side and Hessian is used for this calculation, and we thus have an *a priori* control of the convergence by specifying convergence threshold for this residual.

If convergence is not met, the residuals are used to form new trial vectors, by use of the preconditioner

$$\begin{pmatrix} b^R \\ b^I \end{pmatrix} = \begin{pmatrix} (\mathbf{E}_0 - \hbar\omega\mathbf{1}) & \hbar\gamma\mathbf{1} \\ \hbar\gamma\mathbf{1} & -(\mathbf{E}_0 - \hbar\omega\mathbf{1}) \end{pmatrix}^{-1} \begin{pmatrix} R^R \\ R^I \end{pmatrix}, \quad (3.102)$$

where $\mathbf{E}_0$ is a diagonal representation of the full Hessian, retaining the difference in orbital energies in the zeroth-order approximation. While such preconditioning is not strictly necessary, it leads to faster convergence as the trial vectors are transformed to a form that points more closely to the directions in the abstract vector space necessary for the calculation of converged solution vectors.

Note that the above discussion have been focused on one single frequency, but there is no restriction to the number of frequencies that can be treated simultaneously. As the solution vectors of frequencies close to each other are very similar, especially far from resonance, it is in fact advantageous to calculate many at the same time, as the subspace required will be very similar. This approach also fits well with a parallel paradigm of computing, as many actions can be carried out on separate threads. In Fig. 3.3 we demonstrate these advantages by considering the UV/vis spectrum of mercury-substituted porphyrin, as discussed in more detail in Paper [V]. Here we have calculated the complex polarizability of a single component for $n=1-19$ frequencies simultaneously, starting close to resonance and expanding the number of frequencies outwards. We report the total number of iterations, the number of iterations per frequency, as well as the size of the final subspace. Strikingly, we see that the total number of iterations required for the convergence of all simultaneous frequencies drops from 30 to 14, for 1 or 19 frequencies, respectively. The number of iterations per frequency lowers monotonously from 30 to 0.74, and it is clear that the approach benefits from treating several frequencies in parallel. We also note that the total size of the final subspace increase with n , and this thus limits the total number of frequencies which can be considered in parallel — the current implementation in Dirac used here has a limit of 20, but recent development¹⁸⁵ in Dalton have illustrated that over 100 frequencies can be treated in parallel.

3.5 Limits of molecular response theory

I must break you.

I. Drago (D. Lundgren), 1985¹⁸⁶

Here we will briefly discuss some of the limits of linear response theory for which the approximations break down and the method may not be reliable. These flaws are mainly related to two approximations that have been made, namely (i) the use of perturbation theory, and (ii) the use of the electric-dipole approximation. For most current experiments neither of these assumptions affects the reliability

Figure 3.3. The convergence properties of the CPP-approach, as illustrated by plotting the number of iterations necessary for convergence of all frequencies, as a function of the number of simultaneous frequencies. Also report the total size of the final subspace. For more details, see Paper [V].

too much, but the latter approximation seems a bit brazen for core-excitations, and we envision the appearance of spectroscopical techniques which will put the reliability of the approach in question.

3.5.1 High-intensity fields

From the perturbative energy expansion in Eq. (3.2) it is clear that non-linear terms will start affecting the molecular property in question. Expanding the electric-field dependent dipole moment we obtain

$$\mu(t) = \mu_0 + \alpha F(t) + \frac{1}{2!}\beta F^2(t) + \frac{1}{3!}\gamma F^3(t) + \dots \quad (3.103)$$

For a simple illustration of the influence of the non-linear terms, let us consider a system for which $\alpha = 1.0$ a.u., $\beta = 10\alpha$, and $\gamma = 100\alpha$, and the static dipole moment $\mu_0 = 0$.^v In Fig. 3.4 we report the induced dipole moment when truncating the expansion of the dipole moment at different orders, using three different field strengths and a sinusoidal perturbing field. In panel (c) we also report the relative contribution of the quadratic and cubic term as compared to the linear contribution. In this case, it is clear that the linear term is sufficient up to field

^vThe relative size of the polarization properties can be rationalized by considering the static properties, with transition energies affecting the properties as ΔE^{-1} , ΔE^{-2} , and ΔE^{-3} , for α , β , and γ , respectively.¹⁴⁵

strengths which macroscopically would be very intense.^{vi} Further, we note that the non-linear contributions destroys the symmetry of the induced dipole moment.

Provided that the use of perturbation theory has not broken down completely, this situation may be solved if higher-order response functions are calculated. However, this may quickly become quite tedious, and an alternative approach is given by the use of real-time propagation methods.¹⁶⁸ Here the real-time response of the molecular system is followed in time, and information on, *e.g.*, the absorption of the sample is obtained from this time-propagation. However, this approach is hampered by difficulties in separating the different-order responses, or different-order molecular properties, and the calculation of transition energies and oscillator strengths for analysis.

Figure 3.4. Induced dipole moment at different field strengths. (a) 1×10^{-5} a.u., (b) 5×10^{-2} a.u., and (c) 1×10^{-1} a.u. Including only α (dashed grey), α and β (dashed black), and α , β and γ (black). Also (c) illustrating the relative intensity of the quadratic (dashed black) and cubic (dashed grey) contributions relative to the linear contribution.

^{vi}As a comparison, a parallel plate capacitor would have to be supplied by a source with a voltage of approximately 5 GV to produce a 1 a.u. electric field for plates separated by 1 cm, a voltage which is exceedingly high indeed.

3.5.2 Ultra-short pulses

A rising field of X-ray sciences is the use of free-electron lasers (FELs), for which superior field intensities and time-resolution is obtained. This technique opens up new possibilities in fs-resolved experiments for following chemical reactions in real time, but the use of such extremely small laser pulses becomes problematic for linear response theory, which assumes that the perturbing field and the material has reached some stable conditions — with a very short pulse, there will simply not be enough time for this. As an example we illustrate the perturbation of a water molecule at *K*-edge resonance energy in Fig. 3.5, as perturbed by a ~ 20 fs pulse (which, with the current development, is not a very short pulse either). Please note that the y-axis is arbitrarily scaled to see the fluctuations, while the x-axis is in distance and the molecule is to scale to this. As can be seen, the pulse consists of less than ten periods of considerable strength, and stable conditions will likely not occur so quickly. For this situation, it is once again possible to move to the realm of real-time propagations of the wave function. However, if the pulse is to interact with a number of molecules — say, a condensed phase — also this approach becomes debatable as the exact form of the laser pulse is no longer known. An alternative approach is in this case given by following the pulse and studying its evolution over time.^{187, 188}

Figure 3.5. Water molecule perturbed by ultrashort X-ray pulse at resonance. The intensity of the pulse is given as a Gaussian distribution.

3.5.3 Short-wavelength perturbations

In Eq. (3.1) we assumed that the perturbing field is homogeneous over the entire molecular system, as per the electric dipole approximation. For low energies this approximation would seem reasonable, as the wavelengths of the field is quite

long — for visible light it will be of several hundreds of nm. However, for core-excitation processes this approximation becomes more questionable, due to the short wavelength of the X-ray photons. This is illustrated in Fig. 3.6, where we compare the wavelength of photons close to the resonance energy of the $1s$ electrons of carbon and silicon, with the total size and the $1s$ orbitals of the specimen in methane and silane. For carbon we see that the perturbation is quite homogeneous over the entire molecule, and very much so over the $1s$ orbital. Any discrepancies due to the neglect of non-dipole field contributions can thus be expected to be small. However, for silicon we see that the field is not homogeneous over the molecule, even if it is so over the $1s$ orbital — we have, in general, a contraction of the $1s$ orbital that somewhat counteracts the decreasing wavelength of the resonant X-ray photon, with increasing Z .

The origin-dependent inclusion of higher-order terms in the perturbative field has been developed by Bernadotte *et al.*,¹⁸⁹ and expanded by List *et al.*¹⁹⁰ It has been demonstrated that an origin-independent inclusion of higher-order contributions can be achieved if all contributions to the same order in the wave vector is included consistently. Higher-order terms can break symmetry rules in the dipole approximations, yielding, *e.g.*, $1s \rightarrow nd$ transitions.

This expansion is done in terms of the oscillator strength^{vii}

$$f_{0n} = f_{0n}^{(0)} + f_{0n}^{(1)} + f_{0n}^{(2)} + \dots, \quad (3.104)$$

for which the term to be expanded is

$$e^{(i\bar{k} \cdot \bar{r})} = 1 + i(\bar{k} \cdot \bar{r}) - \frac{1}{2}(\bar{k} \cdot \bar{r})^2 + \dots, \quad (3.105)$$

i.e. the spatial part of the radiation field, in orders of the wave vector $\bar{k}$. From this it is clear that the corrections becomes more important as kr increases (*i.e.* for short wavelengths), and that the electric dipole approximation breaks down when kr exceeds unity.

kr values determined by balance between the shorter wavelengths and the contraction of the orbitals. In Ref. [190] it was demonstrated that the contraction is almost inversely proportional to Z , while the transition energy goes as Z^2 — as expected for hydrogenic systems. This gives a kr depending close to linearly with Z . However, extrapolation indicates that kr retains values less than unity for all elements in the periodic table, never reaching a value of 0.6 even for $Z = 119$ — as such, the electric dipole approximation has been estimated to yield an error of at the most 20% for $1s \rightarrow np_x$ transitions within the periodic table. Further analysis on extended polyenes shows a surprising insensitivity to ED in terms of overall band profiles.

The influence on the oscillator strength can be substantial, especially for metal K -edge spectroscopy — the higher-order terms have been shown to have the similar contribution as the electric dipole to the oscillator strength of the iron K -edge (approximately at 7 keV) in vinylferrocene.¹⁸⁹ Can also be necessary to go beyond the dipole approximation for extended systems. For low-energy transitions, it can

^{vii}Rewritten as $f^{0 \rightarrow n} = f_{0n}$, as compared to Eq. (3.26).

be noted that the transitions allowed in the electric dipole approximation can be expected to get lower intensity if higher-order terms are included, as intensity is moved to the previous symmetry-disallowed transitions.

None of the results presented in this thesis have included effects beyond the electric dipole approximation, but such effects are expected to be small for the relatively light elements and small molecules considered here.

Figure 3.6. Comparison of the wavelength of near-resonant photons to the size of methane and silane and the distribution of the 1s electrons ($r^2\rho$). Orbital density obtained at an uncontracted cc-pVQZ/HF level of theory.

CHAPTER 4

K-edge X-ray absorption spectroscopy

Truth is ever to be found in simplicity, and not in the multiplicity and confusion of things.

I. Newton¹⁹¹

For the consideration of *K*-edge X-ray absorption spectroscopy we will first consider the theoretical aspects of core excitation processes, with focus the influence of relaxation and electron correlation. An analysis of ionization potentials along the periodic table is used to illustrate the influence of relaxation, self-interaction errors, and spin-orbit splittings with increasing *Z*. With these basic concerns illustrated, the performance of the CC hierarchy and more approximate methods will then be discussed, followed by a discussion on dynamical and environmental effects. Finally, the X-ray absorption spectrum of water will be discussed, with focus on the influence of H-bonds and new state-of-the-arts results presented in Paper [V].

4.1 Relaxation effects

For X-ray absorption processes, relaxation affects the molecule in two distinct physical manners, as a 'direct' relaxation and as a polarization/screening effect. The 'direct' relaxation originate from the reduced screening of the core as experienced by the valence electrons, and it is thus an attractive effect. The polarization/screening is instead a repulsive effect, resulting from the interaction between the excited electron and the valence electrons. Since the former effects dominates over the latter in terms of energetics, schemes by which only the 'direct' effect is accounted for are in use.^{17, 18} While this gives reasonably good spectra, the features becomes compressed and it is thus a method we will not pursue further — illustrations of this can be found in Paper [III].

4.1.1 Electron density of ground and core-ionized systems

In Fig. 4.1 we report the orbital densities of krypton, as obtained in a non-relativistic and relativistic setting. The different 'shells' are clearly visible, and we see minor shifts in the densities when relativistic effects are included, for which all orbital densities are contracted by a factor of 1.000–1.029 when comparing the position of the $r^2\rho$ maxima. The larger values are for the $1s$, $2s$, $2p$, and $3s$ orbitals, *i.e.* the mostly tightly bound electrons. If a resolution of the individual spin states of the orbitals with $l \geq 1$ was included, this trend of contractions would disappear, as, *e.g.*, the $p_{1/2}$ orbitals are more contracted than the $p_{3/2}$ orbitals, and the latter are thus decontracted.⁸⁰ In general, for any system, there are trends of s and p orbitals being contracted and the higher orbitals being decontracted, and $j = 1/2$ more contracted, but there is no clear, unambiguous systematic in the behaviour. As a result of this, the effective radii of atoms shrink downward in a group in the periodic table, with *e.g.* the silver atom being larger than the gold atom.

