

Optical Properties of the 11-cis Retinal Molecule from Time-Dependent Density Functional Theory

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A dissertation submitted to the Faculty of Science, University of the Witwatersrand,
in fulfillment of the requirements of the degree of Master of Science.

May 6, 2010

Declaration

I declare that this dissertation is my own, unaided work and it is being submitted for the degree of Master of Science in the University of Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other university.

6th day of May, 2010.

Abstract

The 11 – *cis* retinal molecule is the primary transducer of light in human eyes. When light is incident on it, the molecule isomerizes from its *cis* configuration to an *all* – *trans* state. Time Dependent Density Functional Theory (TDDFT) happens to be at a momentous stage of its development, paralleled by the production of powerful and very fast computers. Such a combination has made it possible to carry out *ab-initio* studies of the ground and excited states of such large molecules. Starting with the ground state properties, TDDFT as implemented in the real space code, Octopus, was used to calculate the optical properties of the molecule. In particular, the optical absorption spectrum was computed in great agreement with experiment, but unexpected extra properties are also predicted. Short and strong laser pulses (in one case $I = 10^{13} \text{ W/cm}^2$ and in the other case $I = 10^{16} \text{ W/cm}^2$) were shot through the molecule theoretically and high harmonic generation (for $I = 10^{13} \text{ W/cm}^2$) and coulomb explosion (for $I = 10^{16} \text{ W/cm}^2$) were observed. For each of the three scenarios studied here, a QM/MM calculation was also carried out. Unfortunately, the overestimating (for ionization) Local Density Approximation (LDA) for the exchange-correlation functional was used throughout, since the more accurate exact exchange (EXX) over-burdened the eight-core machine that was used in this work.

Dedication

This dissertation and the MSc degree are dedicated to the very reason why I did it – my loving mother and my highly-inspiring uncle, Mr. W. P. Lugube. Thank you very much.

Acknowledgments

First and foremost, I would like to acknowledge my highly supportive supervisor, Professor D. P. Joubert, who always went an extra mile to see me get this work done right. I can never thank him enough. The National Research Foundation (NRF) and the National Institute of Theoretical Physics (NITheP) are accredited for nearly all the financial support, and so is the Center for High Performance Computing (CHPC) for providing the machines that were initially used for the work. I am also very thankful to Professor D. C. Levendis from the School of Chemistry for some very fruitful discussions as well as providing me with the input coordinates of the molecule from the Cambridge Structural Database. Dr. K. Goldstein's help in generating the movies in this work is highly appreciated. Many thanks go to the School of Physics staff – most notably, Professors J. Carter, J. A. P. Rodrigues, J. Lowther (who practically brought me to Wits and first got me interested in condensed matter physics), R. de Mello Koch and D. Comins. Last, but definitely not the least, I am greatly indebted to my fellow colleagues and friends in the school for many fruitful discussions. Space limitations do not allow me to mention each and every one of them by name, unfortunately.

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Chapter 1

Introduction

The 11 – *cis* retinal molecule, shown schematically in figure 1.1 ¹ in its ground (cis) and excited (all trans) states after the absorption of a light photon, is the primary light transducer in the mammalian eye. In other words, it is the primary molecule responsible for human vision. When light is incident on it, it isomerizes from its cis form to the all-trans form as shown. The alternating single and double bonds that are clearly visible in figure 1.1 are the signature of the carotenoid structures of which the 11 – *cis* retinal molecule is a member.

As the name suggests, the 11 – *cis* molecule is situated in the retina, at the back of the human eye (figure 1.2).

Inside the retina are rods and cones, two different cell types that house the retinal molecule, but the 11 – *cis* retinal is still the basic chromophore in either case.

Figure 1.3 shows a three-dimensional model of rhodopsin (found in rod cells) which is responsible for night vision, and as such, it is only sensitive to “black-and-white light”

¹Figure 1.1 was taken from <http://hu.wikipedia.org/wiki/Foton>.