Figure 4.1. Orbital densities of krypton, as obtained at a HF/decontracted cc-pCVQZ level of theory. Full lines indicates results obtained in a relativistic setting, and dashed lines indicates results obtained in a non-relativistic setting. Density scaled as $r^2\rho$.

Returning to the relativistic mass expressed in Eq. (2.60), the shrinking of the $1s$ orbital should be of similar factor as the mass increase.⁷¹ Using the relativistic HF orbital energy, we obtain a factor of 1.029, *i.e.* in perfect agreement with the contraction of the orbital.

Considering $1s$ orbital densities, Fig. 4.2 illustrate the densities of neutral and ionized helium, as compared to the Li $1s$ orbital density of lithium hydride. It is clear that the remaining $1s$ electron of He^+ is more strongly attracted to the nucleus, as the screening is now significantly reduced. Comparing to lithium, the He^+ results encloses the Li orbital density, but the $Z + 1$ approximation does not appear to perform that well for this system. This is not very surprising, seeing that these are very small molecular systems, more heavily influenced by the environment and in general more delocalized. The $Z + 1$ approximation will perform better for heavier elements.

Instead considering the total electron density of a core-ionized system, Fig. 4.3 illustrate the neutral and carbon and oxygen core-ionized densities of formalde-

Figure 4.2. $1s$ orbital densities of neutral and ionized helium, as compared to lithium hydride, obtained at a HF/decontracted cc-pCVQZ level of theory. Densities scaled as $r^2\rho$, with the He^+ results rescaled for the same area.

hyde. Reported here are the isosurfaces for isosurface values of 0.1, *i.e.* the points in space in which $\rho = 0.1$. Looking first at the neutral system, it is clear that oxygen has the most charge, seeing that it is both heavier and more electronegative. Removing then a core electron from oxygen, the reduced screening of the oxygen nucleus now attracts more electrons from $-\text{CH}_2$, depleting mainly the carbon-site electron density. In the $Z + 1$ this ionization effectively yield fluorine on the left-hand side, which is very effective in attracting charge. For carbon core-ionization, the charge is instead attracted towards the carbon with the depletion seeming most significant for the hydrogen sites. In the $Z + 1$ approximation the carbon atom is replaced by nitrogen, which is still less electronegative than oxygen.

4.1.2 Correlation effects of core electrons

As discussed in Section 2.1.2, a mean-field theory such as Hartree–Fock lack the correlation effects of the electronic system. As this is one of the key properties in modern quantum chemistry, we will now consider the correlation effects of the core electrons, both for a set of neutral and heavily ionized noble gases.

In Table 4.1 the correlated and uncorrelated total energies of the neutral gases are reported, explicitly correlating all, only the $1s$, or all except the $1s$ electrons. From this we can investigate the total correlation energy, as well as the core-core and valence-valence correlation energy. First, the total energies of the noble gases are seen to increase significantly, as well as the influence of relativity. For the latter, the total relativistic effects increase from 0.0 to 36.8 Hartree, or 0.003 to 1.3% of the total energy. By comparison, the total correlation effects goes from 0.0 to 1.0 Hartree, or 1.4 to 0.04% of the total energy, thus decreasing its relative significance markedly with growing Z . In terms of orbital densities, orbital

Figure 4.3. Density isosurfaces of neutral and core-ionized formaldehyde, as obtained at a HF/decontracted cc-pCVQZ level of theory. Core-hole indicated by +, and the isosurface values selected as 0.1.

contractions amounts to 1.00–1.04. We note that the total contraction of the orbital density increase close to linearly with Z , with $Zr_{\max}^i$ amounting to 1.0–1.1 for the atoms in consideration. This is in good agreement with the results presented in Ref. [190].

Focusing on the correlation energy, the freezing of the $1s$ or valence orbitals yields estimates of the valence-valence and core-core correlation energy, respectively, with remaining discrepancy to the total correlation energy an effect of core-valence correlation. For the isolated core-core correlation, the correlation energies are found to be close to independent on the atomic system. This can be understood as a balance between the increasing correlation between the contracted $1s$ orbitals (increasing with Z), balanced against the decreased volume with is to be integrated over to obtain the correlation energy (decreasing with Z) — the correlation energy *density* increase, but this is integrated over a smaller volume and thus yields only minor effects for the *total* energy. By comparison, the valence-valence correlation energy increases with Z , but if we consider the valence-valence correlation energy per valence electron, the measure instead decrease with Z . Again, we note the difference between the correlation energy density and the total correlation energy, and further note that while CCSD is exact for two electrons, it will give a small error for other cases. Finally, we observe that the core-valence correlation energy is seen to increase with Z , superseding the pure core-core correlation energy for krypton.

In order to remove the influence of the valence-valence and core-valence correlation effect we now consider the same noble gases when only the $1s$ orbitals are occupied. The HF and CCSD results for these systems are found in Table 4.2, and we here note that CCSD gives the full CI results, *i.e.* corresponds to the highest

ⁱ $r_{\max}$ is here defined as the maximum of $r^2\rho$, as expressed in Bohr radius.

Table 4.1. Correlation energies of noble gases, comparing HF results with results obtained at a CCSD level of theory. HF orbitals relaxed of partially frozen to obtain orbital-explicit correlation energies. Also include relativistic energetics and contractions of the $1s$ orbitals. CCSD results obtained using the DKH2 scalar relativistic Hamiltonian, with comparisons done to HF results at the same level. Reported HF relativistic energies and $r_{\max}$ obtained using a fully relativistic Hamiltonian — thus note that the correlation energies are not from a comparison to the reported HF energies. All energies expressed in E_h , and distances in a_0 .

Mol.		HF		Correlated			Δ_{corr}^b
		Rel.	NR	All	Valence	Core	
He	E_{tot}	2.862	2.862	2.903	-	2.903	0.000
	E_{corr}			0.041	-	0.041	
	$r_{\max}^a$	0.568	0.568				
Ne	E_{tot}	128.688	128.543	129.034	128.978	128.716	0.021
	E_{corr}			0.353	0.297	0.035	
	$r_{\max}^a$	0.103	0.103				
Ar	E_{tot}	528.683	526.816	529.060	529.010	528.661	0.016
	E_{corr}			0.433	0.383	0.034	
	$r_{\max}^a$	0.056	0.057				
Kr	E_{tot}	2788.882	2752.039	2788.045	2752.055	2789.058	0.059
	E_{corr}			1.023	0.926	0.038	
	$r_{\max}^a$	0.027	0.028				

^a r of $[r^2\phi_{1s}^2]_{\max}$. ^b $\text{CORR}_{\text{all}} - \text{CORR}_{\text{valence}} - \text{CORR}_{\text{core}}$

level of theory on the N -particle axis in Fig. 2.1. The correlation energies obtained here are similar to the core-core correlation energies reported in Table 4.1, differing by up to 0.016 Hartree. Correspondingly, the $r_{\max}$ values are left relatively unaffected by the removal of all valence electrons. Comparing instead the HF orbital energies, the ionized atoms have an increase in energies by 36, 28, and 21% for neon, argon, and krypton, respectively (the helium energies differ by less than 0.1%, due to the use of different basis sets). Relativistic corrections now amount to 0.0–22.1 Hartree, differing by 0.006 Hartree for krypton at a HF or CCSD level of theory. From this, we see that the relativistic effects of the Kr^{+34} and Kr are very similar, as $1s$ is most strongly affected, and that relativistic and correlation effects are non-additive. Further, we again see that correlation effects dominate over relativistic effects for helium (with a relation 410:1) while the opposite is the case for ionized krypton (1:440).

4.1.3 Ionization potentials along the periodic table

In order to obtain an estimate of the ionization potentials (IPs), the orbital energies can be used as per Koopmans' theorem. However, this gives a reasonable

Table 4.2. Correlation energies of ionized noble gases, as obtained at a HF and CCSD level of theory. Results obtained using a non-relativistic and DKH2 scalar relativistic Hamiltonian, and we further report maxima of non-relativistic and and fully relativistic HF densities. A decontracted cc-pVQZ developed for krypton used for all systems. All energies expressed in E_h and distances in a_0 .

Mol.		$r_{\max}^a$	HF	CCSD	E_{corr}
He	Rel.	0.570	2.8616	2.9029	0.0413
	Non-rel.	0.570	2.8615	2.9028	0.0413
Ne ⁺⁶	Rel.	0.102	93.9766	94.0210	0.0444
	Non-rel.	0.103	93.8611	93.9051	0.0440
Ar ⁺¹⁶	Rel.	0.056	314.1588	314.2044	0.0456
	Non-rel.	0.057	312.8611	312.9053	0.0442
Kr ⁺³⁴	Rel.	0.027	1295.6623	1295.7119	0.0496
	Non-rel.	0.028	1273.6110	1273.6551	0.0441

^a r of $[r^2\phi_{1s}^2]_{\max}$.

approximation only for the higher valence electrons, as these orbital energies lacks any relaxation effects. More accurate measures can be obtained by, for example, using a Δ SCF approach (*i.e.* comparing neutral and ionized total energies) or using response theory. The latter can be obtained by calculating the excitation energy for transitions to a very diffuse state, approximating excitations to the continuum.^{156,192} However, for single-determinant electronic structure methods, no relaxation effects are obtained. This is as a single electron can be excited, but no electron can simultaneously be relaxed — by comparison, including doubles in the coupled cluster manifold a simultaneous excitation and relaxation can occur, as will be described later. As such, linear response ionization potentials at a TDHF or TDDFT level of theory should be identical to orbital energies, as has been investigated for ethene in Table 4.3. Excellent agreement is found, with only a minor discrepancy for HF, and it is thus possible to obtain TDHF and TDDFT estimates of IPs from ground state HF and KS-DFT orbital energies.ⁱⁱ

With this approach established, in Fig. 4.4 we report the experimental ionization potentials and the orbital energies from HF and KS-DFT, considering the elements of the periodic table up to $Z = 54$ (xenon). Here we illustrate the IPs of $1s$, $2s$, $2p_{1/2}$, and $2p_{3/2}$, as well as investigating scalar and spin-orbit relativistic effects and error in the theoretical K -edge IPs. Turning to the analytical solution of the hydrogenic system given in Eq. (2.63), we see that the IP should have an approximate quadratic dependence on Z . This is indeed observed, with IP/Z^2 of the K -edges being equal to 13.6 for hydrogen and 11.9 for xenon. In terms of the

ⁱⁱFormally the KS orbitals and orbital energies are mere constructs for the total density, but from the ethene example we see that they indeed can be given some physical interpretation.

Table 4.3. Carbon 1s ionization potential of ethene, as estimated using orbital energies and transitions to very diffuse states (10^{-8}), compared against experiment. Results obtained using a double- ζ basis set, and all energies are expressed in eV.

Method	Orbital energy	Excitation energy
HF	305.85	305.84
BLYP	269.95	269.95
CAM-B3LYP	279.17	279.17
Experiment ¹²⁹	290.8

Figure 4.4. Ionization potentials in the periodic table for $Z = 1-54$, as estimated from KS-DFT (red) and HF (green) orbital energies, obtained in a relativistic setting. Experimental¹⁹³ ionization potentials of the K -edge given as black line. Ionization potentials of K -, L_1 -, and $L_{2,3}$ -edges in panels (a), (b), and (c), respectively. Relativistic effects of K -edge in panel (d) and of L_1 -edge in panel (e). Spin-orbit splitting of $2p$ in panel (f). Absolute and relative errors of the theoretical K -edge in panels (g) and (h), respectively. Theoretical result obtained using a decontracted 3-21G basis set.

influence of relativity, the scalar effects of the K - and L_1 -edges are reported in panel (d) and (e), respectively, and the spin-orbit splitting of the $L_{2,3}$ -edge is found in panel (f). The scalar relativistic effects are most prominent for the contracted 1s orbitals, amounting to up to 1200 eV (or 3.6% of the total energy). Considering the hydrogenic system, Eq. (2.63), the relativistic effects should increase as Z^4 , and for neon the IP/Z^4 value is reported as 1.0×10^{-4} , and corresponding value for

xenon is 1.4×10^{-4} . For the spin-orbit splitting Eq. (2.63) again give a Z^4 dependence for the hydrogenic system, and the Z^4 here are reported as 7.0×10^{-5} and 3.0×10^{-4} for neon and xenon, respectively. As such, the trends of the hydrogenic system are qualitatively well reproduced, with somewhat higher discrepancies for the higher orbitals.

Comparing the *K*-edge IPs to experimental values, panel (g) show the absolute error for HF and DFT, and panel (h) illustrates the relative errors. For low Z HF overestimation the IPs for low Z , and underestimates them for high Z . The former is due to the lack of relaxation effects, leading to a too unstable core-ionized state, and the latter is likely due to difficulties in correctly reproducing the electronic structure of the high electron density specimen. In comparison, the self-interaction error of approximate exchange-correlation functionals in DFT leads to underestimations of IPs. Approximate fitting of the DFT error (attributed mainly to the SIE, even if lack of relaxation, insufficient basis sets, and other factors also are in effect) to Z shows a $Z^{1.7}$ behaviour for $Z \geq 10$.ⁱⁱⁱ For lighter elements the error behaves more erratically, such that no good estimation can be obtained. As a result of SIE behaviour and the Z^2 behaviour of the IP, the relative discrepancy due to the SIE decrease with Z , as demonstrated in panel (h). For the relative errors, the DFT orbital energies of hydrogen and helium are significantly underestimated, as the self-interaction error is more substantial if there are no other electron-electron interactions available. The large absolute energy dependence of low- Z atoms further yields large errors for HF and, to a smaller degree, DFT estimates of lithium and beryllium. In terms of HF, the apparent decrease in relative relaxation effects can be understood as a result of the reduced screening being less influential for the very compact, high- Z elements — a very simple analysis can be given by considering $1s$ orbital energies combining Eq. (2.63) with the $Z + 1$ approximation

$$\frac{\Delta E_{\text{relaxation}}}{E} \propto \frac{Z^2 - (Z - 1)^2}{Z^2} = \frac{2}{Z} - \frac{1}{Z^2}, \quad (4.1)$$

which goes to 0 as $Z \rightarrow \infty$.

4.1.4 Relaxation in the coupled cluster hierarchy

In connection with the construction of the exact state linear response function in Eq. (3.20) it was concluded that the calculation of complex polarizability by this mean is in principle exact. As such, the relaxation effects for any approximate state damped linear response functions depends only on the quality of the electronic structure method and is thus treated on par with electron correlation. In coupled cluster, the electron correlation is included by excitations to virtual orbitals, and relaxation effects are thus included by the use of an appropriately large excitation manifold. Noting that an excitation manifold of single excitations can describe only the excitation of the core electrons, *i.e.* no relaxation effects, it is clear that at least an approximate doubles excitation manifold is necessary.

ⁱⁱⁱMore explicitly, $|\Delta E/Z^{1.7}|$ is equal to 0.58, 0.53, 0.46, and 0.52 for neon, argon, krypton, and xenon, respectively.

In Fig. 4.5 the carbon K -edge X-ray absorption spectrum is investigated using the hierarchy of coupled cluster methods CCS, CC2, CCSD, and CCSDR(3), as compared against experiment.¹²⁹ Since the CCSDR(3) method only corrects the CCSD energetics and leaves the transition energies unaffected, the results are included as the CCSDR(3) shifts in the panel for CCSD. The integrated absorption cross-sections I_S are also reported, in order to investigate the non-variational nature of coupled cluster. Similar comparisons for other molecular systems can be found in Papers [I-III]. method in turn.

At the CCS level of theory, the error in absolute energy amounts to 10.09 eV, consistent with previous findings of 7–21 eV.^[I-III] These overestimations are mainly due to the lack of relaxation effects, and especially of the 'direct' relaxation effects. Comparing the discrepancies of the different edges, the relaxation effects increase with the excitation energy, amounting to 7–11, 14, 16–17, and 21 eV for excitations from the core of carbon, nitrogen, oxygen and neon, respectively. In relation to the experimental excitation energies, this amounts to discrepancies of 2–4%. In principle, an error in absolute features could be acceptable, provided that the relative features are of sufficiently high quality — the different edges of the different elements are typically separate enough in terms of energies such that mistaken the edges is very improbable. Unfortunately, the flaws of CCS are not restricted to an error in absolute energies, but the spectral features are also erroneous, and the method is thus unreliable. This is by no means unexpected.

Including approximate double excitations with the CC2 method, the error in absolute energy is decreased by over 7 eV and overall spectral features are significantly improved, but the fine structure details are still unreliable. In general, the absolute energies of CC2 are typically in good qualitative agreement with experiments, in some cases out-performing that of CCSD, but the spectral region is often compressed.^[I-IV] While investigated chemical shifts are in excellent agreement with experiment,^[II] the high-frequency features of an individual core are often too close in energy, and this is partially attributed to insufficient polarization effects. Approaches which does not account for the polarization effects typically gives a too compressed spectrum,^{17, 18} An additional discrepancy observed for CC2 is that the intensity of the features are underestimated as compared to CCSD for all considered systems save π -conjugated molecules. The reason for this behaviour is currently not understood. In general, CC2 is seen to be a viable option for the study of intense features, especially for $1s \rightarrow \pi^*$ transitions, but care must be taken for any fine structure details.

With the full double excitation manifold included in the CCSD method, the error in absolute energy is decreased further and, more importantly, the spectral features are now in excellent agreement with experiment. The CCSD energetics are then further improved by the CCSDR(3) method, approximately accounting for the triple excitations and decreasing the $1s \rightarrow \pi^*$ transition energy by 0.71 eV. It is to be noted that the CCSDR(3) method requires well converged eigenvectors, thus requiring the Lanczos chain length to be large to ensure convergence of the pseudovectors, or enforcing the use of a core-valence separation scheme.¹⁵⁶

The total integrated absorption cross-section is observed to undershoot the correct value (C_2H_4 , *i.e.* 16 electrons) for CCS, overestimate the necessary positive

correction at a CC2 level and instead overshooting the correct value, and bringing it down slightly at a CCSD level. This again illustrates the non-variational nature of CC, and the remaining discrepancy can be understood as a combination of an insufficient treatment of the CC excitation manifold and an incomplete basis.

Figure 4.5. Relaxation effects in the CC hierarchy, as illustrated for the spectrum of ethene. TZ basis set. X-ray absorption spectra of ethene as obtained with a hierarchy of CPP-CC methods and compared against experiment.¹²⁹ The results are aligned against the first experimental transition, with corresponding shifts given beneath each model label, as expressed in eV. Included is also the total integrated absorption cross-section I_S . Basis set chosen as aug-cc-pCVTZ/cc-pVTZ for C/H, augmented by Rydberg ($3d3p3d$) functions at the centre of the C–C bond. Lanczos chain lengths $j = 6000$ and 8000 for CC2 and CCSD, respectively, and the full excitation space was utilized for CCS. Shift for CCSDR(3): -0.74 eV.

4.2 Treating larger systems

As the coupled cluster method is too computationally demanding to treat systems of any larger sizes, it is in the discussed form unviable for anything but small molecules in gas phase (consider the scaling of the method illustrated in Table 2.1). In order to consider larger molecules or condensed phase, we will first consider the benchmarking of more approximate electronic structure methods. Following this, a brief discussion on the challenges of including molecular dynamics and long-range corrections will be included.

In order to include correlation effects in a computationally favourable manner, one is well advised in turning to density functional theory. In fact, as discussed in Section 2.2, a large part of the great developments in quantum chemistry in the last decades is due to advances in DFT, especially in terms of enabling quantum chemical calculation for non-experts. However, in order to utilize such more approximate method, it must first be established that they yield sufficiently reliable correspondence to high-quality calculations or to experimental measurements. This is especially the case for DFT, for which the quality of any calculation is very much dependent on the exchange-correlation functional.

Focus here will be on the use of TDDFT for X-ray absorption spectra, as compared to coupled cluster calculations and experiments. It is to be noted that TDDFT is not the only DFT-based method applicable to core-excitation processes, nor is the linear response formalism the only way of formulating TDDFT — for the latter we have earlier discussed the possibility of real-time propagation,^{33, 168} and for the latter there exists state-specific methods based on ground state DFT (one of which is used in Paper [IV]).^{13, 15, 16} A major concern here is that TDDFT lacks relaxation effects, as has been discussed in connection to the ethene example of Table 4.3, and one would thus assume that TDDFT is relatively useless for the simulation of X-ray absorption spectra. However, as we shall see, this is not the case.

In Fig. 4.6 the X-ray absorption spectrum of 1,1-difluoroethene is reported, as obtained using TDDFT and CCSD and compared against experiment.¹²⁹ For TDDFT a Coulomb-attenuated B3LYP functional with parameters tailored as from Ref. [194] was used, designated CAM-B3LYP_{100%},¹⁹⁰ for which good results have been found against experiment. This functional has 100% asymptotic exact exchange, *i.e.* $\alpha = 0.19$, $\beta = 0.81$, and $\gamma = 0.33$, which change mainly the relative features while the absolute energies are similar to that of standard CAM-B3LYP ($\beta = 0.46$). The comparison to experiment and CCSD in terms of relative features is excellent, with well reproduced chemical shift for both methods. Comparisons for the spectra of vinylfluoride and trifluoroethene can be found in Paper [III], showing the same behaviour for DFT and CCSD as for 1,1-difluoroethene. Focusing on the chemical shifts, it has been demonstrated that TDDFT gives excellent shift for all three systems, with discrepancies of 0.03–0.08 eV, while CC performs slightly worse, 0.03–0.09 and 0.07–0.23 eV for CC2 and CCSD, respectively. The systems were selected as the chemical shifts are substantial owing to the influence of the very electronegative fluorine atoms — the valence electrons are strongly attracted and thus reduced the screening experienced by the carbon core elec-

trons, increasing the binding energies. As such, the relaxation effects following core excitations are very site-specific and this thus offers a good test of theoretical methods. The molecules are also good examples of the important class of π -conjugated systems, interesting especially for the study of bio-molecules. These molecules possess easily identified $1s \rightarrow \pi^*$ transitions, which was the focus of the comparative study.^[III]

Figure 4.6. Carbon K -edge spectra of 1,1-difluoroethene obtained by TTDFT and CCSD calculations and compared to experiment. Theoretical $1s \rightarrow \pi^*$ have been align to experiment,¹²⁹ with shift reported beneath each model label as expressed in eV. Basis set aug-cc-pCVDZ for carbon, cc-pVDZ for the remaining elements, and additional Rydberg ($3s3p3d$) have been centered at the center of the C-C bond. Lanczos chain length $j = 4000$. Vertical dashed line second experimental $1s \rightarrow \pi^*$ energy.

Considering the influence of different exchange-correlation functionals, the carbon K -edge X-ray absorption spectrum has been calculated using a number of different exchange-correlation functionals, as reported in Fig. 4.7. These results can be compared to those of Fig. 2.3, where only the absolute transition energy of $1s \rightarrow \pi^*$ of ethene was considered. Again, it is seen that at least a GGA functional is necessary for any qualitative agreement to experiment, and the hybrid functionals improve the relative features even more. The range-separation scheme

of CAM-B3LYP leaves the absolute energy close to unaffected, correcting mainly relative features. It is noted that CAM-B3LYP and CAM-B3LYP_{100%} yield similar features, with some improvement in the CAM-B3LYP_{100%} features for the experimental band at ~ 288.3 eV and the high-energy features.

As can be seen, TDDFT can indeed yield excellent agreement to experiment in terms of relative features, even if the self-interaction error yields improper absolute energies. The self-interaction error will be discussed in some detail in Section 5.2, but we here note that it can, in principle, be decreased by use of self-interaction correction methods or by using functionals tailored for core-excitations. Studies on the performance of TDDFT for electronic transitions are numerous, especially for valence transitions for which Ref. [195] is a good starting point, with smaller numbers dedicated to core-excitations.¹⁹⁶ Additional considerations can be found in the review of Besley and Asmuruf,⁹ and it is further noted that the computational costs of TDDFT can be decreased further by using the Tamm–Dancoff approximation, and by relaxing the resolution of the numerical integration grid and the threshold of two-electron integrals.¹⁹⁵

4.3 Calculating the X-ray absorption spectrum of water

You can't cross the sea merely by standing and staring at the water.

R. Tagore, 1910¹⁹⁷

As previously stated, X-ray absorption spectroscopy gives a tool highly suitable for the investigation of local structure, due to the very element specific absorption energies and probing of local unoccupied states. As such, it is not surprising that a X-ray absorption study⁴² was the spark that awoken a discussion on the local structure of water, a debate that remains ongoing. In Paper IV we addressed concerns on the ability of methods used for calculating the X-ray absorption spectra of liquid water, as well as produced state-of-the-arts TDDFT results. In this section we will discuss the hydrogen-bond (H-bond) effects on the absorption spectrum, as well as the spectra of different phases of water.

4.3.1 Effects of hydrogen-bonding

Due to the hybridization of the LUMOs of gas phase water, the lowest excited states are sensitive mainly to H-bond donation, and remains relatively unaffected by H-bond acceptance.^{14,198} In Fig. 4.8 this is illustrated at a TDDFT and CCSD level of theory, reporting the spectra of gas phase water as well as of a water dimer. If the probed water molecule accepts a H-bond, a small blue-shift and minor changes in high-energy features occur. However, if the molecule instead donates a H-bond, significant changes in the spectral features result. The low-frequency transition energies are now similar to that of gas phase water, but these features are markedly reduced, and some intensity is instead found in the high-energy region. In Paper [IV] it is demonstrated that this decrease in low-energy

Figure 4.7. Carbon *K*-edge spectra of 1,1-difluoroethene obtained by TTDFT calculations and compared to experiment. Theoretical results aligned to experiment, with shift reported beneath each model label as expressed in eV. Vertical dashed line second experimental $1s \rightarrow \pi^*$ energy.

features is even larger for water trimers, especially when two H-bonds are donated. This is due to the LUMOs being directed towards the hydrogens, and these gain *s*-character due to H-bond donation, which decrease the transition moment of the

low-energy excitations. From this, we can immediately expect a H-bonded water system to have intensity moved to higher energies, and should thus be able to use the spectral features as a measure on the amount of H-bonded molecules.