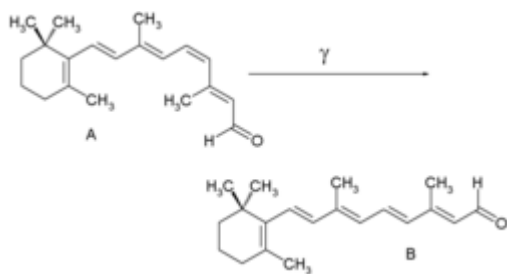


Figure 1.1: The 11 – *cis* retinal molecule.

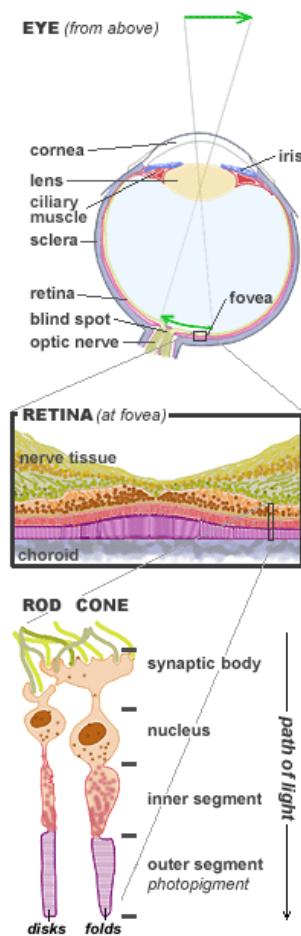


Figure 1.2: The human eye.

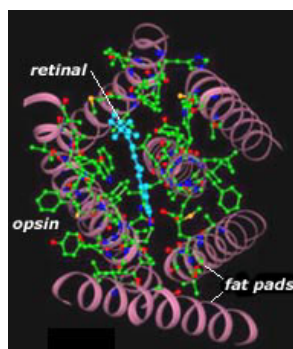


Figure 1.3: Three dimensional model of rhodopsin with the retinal molecule well-labeled inside.

just as we see it at night or in deem light. As is evident here (in figure 1.3), the molecule is normally attached to a particular protein base called opsin [10, p968].

In the case of the colour-sensitive cone cells, the protein “intelligently” alters the molecule’s photo-absorption spectrum linearly, thereby determining the wavelength (colour) of visible light that we see. Three basic opsins are found attached to the retinal molecule, each with a sensitivity that thrives with a particular wavelength of light.² That way, the three primary colours of visible light are well-covered – the rest of the colours that we see are mixtures of these three primary ones.

With this in mind, it should go a long way in satisfying one’s general curiosity about the process of vision to study only the primary 11 – *cis* retinal molecule under different conditions. In this particular study, the molecule was not only studied under the illumination of normal light, but also with the molecule placed in a strong laser field ($10^{16}W/m^2$ and $10^{13}W/m^2$). The reason for this latter study was to establish what really happens when one gets a strong laser shone into one’s eye, i.e. what really happens in this case as one goes blind (presumably).

This way, two primary problems are well outlined:

- i) what is the theoretical photo-absorption spectrum of the 11 – *cis* retinal molecule? What colour of light are our eyes primarily sensitive to (loosely speaking)?
- ii) what happens when the 11 – *cis* retinal molecule is placed in a strong laser field? How do we go blind when a strong laser shines into our eyes? Can the eye (molecule) “heal” after this illumination as do some molecules which heal after staying in the dark for some time?

Well, it turns out that an *ab-initio* study of the molecule under the two cases is currently the best way to provide answers to these questions. This comes in the form of Quantum Mechanics in its Time Dependent Density Functional Theory formulation – for reasons discussed in later chapters.

In the interest of space, while it is highly appreciated that DFT and TDDFT are big subjects of interest in their own right, only those parts that have direct relevance to the calculations carried out in this work will be discussed. As such, all formulae will be written in the highly readable spin-saturated format. Spin should be easy to include whenever necessary.

²More on this in Chapter 4.