Figure 4.8. H-bond effects on water X-ray absorption spectra. Using a $6s6p6d$ set of diffuse functions. Include pictures of structures in the figure.

4.3.2 The different phases of water

The theoretical and experimental spectra of gas phase water, liquid water and ice are reported in Fig. 4.9, as obtained using TDDFT as well as transition state DFT. The difference in spectral features is striking, with especially gas phase water exhibiting significantly dissimilar spectrum. Moving to the liquid phase, it is first clear that the pre-edge onset is blue-shifted, and intensity is moved to higher energies. The spectrum consists of mainly three features, designated as the pre-, main-, and post-edge region at approximately 535, 535, and 541 eV, respectively. For the solid phase, a reasonable first expectation could be that the spectrum is similar to that of the liquid, save for less defined features due to vibrational and other dynamical effects in the liquid smearing out the features. However, this is not observed for water, instead exhibiting a redistribution of low-energy intensity to the post-edge. The ice spectrum then shows a very weak pre-edge, expected to decrease further for a ice sample with less impurities. This somewhat unexpected difference compared to liquid phase is part of the argument for liquid consisting of two underlying structural motifs. In general, the agreement to experiment is very good for TDDFT, here considering that the ice spectra were obtained using a single structure, and more difficult to resolve using transition potential DFT.

For the latter the gas phase spectrum is good, but there are general difficulties in identifying the pre- and post-edge features of the condensed phases. Furthermore, it can be noted that the theoretical results — especially at the TDDFT level of theory — shows a splitting of the post-edge feature of ice, as well as a forth feature in the TDDFT spectrum of liquid water at ~ 544 eV. The former has been experimentally resolved,⁵⁹ while it is currently unknown if the latter is a physical feature or a computational artifact.

Figure 4.9. X-ray absorption spectra of the different phases of water. Using a 19s19p19d set of diffuse functions.

For both the dynamics and response calculations it is desirable to utilize an as big cluster as possible, be that using periodic cells or finite clusters. Ideally, the entire cell/cluster should be treated at a quantum mechanical level of theory, but this would restrict any treatments to very small samples. In order to capture long-range effects it is thus possible to add a region which is not considered at a QM level of theory. This can be done using different embedding schemes, and using explicit embedding, interactions with long-range structure can be included, and many schemes and levels of approximations can be used^{155, 199–201} — recent development also includes the possibility of using densities from DFT calculations in order to calculate the potential affecting the QM region.²⁰² In this thesis we have utilized polarizable embedding as developed by Kongstedt *et al.*,²⁰⁰ for which a self-consistent way of treating the interaction between the MM region and the excited state is included.

In order to account for long-range interactions in a computationally feasible manner, a polarizable embedding scheme can be highly beneficial. In Paper [IV] the performance of such a subdivision is investigated, and some of the most important results are reproduced in Fig. 4.10. Here the average spectra of ten structures

are illustrated, using four different divisions. First, a pure QM calculation with 32 molecules is considered, compared mainly to QM/MM calculations for which 24 molecules are treated quantum mechanically, and a classical layer is placed outside of this such that the total cluster has a radius of 30 Å. Good agreement are obtained between these divisions, with the QM/MM calculation exhibiting somewhat sharper features. As demonstrated in Paper [IV], it is thus clear that it is possible to decrease the number of QM molecules while retaining the reliability of the theoretical spectra, potentially leading to significant reductions in computational costs. The gas phase spectrum is additionally included for comparisons, and it is clear that the liquid exhibits more intensity in the high-energy region (note that the gas phase spectra is rescaled), as well as a blue-shift of 1 eV. Additionally, using the QM/MM division from Ref. [155], with a single QM water molecule, some of the blue-shift is retained, but the overall spectral features are too similar to the gas phase spectrum. This was indeed expected, and the division was never meant to reproduce experimental values, but rather illustrate the performance of QM/MM coupled cluster calculations.

Figure 4.10. QM/MM of water. 10 structures. Shift towards experimental pre-edge, expressed in eV.

CHAPTER 5

L-edge X-ray absorption spectroscopy

As of yet, the discussion has been limited to core-excitations from s orbitals, for which relativistic effects are restricted to a scalar shift in energy. Considering now excitations from p orbitals, it becomes necessary to include spin-orbit coupling in order to obtain the splitting from the $p_{1/2}$ and $p_{3/2}$ orbitals. Such a splitting can be included in a perturbative manner, but this is only viable for weak spin-orbit coupling. Instead, a four-component setting can be utilized in which the spin-orbit coupling is included in the zeroth-order Hamiltonian and thus arise naturally. The performance of damped TDDFT in such a setting has been investigated for valence-excitations in Paper [V], and for core-excitations in Paper [VI]. Focusing now on core-excitations, the performance of this method will be demonstrated for silane derivatives, and an anomalous discrepancy in absolute energy observed for the $L_{2,3}$ -spectra of silicon tetrafluoride will be discussed in some detail.

5.1 Reproducing experimental measurements

If it disagrees with experiment it is wrong. In that simple statement is the key to science. It does not make any difference how beautiful your guess is. It does not make any difference how smart you are, who made the guess, or what his name is — if it disagrees with experiment it is wrong. That is all there is to it.

R. P. Feynman, 1965⁷²

Before moving on to a discussion on how to reproduce the experimental spectrum of silicon tetrachloride (SiCl_4), we need to address an unfortunate basis set dependence noticed for some of the systems and basis sets considered here. In Fig. 5.1 the $L_{2,3}$ -spectrum of SiF_4 is reported, as obtained with no restriction of the excitation channels, as well as restriction to the $2p$ orbitals or all orbitals with above $2p$.

In general, the core-excited states are embedded in the continuum, and they can thus be plagued by unphysicalⁱ valence-valence excitations. However, in all cases reported thus far this has not been the case, as the energies are sufficiently high such that any virtual states of corresponding energies likely have too small overlap with the occupied valence states. However, comparing the different restrictions of the excitation channels in Fig. 5.1, it is clear that unphysical valence-valence excitations significantly affect the energy region of interest. These features occur mainly for basis sets of triple- ζ quality, being absent for double- ζ calculations. If the basis set is sufficiently well saturated, they are expected to more or less disappear, as this would lead to a more smooth continuum with low intensity over large regions. At present, the most practical manner by which they can be avoided is to restrict the excitation channels to the relevant orbitals, which somewhat counteracts one of the most important advantage of the damped linear response method. However, as will be shown, the total density-of-states even with such a restriction still remains large and gives difficulties for a resolution of eigenstates.

Figure 5.1. Basis set dependence of four-component TDDFT spectrum calculation of the $L_{2,3}$ -edge of SiF_4 . Results obtained at a CAM-B3LYP_{100%}/triple- ζ level, augmented with core-polarizing functions and a double set of diffuse function for silicon.

With this issue accounted for, let us now consider the reproduction of reliable SiCl_4 $L_{2,3}$ -spectra, as reproduced using a number of different approximations in Fig. 5.2, compared against vibrationally resolved experiment.²⁰³

5.1.1 Electron correlation

In panels (a) and (b) TDHF and TDDFT results are reported, as obtained in a non-relativistic setting. These and all other theoretical results have been aligned

ⁱFor any calculation using an incomplete set of localized basis functions, as the continuum is then falsely discretized.

to experimental a_1 feature (for the non-relativistic results in-between the two features). Temporarily disregarding the issue of spin-orbit splitting, both TDHF and TDDFT gives reasonable relative energies and intensities of the a_1 and t_2 features, but TDHF exhibits difficulties to properly reproduce high-energy features. This is not surprising, seeing the very approximate nature of HF, lacking the important electron correlation effects.

5.1.2 Spin-orbit effects

From the projected total angular momentum in Eqs. (2.66) and (2.66), and the related discussion, it is clear that $2p_{3/2}$ of silicon is populated by four electrons, and $2p_{1/2}$ by two electrons. Furthermore, $2p_{3/2}$ is higher in energy, and a very naive account of spin-orbit effects in the $L_{2,3}$ -spectrum can be achieved by shifting two thirds of the intensity to lower transition energies, and one third to higher transition energies. The total relative shift should be equal to the spin-orbit splitting, as can be obtained from approximate spin-orbit expressions, corrected ground state calculations, or experiments. For simplicity the shift in either direction is here taken to be identical, amounting to 0.3 eV. The result is illustrated in Panel (c), and it is clear that the low-energy features are erroneous, with experimental measurements yielding approximately an intensity relation of 1:2 instead of 2:1. This non-statistical branching ratio can be found for a number of systems, and has been attributed to the delicate balance of between core-hole spin-orbit interaction and electron-hole exchange interaction.^{18,204–207} If only core-hole spin-orbit interactions are in effect, the branching ratio should be the statistical 2:1, but electron-hole exchange effects change the situation. This can be demonstrated by restricting the excitation channels in a relativistic calculation to only allow excitations from $2p_{1/2}$ or $2p_{3/2}$, and the results of such a division is demonstrated in panel (d). The erroneous 2:1 branching ratio from panel (c) is then reproduced. Instead simultaneously allowing excitations from $2p_{1/2}$ and $2p_{3/2}$, reported in panel (e), excellent branching ratio is achieved, and the theoretical spectrum is in good agreement to experiment, barring the lack of vibrational resolution. It is especially gratifying to see that the non-statistical intensity distribution is accounted for in the theoretical spectrum.

Figure 5.2. $L_{2,3}$ spectra of SiCl_4 , as obtained using damped linear response theory in the four-component regime and compared to experiment²⁰³ (f). Theoretical results obtained using (a) non-relativistic TDHF, (b) non-relativistic TDDFT, (c) non-relativistic TDDFT with a naive spin-orbit correction (as explained in the text), (d) relativistic TDDFT, and (e) vibrationally corrected TDDFT. Theoretical results obtained using a triple- ζ basis set with core-polarizing functions and triple set of diffuse functions on silicon. Theoretical results aligned to experiments using shift given beneath each panel label. TDDFT results obtained using the CAM-B3LYP_{100%} functional.

5.2 Anomalous energy discrepancy of silicon tetrafluoride

The most exciting phrase to hear in science, the one that heralds new discoveries, is not 'Eureka!' but 'That's funny...'

I. Asimov²⁰⁸

The $L_{2,3}$ -edge X-ray absorption spectra of SiH_4 , SiF_4 , and SiCl_4 have been considered in a fully relativistic setting, as compared against experiment²⁰³ in Fig. 5.3. The first experimental a_1 features to which the theoretical results have been aligned are estimated to be at 102.6, 106.1, and 104.4 eV for SiH_4 , SiF_4 , and SiCl_4 , respectively. In general, the agreement to experiment is good, especially for the low-energy features. However, the energy shift required to align to experimental spectra differs noticeably, with that of silicon tetrafluoride diverging from those of the other two molecules by almost 1 eV, or by approximately 20%.

Figure 5.3. $L_{2,3}$ -edge X-ray absorption spectra of silanes, as obtained using TDDFT and compared against experiment.²⁰³ Results obtained at a CAM-B3LYP_{100%}/triple- ζ level of theory with additional core-polarizing and double set of diffuse functions. Theoretical spectra aligned to first a_1 feature with shifts reported beneath each system label.

Previous studies on a set of exchange-correlation functionals have been reported to exhibit relative errors as compared to experiment of 0.03–1.75, or 0–88%. Here the results of the BHH and BHHLYP functionals were seen to be most erroneous, and removing those results yielded discrepancies of 0.03–0.88 eV, or 0–10%. The largest relative errors were in most cases exhibited by the $\text{C } 1s \rightarrow \pi^*$ of CO as compared to $\text{C}_2\text{H}_4/\text{CHFO}$, or the $\text{O } 1s \rightarrow \pi^*$ of N_2O versus CHFO. Here $\text{C}_2\text{H}_4/\text{CHFO}$ exhibits the smallest error as compared to experiment for C. By

comparison, the self-interaction correction has previously been seen to vary by, at most, 0.2 and 0.4 eV for oxygen and carbon *K*-edge ionization potentials, considering 14 different molecular systems.¹¹¹ For the CAM-B3LYP_{100%} functional no significant variations have been observed for other molecular systems. While this variation in energy discrepancy is not a major concern for the results in Fig. 5.3, such variations need to be addressed if any systems considering several chemically inequivalent core atoms are to be considered — as previously stated, the priority is that the relative features are reliable. As such, this anomaly of silicon tetrafluoride need to be investigated, and we will now expand on the analysis presented in Paper [VI].

The total error in energetics is a result of not only the SIE, including errors from, *e.g.*, incomplete basis sets, lack of relaxation, and additional errors in TDDFT. As such, there are a number of possible origins for the anomaly. Focusing instead on the different substitutions, it is to be noted that the system with fluorine gives the divergent results. Being the most electronegative element in the periodic table, fluorine is highly proficient in attracting electrons from other atoms, strongly affecting the valence electron density. A substitution with four fluorine atoms would thus give a significant effect in the electronic structure, and this hints on the source of the anomaly. Nevertheless, considering the computational set-up, calculations using different sets of basis functions are reported in Paper [VI], and it is clear that this is not the origin of the discrepancy. Considering instead the electron density of the core electrons, results obtained for all three silane derivatives are reported in Fig. 5.4. Considering the changes due to the different substitutions, it is clear that the HF densities are not adversely affected, with some minor contraction of the orbital densities observed for the substituted silanes. Interestingly, the results indicate that silicon-substitution has a more significant effect on the core electron densities than fluorine-substitution. Considering the different orbitals, *1s* is affected the least, while the *2s* and *2p* electrons are similarly affected — note here that there are three times as many *2p* electrons as *2s* electrons, so the difference in scale is explained mainly by this.

Considering instead the densities obtained at a DFT level of theory, the change in densities as compared to the HF results is significant, far superseding the differences due to substitutions. The main effect is a decontraction of the core electron densities, as could be expected due to the erroneous self-repulsion discussed in Section 2.2.3. As such, it would appear plausible that DFT calculations could be more affected by substitution than HF calculations.

If more complex molecular systems are to be considered, it is vital to know to which degree the results are reliable, *i.e.*, at which level of substitution the discrepancy is unacceptable. Furthermore, studying partially substituted systems could give more understanding on the behaviour of the anomaly. As such, Fig. 5.5 reports the theoretical ionization potentials (IPs) of silane substituted by zero to four fluorines, as well as population analysis. Unfortunately, no experimental measurements on partly substituted silanes have been found, and we instead interpolate the available IPs and approximate the proper changes as occurring along this line. Panel (a) reports the theoretical and experimental IPs, the latter as obtained using HF and DFT with three different exchange-correlation functionals,

Figure 5.4. Core orbital densities of silane derivatives, as obtained at a decontracted cc-pVQZ level of theory. Results reported in the first two columns obtained using HF, and comparisons to DFT using the CAM-B3LYP_{100%} reported in the third column. Orbital densities scaled as $r^2\rho$.

and panel (b) show the divergence from the interpolated experimental lines. From panel (b) it can be seen that also HF gives an erroneous IP for silicon tetrafluoride, diverging by close to 0.4 eV, while the three DFT results diverge by 0.6–1.0 eV. The divergence from the interpolated trend lines is continuously, amounting to approximately 0.0–0.2 eV for substitution with a single fluorine atom, and 0.2–0.4 eV for substitutions with two atoms. The DFT results of the GGA functional performs the worst, and the long-range corrected hybrid gives best correspondence to experimental estimates. As both the HF and DFT results lacks relaxation, it is clear that part of the DFT discrepancy can be explained by this approximation, but DFT have some additional difficulties. As HF lacks electron correlation and good DFT functionals should possess this, this does not seem to yield the answer either. While the HF results are erroneous in absolute energy mainly due to the lack of relaxation, the self-interaction error of the DFT calculations are even more significant, leading to a total underestimation of transition energies and ionization potentials. We thus attributes the anomaly of the $L_{2,3}$ -edge spectra as being due to difficulties in correctly reproducing the complicated electronic structure when

significant changes are imposed due to fluorine-substitutions, taking the form of erroneous relaxation and self-interaction effects.

Figure 5.5. Ionization potential and population analysis of partially fluorine-substituted silane. (a) Silicon $L_{2,3}$ -edge ionization potentials of partially fluorine-substituted silanes obtained using HF and KS-DFT orbital energies, as compared against experiment (black).²⁰³ Full line indicates interpolated experimental data, and the dashed lines are this interpolated trends lines vertically translated, such that the left-hand end overlaps the IPs of silane on the corresponding theoretical models. (b) Deviation from interpolated IPs. (c) Net Mulliken charge of silicon atom. (d) Population of pure 2p orbitals. Theoretical results using HF (blue), and KS-DFT with the BLYP (magenta), PBE0 (green), and CAM-B3LYP_{100%} (red) functionals. IPs obtained using a decontracted cc-pVTZ basis set and and population analysis obtained at cc-pVQZ level of theory.

In conclusion, there is currently no simple way of removing the differences in the SIE, but we believe that this will, in practice, not be very influential, as most systems of importance will not exhibit such a substantial fluorine-substitution. A more realistically system of interest would likely include a substitution of one or two fluorines at the same site, in which case the electronic structure at silicon (or any other element) will not be as effected, leading to smaller variations of absolute energies — substituting with a single fluorine should yield an error of ~ 0.1 eV, and if the error tolerance can be decreased to ~ 0.3 eV, substitutions of up to two molecules should be viable.

CHAPTER 6

K-edge X-ray emission spectroscopy

Physics is about questioning, studying, probing nature. You probe, and, if you're lucky, you get strange clues.

L. Hau, 2007²⁰⁹

Considering the decay of the core-hole state measured through photoemission, X-ray emission spectroscopy can broadly be divided into a resonant and non-resonant form. For resonant XES, also designated resonant inelastic X-ray scattering (RIXS), the excited core-electron is still bound to the molecule and need to be taken into account in the construction of the wave function. By comparison, non-resonant is theoretically more easy to consider, as the core-electron is excited to the continuum and only a core-ionized system need to be considered. As such, this chapter will consider non-resonant XES, presenting the first applications of the damped linear response function for such calculations.

More accurate calculations have been reported using equation of motion coupled cluster theory, featuring an mean absolute deviation of 0.4 eV,²¹⁰ but the method suffers from an unfavorable computational scaling and difficulties in converging the core-hole reference wave function.²¹¹ More approximate method are thus needed for large-scale applications.

6.1 Damped linear response calculation of X-ray emission

For non-resonant X-ray emission spectroscopy a theoretical consideration is achieved merely by using linear response theory on a core-ionized system, for which the negative-energy solutions are the first solutions found if a bottom-up resolution

of the eigenstates is used.⁹ Restrictions in the excitation channels are thus unnecessary, simplifying the use of standard linear response formulations. However, the optimization of the core-hole state can be difficult, as this state will easily tend to collapse to an energetically favoured valence-ionized state. Further, even while no restrictions of the excitations channels are needed, it is still necessary to localize the core-hole, and we thus need to consider each non-equivalent atom in turn. As such, the previous advantages of a damped linear response function are partially moot, even if we still anticipate advantages for condensed phases and large molecules, where the density of states remains high.

For damped TDDFT calculations of XES, tests highlight the need of theoretical developments before such results can be obtained at a TDDFT level of theory, due to difficulties in obtaining a converged ionized state: using standard optimization with direct inversion of the iterative subspace, the core-hole collapse to a valence-hole. However, by relaxing the valence and core electrons in turn, the obtained reference wave function is sufficiently well converged for a calculation of the eigenstates, but a damped linear response calculation fails to converge. A better reference wave function is needed for the complex polarization propagator, as can be obtained using quadratic convergent self-consistent field routines. Unfortunately, these routines are only available for HF in the current version of Dalton.

As an illustration, Fig. 6.1 reports the absorption cross section of core-ionized carbon monoxide, as obtained using the damped linear response function at a HF level of theory. Valence-to-core transitions are seen at the low-energy region, featuring negative absorption due to the emission of photons. At higher energies positive absorption cross section is found, signifying the excitation of the remaining $1s$ electron, *i.e.* the X-ray absorption spectra of core-ionized carbon monoxide. Experimentally, this absorption will be exceedingly weak, as the life-time of the core-hole state before collapsing to a valence-hole state is of the order of femtosecond. With this method, it is thus possible to simultaneously obtain an emission spectrum and an core-hole ionized absorption spectrum. However, in both cases there is currently no electron correlation and, more importantly, relaxation effects, such that the de-excitation energies are underestimated (the final valence-ionized state is too compact) and the excitation energies are overestimated (the final excited two-core-hole state is too diffuse). More accurate methods would instead obtain positive and negative features closer in energy, and these could affect each other for some systems, making the analysis more complicated. It is thus possible that a restriction of the excitation channels could be desirable also for these systems.

For reference, it is noted that the reference wave function used here, which has been optimized using quadratic convergent SCF, gives a final total energy diverging from that of a partially optimized state by less than 0.001 Hartree. The partially optimized state is constructed by sequential freezing of the singly-occupied core orbital and all other occupied orbitals. The latter approach is thus deemed sufficient for standard response calculations, even if it is insufficient for damped linear response calculations.

Figure 6.1. Absorption cross section of core-ionized carbon monoxide, as obtained at a HF/daug-cc-pVDZ level of theory. A larger damping parameter $\gamma = 0.5$ eV is used for esthetic reasons.

6.2 Performance of Hartree–Fock and density functional theory

Using a partially optimized core-ionized state, as is also available for KS-DFT calculations, a bottom-up resolution of TDDFT eigenstates remains viable, even as a damped formulation is not. While applying TDDFT for XAS, the use of this approach for considerations of XES is a relatively recent development, and the applications^{9, 211, 212} found thus far have all used the Tamm–Dancoff approximation (see Eqs. (3.66) and (3.69) and the associated discussion). In Fig. 6.2 the X-ray emission spectrum of gas phase water is reported, as obtained using the full RPA in TDDFT, compared against TDHF and experiment.²¹³ It is immediately striking how few features the X-ray emission spectra contains, as compared to the X-ray absorption spectra of water, as transitions from valence states are now investigated. As previously stated, X-ray emission spectroscopy thus probe the occupied states, while X-ray absorption spectroscopy probe the unoccupied states — the different spectroscopies gives complementary information. Compared to XAS calculations, TDHF now underestimates the emission energies, while TDDFT yields an overestimation. This is due to the opposite influence of relaxation and self-interaction errors when considering de-excitation events: the final state is too compact when relaxation is regarded, yielding too high energy of this state, and the self-interaction error of the final state is underestimated in comparison to that of the initial state, yielding too high energy difference. In terms of performance for relative features, HF and the LDA gives too high and too low energy spacings, respectively. Moving to a GGA functional, the results are partially improved, but good agreement is only found using the hybrid exchange-correlation functionals. All three hybrides used here gives similar results (as the long-range correction gives

small effects here, since we probe the local valence to core de-excitation), with the main difference being the absolute energy of CAM-B3LYP_{100%}. This is consistent with previous results.²¹¹

Figure 6.2. X-ray emission spectrum of water, as obtained using TDHF and TDDFT with different functionals, compared to experiment.²¹³ Theoretical results have been aligned to experiment, with shifts reported beneath each method label, expressed in eV. Dashed vertical lines indicates experimental transition energies. Theoretical results obtained using a partially optimized core-ionized reference state and daug-cc-pVDZ basis set.

In conclusion, we see that TDDFT can be used for XES calculations, even if there are a number of additional concerns when compared to XAS calculations. The damped linear response approach loses some of the very favourable advantages observed for XAS calculations, but we argue that it may still be useful for systems with a large number of valence orbitals. However, before any production calculations can begin, the currently used quantum chemical program require software development.

CHAPTER 7

Conclusions

The performance of the damped linear response function in coupled cluster and time-dependent density functional theory (TDDFT) has been evaluated for applications in X-ray absorption spectroscopy and, for TDDFT, X-ray emission spectroscopy. It has been shown that the damped formalism of response theory has the advantage of being able to directly target any frequency region of interest, thus removing both the need for restrictions of the excitation channels and the need to consider unimportant valence excitations.

In coupled cluster theory, the vital relaxation effects exhibited by core-excitation processes are retrieved by including doubles in the coupled cluster excitation manifold, yielding results at a CCSD level of theory in excellent agreement with experiments. Using the approximate doubles method of CC2, term values are typically underestimated, attributed to an insufficient description of the polarization *vis-à-vis* the excited electron, and the spectrum intensities are underestimated for all but π -conjugated systems. The reason for the latter discrepancy remains unknown.

At the TDDFT level of theory, excellent relative spectral features are obtained using a tailored exchange-correlation functional with 100% asymptotic exact exchange, designated CAM-B3LYP_{100%}. The damped formalism is available in both a non-relativistic and a four-component relativistic setting, with the latter enabling the inclusion of spin-orbit splitting in, *e.g.*, $L_{2,3}$ -spectra. For this spectroscopy, a good reproduction of the experimental intensity ratio is demonstrated — while a 2:1 ratio for the L_3/L_2 features can be expected on statistical grounds, exchange interactions in the excited states can significantly alter the situation. With this method, we thus have a black-box scheme by which K - and L -edge X-ray absorption spectra can be calculated on an equal footing. However, a disadvantage of this method is the self-interaction error of standard exchange-correlation functionals, which ensures that the transition energies are significantly underestimated. This could, in principle, be accounted for using self-interaction corrections, or mini-

mized using tailored functionals, but it is argued that it is of highest importance to obtain good *relative* features, and that the *absolute* features are a second priority. As such, we recommend the use of a well-tested functional, even if the absolute energy is erroneous. Potentially more troublesome, however, is the lack of relaxation in TDDFT and an anomalous error in absolute energy obtained for the $L_{2,3}$ -spectra of silicon tetrafluoride (an error of ~ 1 eV, or 20% compared to other silane derivatives). The former aspect is indeed a significant principal problem, but studies have shown that very good features can be obtained nonetheless. For the latter it is argued that the very electronegative nature of fluoride makes it very difficult to emulate the correct electronic structure. The discrepancy will likely be small for systems where silicon is bonded to up to two fluorine atoms, such that larger, more complex, molecules can be considered with the present approach.

Using coupled cluster theory, the performance of TDDFT and transition potential DFT (TP-DFT) have been investigated for small water complexes. Having established similar performance on the complexes for all three methods, TDDFT and TP-DFT have been utilized for calculation of spectra of liquid water and ice, and especially good results at a TDDFT level of theory are reported, as compared to experimental measurements. Using this, spectral features are to be related to local structure, contributing to the active debate on the structure and dynamics of liquid water.

For non-resonant X-ray emission spectra, it has been demonstrated that the damped linear response method can capture both the de-excitation of valence electrons, as well as the absorption spectrum of a core-ionized state. Before damped TDDFT calculations can be applied, however, software development is needed in order to optimize a core-ionized state without it collapsing to a valence-ionized state. Using standard non-resonant response theory, time-dependent Hartree–Fock and TDDFT have been utilized for the non-resonant spectrum of gas phase water, showing good agreement to experiment.

In closing, let us start as we began, by yet again consider the words of arguably the greatest scientist of all time. Maybe this thesis can at least be a tiny, minuscule addition to our attempts of understanding this vast ocean:

What we know is a drop, what we don't know is an ocean.

I. Newton²¹⁴

Bibliography

- [1] Letter from Isaac Newton to Robert Hooke, 5 February 1676, as transcribed in J.-P. Maury's *Newton: Understanding the Cosmos*, New Horizons, London, 1992.
- [2] Voltaire. *Le dîner du comte de Boulainvilliers*, 1767.
- [3] A. Comte. *Philosophie Positive*, 1830.
- [4] P. Norman. *Nonlinear Optical Properties of Fullerenes, Oligomers, and Solutions*. Linus & Linnea AB, Linköping, Sweden, 1998.
- [5] J. P. Marangos. *Contemp. Phys.*, 52:551–569, 2011.
- [6] J. Ullrich, A. Rudenko, and R. Moshammer. *Annu. Rev. Phys. Chem.*, 63:635–660, 2012.
- [7] C. J. Milne, T. J. Penfold, and M. Chergui. *Coord. Chem. Rev.*, 277-278:44–68, 2014.
- [8] J. Stöhr. *NEXAFS Spectroscopy*. Springer, Berlin, 1992.
- [9] N. A. Besley and F. A. Asmuruf. *Phys. Chem. Chem. Phys.*, 12:12024–12039, 2010.
- [10] A. Nilsson, D. Nordlund, I. Waluyo, H. Ogasawara, S. Kaya, U. Bergmann, L.-Å. Näslund, H. Öström, Ph. Wernet, K. J. Andersson, T. Schiros, and L. G. M. Pettersson. *J. Elec. Spec. Rel. Phenom.*, 177:99–129, 2010.
- [11] G. Hähner. *Chem. Soc. Rev.*, 35:1244–1255, 2006.
- [12] N. A. Besley and F. A. Asmuruf. *Phys. Chem. Chem. Phys.*, 12(12024), 2010.

- [13] L. Triguero, L. G. M. Pettersson, and H. Ågren. *Phys. Rev. B*, 58:8097–8110, 1998.
- [14] M. Leetmaa, M. P. Ljungberg, A. Lyubartsev, A. Nilsson, and L. G. M. Pettersson. *J. Elec. Spec. Rel. Phenom.*, 177:135–157, 2010.
- [15] J. C. Slater. *Adv. Quant. Chem.*, 6(1), 1972.
- [16] J. C. Slater and K. H. Johnson. *Phys. Rev. B*, 5(844), 1972.
- [17] H. Ågren, V. Carravetta, O. Vahtras, and L. G. M. Pettersson. *Chem. Phys. Lett.*, 222:75–81, 1994.
- [18] U. Ekström, P. Norman, and V. Carravetta. *Phys. Rev. A*, 73:022501, 2006.
- [19]
- [20] E. L. Shirley. *J. Elec. Spec. Rel. Phenom.*, 144-147:1187–1190, 2005.
- [21] J. Vinson, J. J. Rehr, J. J. Kas, and E. L. Shirley. *Phys. Rev. B*, 83(115106), 2011.
- [22] K. Gilmore, J. Vinson, E. L. Shirley, D. Prendergast, C. D. Pemmaraju, J. J. Kas, F. D. Vila, and J. J. Rehr. *Comput. Phys. Commun.*, 197:109–117, 2015.
- [23] M. Nooijen and R. J. Bartlett. *J. Chem. Phys.*, 102:6735–6756, 1995.
- [24] J. Brabec, K. Bhaskaran-Nair, N. Govind, J. Pittner, and K. Kowalski. *J. Chem. Phys.*, 137(171101), 2012.
- [25] B. Peng, P. J. LeStrange, J. J. Goings, M. Craicato, and X. S. Li. *J. Chem. Theory Comput.*, 11:4146–4153, 2015.
- [26] K. Kuramoto, M. Ehara, and H. Nakatsuji. *J. Chem. Phys.*, 122(014304), 2005.
- [27] Y. Ohtsuka and H. Nakatsuji. *J. Chem. Phys.*, 124(054110), 2006.
- [28] J. Schirmer. *Phys. Rev. A*, 26:2395–2416, 1982.
- [29] J. Wenzel, M. Wormit, and A. Dreuw. *J. Comp. Chem.*, 35:1900–1915, 2014.
- [30] E. Runge and E. K. U. Gross. *Phys. Rev. Lett.*, 52:997–1000, 1984.
- [31] M. E. Casida. Time-dependent density-functional response theory for molecules, in: D. P. Chong (Ed.), *Recent Advances in Density Functional Methods Part I*, World Scientific, Singapore, 1995.
- [32] Y. Zhang, J. D. Biggs, D. Healion, N. Govind, and S. Mukamel. *J. Chem. Phys.*, 137:194306, 2012.
- [33] T. Akama and H. Nakai. *J. Chem. Phys.*, 132:054104, 2010.

- [34] M. Kadek, L. Konecny, B. Gao, M. Repinsky, and K. Ruud. *PhysChem-ChemPhys*, 17:22566–22570, 2015.
- [35] U. Ekström, P. Norman, V. Carravetta, and H. Ågren. *Phys. Rev. Let.*, 97(143001), 2006.
- [36] U. Ekström and P. Norman. *Phys. Rev. A*, 74(042722), 2006.
- [37] J. W. von Goethe (1749-1832). Exact origin unknown.
- [38] M. F. Chaplin. Water Structure and Science. <www1.lsbu.ac.uk/water/index.html>.
- [39] A. Nilsson and L. G. M. Pettersson. *Chem. Phys.*, 389:1–34, 2011.
- [40] G. N. I. Clark, C. D. Cappa, J. D. Smith, R. J. Saykally, and T. Head-Gordon. *Mol. Phys.*, 108:1415–1433, 2010.
- [41] A. K. Soper. *Pure Appl. Chem.*, 82:1855–1867, 2010.
- [42] Ph. Wernet, D. Nordlund, U. Bergmann, M. Cavalleri, M. Odelius, H. Osagawara, L.-Å. Näslund, T. K. Hirsch, L. Ojamäe, P. Glatzel, L. G. M. Pettersson, and A. Nilsson. *Science*, 304:995–999, 2004.
- [43] A. Nilsson and L. G. M. Pettersson. *Nat. Commun.*, 6:8998, 2015.
- [44] C. Huang, K. T. Wikfeldt, T. Tokushmia, D. Norlund, Y. Harada, U. Bergmann, M. Niebuhr, T. M. Weiss, Y. Horikawa, M. Leetmaa, M. P. Ljungberg, O. Takahashi, A. Lenz, L. Ojamäe, A. P. Lyubartsev, S. Shin, L. G. M. Pettersson, and A. Nilsson. *Proc. Natl. Acad. Sci. (USA)*, 106:15214–15218, 2009.
- [45] A. Nilsson, C. Huang, and L. G. M. Pettersson. *J. Mol. Liq.*, 176:2–16, 2012.
- [46] J. A. Sellberg, C. Huang, T. A. McQueen, N. D. Loh, H. Laksmono, D. Schlesinger, R. G. Sierra, D. Nordlund, C. Y. Hampton, D. Starodub, D. P. DePonte, M. Beye, C. Chen, A. V. Martin, A. Barty, K. T. Wikfeldt, T. M. Weiss, C. Caronna, J. Feldkamp, L. B. Skinner, M. M. Seibert, M. Messerschmidt, G. J. Williams, S. Boutet, L. G. M. Pettersson, M. J. Bogan, and A. Nilsson. *Nature*, 510:381–384, 2014.
- [47] L. Kong, X. Wu, and R. Car. *Phys. Rev. B*, 86(134203), 2012.
- [48] J. D. Smith, C. D. Cappa, K. R. Wilson, B. M. Messer, R. C. Cohen, and R. J. Saykally. *Science*, 306:851–853, 2004.
- [49] J. D. Smith, C. D. Cappa, B. M. Messer, R. C. Cohen, and R. J. Saykally. *Science*, 308(793B), 2005.
- [50] J. D. Smith, C. D. Cappa, B. M. Messer, W. S. Drisdell, R. C. Cohen, and R. J. Saykally. *J. Phys. Chem. B*, 110:20038–20045, 2006.

- [51] D. Prendergast and G. Galli. *Phys. Rev. Lett.*, 96(215502), 2006.
- [52] J. S. Tse, M. Shaw, D. D. Klug, S. Patchkovskii, G. Vankò, G. Monaco, and M. Krisch. *Phys. Rev. Lett.*, 100(095502), 2008.
- [53] W. Chen, X. Wu, and R. Car. *Phys. Rev. Lett.*, 105(017802), 2010.
- [54] J. Vinson, J. J. Kas, F. D. Vila, J. J. Rehr, and E. L. Shirley. *Phys. Rev. B*, 85(045101), 2012.
- [55] A. Nilsson, Ph. Wernet, D. Nordlund, U. Bergmann, M. Cavalleri, M. Odelius, H. Ogasawara, L.-Å. Näslund, T. K. Hirsch, L. Ojamäe, P. Glatzel, and L. G. M. Pettersson. *Science*, 2005(793A), 308.
- [56] M. Odelius, M. Cavalleri, A. Nilsson, and L. G. M. Pettersson. *Phys. Rev. B*, 73(024205), 2006.
- [57] M. Leetmaa, M. Ljungberg, H. Ogasawara, M. Odelius, L.-Å. Näslund, A. Nilsson, and L. G. M. Pettersson. *J. Chem. Phys.*, 125(244510), 2006.
- [58] I. Waluyo, D. Nordlund, U. Bergmann, D. Schlesinger, L. G. M. Pettersson, and A. Nilsson. *J. Chem. Phys.*, 140(244506), 2014.
- [59] J. A. Sellberg, S. Kaya, V. H. Segtnan, C. Chen, T. Tyliszczak, H. Ogasawara, D. Nordlund, L. G. M. Pettersson, and A. Nilsson. *J. Chem. Phys.*, 141(034507), 2014.
- [60] L. Weinhardt, O. Fuchs, Blum, M., M. Bär, M. Weigand, J. D. Denlinger, Y. Zubavichus, M. Zharnikov, M. Grunze, C. Heske, and E. Umbach. *J. Elec. Spec. Rel. Phenom.*, 177:206–211, 2010.
- [61] M. Odelius. *Phys. Rev. B*, 79:144204, 2009.
- [62] L. Weinhardt, M. Blum, O. Fuchs, A. Benkert, F. Meyer, M. Bär, J. D. Denlinger, W. Yang, F. Reinert, and C. Heske. *J. Elec. Spec. Rel. Phenom.*, 188:111–120, 2013.
- [63] T. Tokushima, Y. Harada, O. Takahashi, Y. Senba, H. Ohashi, L. G. M. Pettersson, A. Nilsson, and S. Shin. *Chem. Phys. Lett.*, 460:387–400, 2008.
- [64] T. Tokushima, Y. Harada, Y. Horikawa, O. Takahashi, Y. Senba, H. Ohashi, L. G. M. Pettersson, A. Nilsson, and S. Shin. *J. Elec. Spec. Rel. Phenom.*, 177:192–205, 2010.
- [65] J. A. Sellberg, T. A. McQueen, H. Laksmono, S. Schreck, M. Beye, D. P. DePonte, B. Kennedy, D. Nordlund, R. G. Sierra, D. Schlesinger, T. Tokushima, I. Zhovtobriukh, S. Eckert, V. H. Segtnan, H. Ogasawara, K. Kubicek, S. Techert, U. Bergmann, G. L. Dakovski, W. F. Schlotter, Y. Harada, M. J. Bogan, P. Wernet, A. Fölich, L. G. M. Pettersson, and A. Nilsson. *J. Chem. Phys.*, 142:044505, 2015.

- [66] T. Fransson. *X-ray absorption spectroscopy through damped linear coupled cluster response theory*. LiU-Tryck, Linköping, Sweden, 2013.
- [67] As quoted in *New Chemisty*, by the editors of *Scientific American*, 1957.
- [68] T. Helgaker, P. Jørgensen, and J. Olsen. *Molecular electronic-structure theory*. John Wiley & Sons Ltd., 2000.
- [69] A. Szabo and N. S. Ostlund. *Modern quantum chemistry: Introduction to advanced electronic structure theory*. Dover Publications, 1996.
- [70] R. Bast and P.-O. Widmark (editors). *European Summerschool in Quantum Chemistry 2013 Book II*. 2013.
- [71] F. Jensen. *Introduction to computational chemistry, 2nd Ed.* John Wiley & Sons Ltd., 2006.
- [72] R. P. Feynman, *The Character of Physical Law*, 1965.
- [73] C. Nordling and J. Österman. *Physics handbook for science and engineering, 8th Ed.* Studentlitteratur, 2006.
- [74] T. H. Dunning. *J. Chem. Phys.*, 90(2), 1989.
- [75] D. E. Woon and T. H. Dunning. *J. Chem. Phys.*, 103(11), 1995.
- [76] R. A. Kendall, T. H. Dunning, and R. J. Harrison. *J. Chem. Phys.*, 96:6796–6806, 1992.
- [77] K. Kaufmann, W. Baumeister, and M. Jungen. *J. Phys. B-At. Mol. Opt.*, 22(2223), 1989.
- [78] P. Strange. *Relativistic quantum mechanics*. Cambridge University Press, 1998.
- [79] P. Pyykkö. *Chem. Rev.*, 112:371–384, 2012.
- [80] J. Autschbach. *J. Chem. Phys.*, 136(150802), 2012.
- [81] T. Saue. *ChemPhysChem*, 12:3077–3094, 2011.
- [82] L. Belpassi, L. Storchi, H. M. Quiney, and F. Tarantelli. *Phys. Chem. Chem. Phys.*, 13:12368–12394, 2011.
- [83] Schwerdtfeger, P., Ed. *Relativistic Electronic Structure Theory. Part I. Fundamentals*. Elsevier, Amsterdam, 2002.
- [84] L. Visscher. *Theor. Chem. Acc.*, 98:68–70, 1997.
- [85] M. Douglas and B. A. Hess. *Ann. Phys. (New York)*, 82(89), 1974.
- [86] G. Jansen and B. A. Hess. *Phys. Rev. A*, 39:6016–6017, 1989.

- [87] P. Norman, B. Schimmelpfennig, K. Ruud, H. J. A. Jensen, and H. Ågren. *J. Chem. Phys.*, 116:6914–6923, 2002.
- [88] M. Ilias and T. Saue. *J. Chem. Phys.*, 126:064102, 2007.
- [89] O. Fossgaard, O. Gropen, M. C. Valero, and T. Saue. *J. Chem. Phys.*, 118:10418, 2003.
- [90] K. Burke. *J. Chem. Phys.*, 136:150901, 2012.
- [91] A. D. Becke. *J. Chem. Phys.*, 140:18A301, 2014.
- [92] K. Burke. *J. Chem. Phys.*, 136:150901, 2012.
- [93] W. Kohn. *Rev. Mod. Phys.*, 71:1253–1266, 1999.
- [94] R. Van Noorden, B. Maher, and R. Nuzzo. *Nature*, 514:550–553, 2014.
- [95] L. H. Thomas. *Proc. Cambridge Phil. Soc.*, 23:542–548, 1927.
- [96] E. Fermi. *Rend. Accad. Naz. Lincei*, 6:602–607, 1927.
- [97] P. A. M. Dirac. *Proc. Cambridge Phil. Roy. Soc.*, 26:376–385, 1930.
- [98] P. Hohenberg and W. Kohn. *Phys. Rev.*, 136:B864–B871, 1964.
- [99] W. Kohn and L. J. Sham. *Phys. Rev.*, 140:A1133–A1138, 1965.
- [100] L. O. Wagner, T. E. Baker, E. M. Stoudenmire, K. Burke, and S. R. White. *Phys. Chem. B*, 90:045109, 2014.
- [101] J. P. Perdew and K. Schmidt. *AIP Conf. Proc.*, 577:1–20, 2001.
- [102] S. H. Vosko, L. Wilk, and M. Nusair. *Can. J. Phys.*, 58:1200–1211, 1980.
- [103] P. M. W. Gill, B. G. Johnson, J. A. Pople, and M. J. Frisch. *Chem. Phys. Lett.*, 197:499–505, 1992.
- [104] A. D. Becke. *Phys. Rev. A*, 38:3098–3100, 1988.
- [105] C. Lee, W. Yang, and R. G. Parr. *Rhys. Rev. B*, 37:785–789, 1988.
- [106] A. D. Becke. *J. Chem. Phys.*, 98:5648–5652, 1993.
- [107] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch. *J. Phys. Chem.*, 98:11623–11627, 1994.
- [108] T. Yanai, D. P. Tew, and N. C. Handy. *Chem. Phys. Lett.*, 393:51–57, 2004.
- [109] J. Klimes and A. Michaelides. *J. Chem. Phys.*, 137:120901, 2012.
- [110] J. P. Perdew and A. Zunger. *Phys. Rev. B*, 23:5048–5079, 1981.
- [111] G. Tu, V. Carravetta, O. Vahtras, and H. Ågren. *J. Chem. Phys.*, 127(174110), 2007.

- [112] G. Tu, Z. Rinkevicius, O. Vahtras, H. Ågren, U. Ekström, P. Norman, and V. Carravetta. *Phys. Rev. A*, 76(022506), 2007.
- [113] Y. Imamura and H. Nakai. *Int. J. Quant. Chem.*, 107:23–29, 2006.
- [114]
- [115] K. L. Bak, J. Gauss, P. Jørgensen, J. Olsen, T. Helgaker, and J. F. Stanton. *J. Chem. Phys.*, 114:6548–6556, 2001.
- [116] G. D. Purvis. *J. Chem. Phys.*, 76(4), 1982.
- [117] T. H. Dunning. *J. Phys. Chem. A*, 104:9062–9080, 2000.
- [118] O. Christiansen, H. Koch, and P. Jørgensen. *Chem. Phys. Lett.*, 243(5), 1995.
- [119] O. Christiansen, H. Koch, and P. Jørgensen. *J. Chem. Phys.*, 105(4), 1996.
- [120] O. Christiansen, H. Koch, and P. Jørgensen. *J. Chem. Phys.*, 103(17), 1995.
- [121] A. B. Trofimov, G. Stelter, and J. Schirmer. *J. Chem. Phys.*, 117:6402–6410, 2002.
- [122] S. Sauer, M. Schreiber, M. Silva-Junior, W. Thiel, and D. Mu. *J. Chem. Theory Comp.*, 5:555–564, 2009.
- [123] M. Silva-Junior, S. Sauer, M. Schreiber, and W. Thiel. *Mol. Phys.*, 108:453–465, 2010.
- [124] M. Schreiber, M. Silva-Junior, S. Sauer, and W. Thiel. *J. Chem. Phys.*, 128(134110), 2008.
- [125] S. Osuna, M. Swart, E. J. Baerends, F. M. Bickelhaupt, and M. Sola. *ChemPhysChem*, 10:2955–2965, 2009.
- [126] Gaussian 03, Revision E.01. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

- [127] L. Serrano-Andres, M. Merchan, I. Nebotgil, R. Lindh, and B. O. Roos. *J. Chem. Phys.*, 98:3151–3162, 1993.
- [128] J. D. Watts, S. R. Gwaltney, and R. J. Bartlett. *J. Chem. Phys.*, 105:6979–6988, 1996.
- [129] R. McLaren, S. A. C. Clark, I. Ishii, and A. P. Hitchcock. *Phys. Rev. A*, 36(1683), 1987.
- [130] T. H. Dunning. *J. Chem. Phys.*, 90:1007–1023, 1989.
- [131] D. E. Woon and T. H. Dunning. *J. Chem. Phys.*, 103:4572–4585, 1995.
- [132] J.-M. Lévy-Leblond. *Commun. Math. Phys.*, 6:286–311, 1967.
- [133] K. G. Dyall. *J. Chem. Phys.*, 100:2118–2127, 1994.
- [134] *Dirac, a relativistic ab initio electronic structure program*. Release DIRAC10 (2010), see <http://dirac.chem.vu.nl>.
- [135] *DALTON, a molecular electronic structure program*. Release DALTON2011 (2010), see <http://daltonprogram.org>.
- [136] N. Kroll and M. Douglas. *Ann. Phys.*, 82:89, 1974.
- [137] B. A. Hess. *Phys. Rev. A*, 33:3742–3748, 1986.
- [138] M. Tsvirko, K. Solovjev, A. Gradyushko, and S. Dvornikov. *Opt. Spectrosc.*, 38:400–404, 1975.
- [139] M. Gouterman and G. Khalil. *J. Mol. Spectrosc.*, 53:88–100, 1974.
- [140] W. van Dorp, W. Shoemaker, M. Soma, and J. van der Waals. *Mol. Phys.*, 30:1701–1721, 1975.
- [141] I. Y. Chan, W. G. van Dorp, T. J. Schaafsma, and J. H. van der Waals. *Mol. Phys.*, 22:741–751, 1971.
- [142] J. A. Kooter and J. H. van der Waals. *Mol. Phys.*, 37:997–1013, 1979.
- [143] L. Edwards, D. H. Dolphin, M. Gouterman, and A. D. Adler. *J. Mol. Spectrosc.*, 38:16–32, 1971.
- [144] R. P. Feynman, *QED: The Strange Theory of Light and Matter*, 1985.
- [145] P. Norman, K. Ruud, and T. Saue. *Response properties of molecular materials*. Wiley. *In manuscript*.
- [146] T. Helgaker, S. Coriani, P. Jørgensen, K. Kristensen, J. Olsen, and K. Ruud. *Chem. Rev.*, 112:543–631, 2012.
- [147] P. Norman. *Phys. Chem. Chem. Phys.*, 13:20519–20535, 2011.
- [148] J. Olsen and P. Jørgensen. *J. Chem. Phys.*, 82:3235–3264, 1985.

- [149] As quoted by D. J. Albers, G. L. Alexanderson and C. Reid in *Mathematical People*, Bostyon, 1985.
- [150] B. H. Bransden and C. J. Joachain. *Quantum mechanics, 2nd Ed.* Pearson Education Limited, 2000.
- [151] P. Norman, K. Ruud, and T. Saue. Lecture notes from *Quantum chemical winter school: Response properties of molecular materials*. Chamonix, France, 2010.
- [152] P. Norman. *Phys. Chem. Chem. Phys.*, 13(20519), 2011.
- [153] P. A. Tipler and R. Llewellyn. *Modern physics, 4th Ed.* W.H. Freeman & Company, 2002.
- [154] O. Christiansen, P. Jørgensen, and C. Hättig. *Int. J. Quantum Chem.*, 68:1–52, 1998.
- [155] N. H. List, S. Coriani, J. Kongsted, and O. Christiansen. *J. Chem. Phys.*, 141(244107), 2014.
- [156] S. Coriani and H. Koch. *J. Chem. Phys.*, 143:181103, 2015.
- [157] J. Kauczor, P. Norman, O. Christiansen, and S. Coriani. *J. Chem. Phys.*, 139(211102), 2013.
- [158] S. P. A. Sauer, I. Ul Haq, J. R. Sabin, J. Oddershede, O. Christiansen, and S. Coriani. *Mol. Phys.*, 112:751–761, 2014.
- [159] J. Cukras, S. Coriani, P. Decleva, O. Christiansen, and P. Norman. *J. Chem. Phys.*, 138(094103), 2013.
- [160] J. Cukras, P. Decleva, and S. Coriani. *J. Chem. Phys.*, 141:174315, 2014.
- [161] M. E. Casida. *J. Mol. Struc. Theochem.*, 914:3–18, 2009.
- [162] J. Schirmer and A. Dreuw. *Phys. Rev. A*, 75(022513), 2007.
- [163] N. T. Maitra, R. van Leeuwen, and K. Burke. *Phys. Rev. A*, 78(056501), 2008.
- [164] J. Schirmer and A. Dreuw. *Phys. Rev. A*, 78(056502), 2008.
- [165] S. Hirata and M. Head-Gordon. *Chem. Phys. Lett.*, 314:291–299, 1999.
- [166] S. Villaume, T. Saue, and P. Norman. *J. Chem. Phys.*, 133(064105), 2010.
- [167] K. Lopata, B. E. Van Kuiken, M. Khalil, and N. Govind. *J. Chem. Theory Comput.*, 8:3284–3292, 2012.
- [168] M. Repinsky, L. Konecny, S. Kadek, M. abd Komorovsky, O. L. Malikn, V. G. Malkin, and K. Ruud. *J. Chem. Theory Comput.*, 11:980–991, 2015.

- [169] L. Triguero, O. Plashkevych, L. G. M. Pettersson, and H. Ågren. *J. Elec. Spec. Rel. Phenom.*, 104:195–207, 1999.
- [170] N. A. Besley, A. T. B. Gilbert, and P. M. W. Gill. *J. Chem. Phys.*, 130:124308, 2009.
- [171] L. Triguero, L. G. M. Pettersson, and H. Ågren. *J. Phys. Chem. A*, 102:10599–10607, 1998.
- [172] W. D. Derricotte and F. A. Evangelista. *Phys. Chem. Chem. Phys.*, 17:14360, 2015.
- [173] U. Ekström, L. Visscher, R. Bast, A. J. Thorvaldsen, and K. Ruud. *J. Chem. Theory Comput.*, 6:1971–1980, 2010.
- [174] A. D. Laurent and D. Jacquemin. *Int. J. Quant. Chem.*, 113:2019–2039, 2013.
- [175] K. Burke, J. Werschnik, and U. K. U. Gross. *J. Chem. Phys.*, 123:062206, 2005.
- [176] E. Wigner (1902-1995). Exact origin unknown.
- [177] E. R. Davidson. *J. Comp. Phys.*, 17:87–94, 1975.
- [178] M. Stener, G. Fronzoni, and M. de Simone. *Chem. Phys. Lett.*, 373:115–123, 2003.
- [179] L. S. Cederbaum, W. Domcke, and J. Schirmer. *Phys. Rev. A: At., Mol., Opt. Phys.*, 22:206–222, 1980.
- [180] K. Lopata, E. van Kuiken, M. Khalil, and N. Govind. *J. Chem. Theory Comput.*, 8:3284–3292, 2012.
- [181] F. A. Asmuruf and N. A. Besley. *J. Chem. Phys.*, 129:064705, 2008.
- [182] Z. Bai, J. Demmel, J. Dongarra, A. Ruhe, and H. van der Vorst. *Templates for the solution of algebraic eigenvalue problems: A practical guide*. Soc. Ind. Math., 1987.
- [183] P. Seidler, M. B. Hansen, W. Gyorffy, D. Toffoli, and O. Christiansen. *J. Chem. Phys.*, 132(16), 2010.
- [184] J. Kauczor, P. Jørgensen, and P. Norman. *J. Chem. Theory Comput.*, 7(1610), 2011.
- [185] J. Kauczor and P. Norman. *J. Chem. Theory Comput.*, 10:2449–2455, 2014.
- [186] D. Lundgren (portraying I. Drago), *Rocky IV*, Metro-Goldwyn-Mayer Studios, Inc., 1985.
- [187] A. Baev, F. Gel'mukhanov, P. Macak, Y. Luo, and H. Ågren. *J. Chem. Phys.*, 117:6214–6220, 2002.

- [188] A. Baev, F. Gel'mukhanov, V. Kimberg, and H. Ågren. *J. Phys. B: At. Mol. Opt. Phys.*, 36:3761–3774, 2003.
- [189] S. Bernadotte, A. J. Atkins, and C. R. Jacob. *J. Chem. Phys.*, 137:204106, 2012.
- [190] N. H. List, J. Kauczor, T. Saue, H. J. A. Jensen, and P. Norman. *J. Chem. Phys.*, 142:244111, 2015.
- [191] From a manuscript published in F. E. Manuel's *The Religion of Isaac Newton*, 1974.
- [192] J. F. Stanton and J. Gauss. *J. Chem. Phys.*, 111:8785–8788, 1999.
- [193] D. R. Lide, (Ed.). *CRC Handbook of Chemistry and Physics, 8:th Ed.* CRC Press, 1998.
- [194] U. Ekström, P. Norman, V. Carravetta, and H. Ågren. *Phys. Rev. Lett.*, 97(143001), 2006.
- [195] S. S. Leang, F. Zahariev, and M. S. Gordon. *J. Chem. Phys.*, 136(104101), 2012.
- [196] Y. Imamura, T. Otsuka, and H. Nakai. *J. Comput. Chem.*, 28:2067–2074, 2007.
- [197] R. Tagore, *The King of the Dark Chamber*, 1910.
- [198] M. Cavalleri, H. Ogasawara, L. G. M. Pettersson, and A. Nilsson. *Chem. Phys. Lett.*, 364:363–370, 2002.
- [199] M. Olsen, K. Aidas, and J. Kongsted. *J. Chem. Theory Comput.*, 6:3721–3734, 2010.
- [200] M. N. Pedersen, E. D. Hedegård, J. M. H. Olsen, J. Kauczor, P. Norman, and J. Kongsted. *J. Chem. Theory Comput.*, 10:1164–1171, 2014.
- [201] M. T. P. Beerepoot, A. H. Steindal, K. Ruud, J. M. H. Olsen, and J. Kongsted. *Comp. Theor. Chem.*, 1040:304–311, 2014.
- [202] J. M. H. Olsen, N. H. List, K. Kristensen, and J. Kongsted. *J. Chem. Theory Comput.*, 11:1832–1842, 2015.
- [203] R. Püttner, M. Domke, and G. Kaindl. *Phys. Rev. A*, 57:297–307, 1998.
- [204] W. H. E. Schwarz. *Chem. Phys.*, 11:217–228, 1975.
- [205] X. Guo, G. Cooper, W.-F. Chan, G. R. Burton, and C. E. Brion. *Chem. Phys.*, 161:471–484, 1992.
- [206] J.-M. Chen, R. Klauser, S.-Ch. Yang, and C.-R. Wen. *Phys. Chem. Lett.*, 246:285–290, 1995.

- [207] K. Ogasawara, T. Iwata, Y. Koyama, T. Ishii, I. Tanaka, and H. Adachi. *Phys. Rev. B*, 94:115413, 2001.
- [208] I. Asimov (1920-1992). Exact origin unknown.
- [209] Interview by H. Blume, *The Boston Globe*, March 17, 2007.
- [210] N. A. Besley. *Chem. Phys. Lett.*, 542:42–46, 2012.
- [211] J. D. Wadey and N. A. Besley. *J. Chem. Theory Comput.*, 10:4557–4564, 2014.
- [212] Y. Zhang, S. Mukamel, M. Khalil, and N. Govind. *J. Chem. Theory Comput.*, 11:5804–5809, 2015.
- [213] L. Weinhardt, A. Benkert, F. Meyer, M. Blum, R. G. Wilks, W. Yand, M. Bär, F. Reinert, and C. Heske. *J. Chem. Phys.*, 136:144311, 2012.
- [214] I. Newton (1643-1727). Exact origin unknown.

List of Figures

1.1	The Fraunhofer lines in the optical spectrum of the Sun	1
1.2	The electromagnetic spectrum	3
1.3	Core spectroscopy processes	4
1.4	Absorption process	6
1.5	Prototypical X-ray absorption spectrum	7
1.6	Hypothesized local structure motifs of liquid water	9
2.1	Theoretical models in quantum chemistry	22
2.2	Popularity of density functional theory	23
2.3	Excitation energies of ethene	36
2.4	Orbital energies of neon	40
2.5	Valence spectra of metallo-substituted porphyrins	42
3.1	Complex polarizability in the vicinity of resonance	49
3.2	Behaviour of the global spectrum using the Lanczos algorithm . . .	64
3.3	Convergence properties of the complex polarization propagator . .	67
3.4	Induced dipole moment at different field strengths	68
3.5	Perturbation by ultrashort X-ray laser pulse	69
3.6	Wavelength of X-ray photons near resonance	71
4.1	Orbital densities of krypton	74
4.2	1s orbital density of neutral and ionized helium	75
4.3	Density isosurfaces of neutral and core-ionized formaldehyde . . .	76
4.4	Ionization potentials in the periodic table	79
4.5	Relaxation effects in the coupled cluster hierarchy	82
4.6	Simulating the X-ray absorption spectrum of ethene	84
4.7	Performance of exchange-correlation functionals for core-excitations	86
4.8	H-bond effects on the water X-ray absorption spectrum	87
4.9	X-ray absorption spectra of the different phases of water	88
4.10	QM/MM calculations on water X-ray absorption spectra	89
5.1	Unphysical continuum features in L -edge X-ray absorption spectra	92
5.2	$L_{2,3}$ -edge X-ray absorption spectra of silicon tetrachloride	94
5.3	$L_{2,3}$ -edge X-ray absorption spectra of silane derivatives	95
5.4	Electron densities of silane derivatives	97

5.5	Ionization potential and population analysis of silane derivatives . . .	98
6.1	X-ray emission spectrum of carbon monoxide	101
6.2	X-ray emission spectrum of water	102

List of Tables

2.1	Scaling of coupled cluster models	35
2.2	Phosphorescence parameters of metallo-porphyrins	41
4.1	Correlation energies of noble gases	77
4.2	Correlation energies of ionized noble gases	78
4.3	Carbon 1s ionization potential of ethene	79

List of included Publications

- [I] **Coupled-cluster response theory for near-edge X-ray-absorption fine structure of atoms and molecules**
S. Coriani, O. Christiansen, **T. Fransson** and P. Norman.
Phys. Rev. A **85**, 022507 (2012).
- [II] **Asymmetric-Lanczos-chain-driven implementation of electronic resonance convergent coupled-cluster linear response theory**
S. Coriani, **T. Fransson**, O. Christiansen and P. Norman.
J. Chem. Theory Comput. **8**, 1616 (2012).
- [III] **Carbon X-ray absorption spectra of fluoroethenes and acetone: A study at the coupled cluster, density functional, and static-exchange levels of theory**
T. Fransson, S. Coriani, O. Christiansen and P. Norman.
J. Chem. Phys. **138**, 124311 (2013).
- [IV] **Requirements of first-principles calculations of X-ray absorption spectra of liquid water**
T. Fransson, I. Zhovtobriukh, S. Coriani, K. T. Wikfeldt, P. Norman. and L. G. M. Pettersson
Phys. Chem. Chem. Phys. **18**, 566-583 (2016).
- [V] **Four-component damped density functional response theory study of UV/vis absorption spectra and phosphorescence parameters of group 12 metal-substituted porphyrins**
T. Fransson, T. Saue and P. Norman.
Submitted.
- [VI] **K- and L-edge X-ray absorption spectrum calculations of closed-shell carbon, silicon, germanium, and sulfur compounds using damped four-component density functional response theory**
T. Fransson, D. Burdakova and P. Norman.
In manuscript.

My contributions to the papers

In Paper [I] we investigated the performance of damped coupled cluster (CC) response theory for the calculation of K -edge X-ray absorption spectra of small molecules and atoms, and I carried out initial test calculations in order to understand the performance of the method. Additionally, I was of assistance in writing the paper and carried out part of the published calculations. In Paper [II] we published the damped CC response method and evaluated it for the calculation of additional molecular properties. I performed all calculations and wrote the first draft for the result section, as well as parts of the theory and conclusions.

Paper [III] was dedicated to the evaluation of the performance of damped CC response theory in terms of chemical shifts in X-ray absorption spectra, featuring comparisons to the more approximate static exchange approach and time-dependent density functional theory (TDDFT). I planned the paper, carried out all calculations and wrote the first draft. In Paper [IV] we continued the evaluation of damped CC response theory and TDDFT for calculation on water, comparing the results to experimental measurements and results using transition potential DFT. I outlined the paper, wrote the first draft, and carried out all TDDFT and CC calculations.

A recently developed formulation of damped TDDFT response theory was evaluated for calculation of valence spectra in Paper [V] and core spectra in Paper [VI]. In Paper [V] we investigated the influence of metal-substitution in porphyrins, in terms of both the UV/vis spectra and phosphorescence parameters. I planned the outline of the paper, wrote the first draft, and carried out all calculations. K - and L -edge spectra of small molecules using four-component TDDFT was investigated in Paper [VI], for which I planned the article, wrote the first draft and carried out all published calculations. Additionally, I supervised a Master student who performed initial test calculations by which we investigated the method.

Papers

The articles associated with this thesis have been removed for copyright reasons. For more details about these see:

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-124272>