Chapter 2

The Ground State: Density Functional Theory¹

Time Dependent Density Functional Theory (TDDFT) is an evolution of some ground state of a given system. This is to say that TDDFT is an initial value problem [81] that can only be solved in the presence of some initial “ground” state of the system. For this reason, it is imperative to discuss first the ground state Density Functional Theory (DFT). From a different view point, TDDFT can be viewed as an extension of the famous and highly successful ground state theory in an attempt to describe time-dependent systems [81].

Now, DFT is a ground state theory. It is a reformulation of the ground state Quantum Mechanics in terms of the electron density rather than the complicated many body wavefunction ($\Psi(\mathbf{r})$) which is very difficult to work with in most of real life systems. To drive the point home, one realizes that for an N -particle system, the many body wavefunction has $3N$ degrees of freedom (excluding spin), while the single particle density has only three degrees of freedom. What this means is that, computationally, the wavefunction is a very complicated object to work with, being computationally more demanding than the density. In other words, if the many body wavefunction, $\Psi(\mathbf{r})$, is used in calculations, the number of processors and the amount of memory needed to complete the calculation (solving the Schrodinger equation) grow exponentially with the number of electrons involved, making it a practically infeasible way of calculating the properties of large quantum systems [70].

Presenting the same problem in a somewhat different way, we notice that the ground state Schrodinger Equation can be solved exactly (analytically) only for a single fermion

¹The bulk of this chapter is based on Walter Kohn’s Nobel lecture [70].

system placed in a classical external potential, e.g. in case of the hydrogen atom. Any other quantum system with two or more interacting particles does not have a well-known analytic solution. Trying to employ computational techniques to the many body problem leads us into a brick (exponential) wall before we can solve many of the systems that occur in nature [70]. In this case, the interesting retinal molecule with forty-nine atoms ($C_{20}H_{28}O$) becomes an insurmountable case.

To overcome this problem, Hohenberg and Kohn [60] reformulated the ground state non-relativistic Schrodinger equation in terms of the more friendly single particle density $n[\mathbf{r}]$ which bore all the information about the quantum system. In their seminal paper, Hohenberg and Kohn proved the very important property of the one-to-one correspondence between the ground state electron density and the external potential affecting the electrons. While this was a very useful thing to do, there was no way of computing this single particle density, until Kohn and Sham put forward their ansatz based on a fictitious non-interacting electron gas in 1965 [71]. These two papers working together, form the basis of the very successful modern Density Functional Theory (DFT).

Now, before we discuss the Hohenberg-Kohn formulation of Density Functional Theory, it makes absolute sense to give a brief description of the background theory on which Hohenberg and Kohn worked, namely, the Thomas-Fermi theory.

2.1 The Thomas-Fermi Theory

Thomas [107] and Fermi [39] published their Density Functional Theory theory in 1927, two years after the completion of the non-relativistic Quantum Mechanics in 1925. Theirs was a very crude theory of electronic energy in terms of the electron density distribution. Its major successes were in the description of qualitative trends such as the total energies of atoms, but it could not describe properties of materials involving valence trends.

The Thomas-Fermi theory considered interacting electrons moving in an external potential $v(\mathbf{r})$. In its description, it provided a highly simplified one-to-one implicit relation between this external potential $v(\mathbf{r})$ and the electron density distribution $n(\mathbf{r})$:

$$n(\mathbf{r}) = \gamma [\mu - v_{eff}(\mathbf{r})]^{\frac{3}{2}} \quad (2.1)$$

where $\gamma = \frac{1}{3\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}}$,

$$v_{eff} = v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (2.2)$$

and μ is the r-representable chemical potential.

Equation (2.1) is based on the expression that

$n = \gamma(\mu - v)^{\frac{3}{2}}$ for the density of a uniform non-degenerate electron gas in a constant electron potential v .

The second term in equation (2.2) is the negated classical electrostatic potential generated by the electron density distribution $n(\mathbf{r}')$.

Note that equation (2.1) does not include gradients of the effective potential v_{eff} . For this reason, we expect the Thomas-Fermi theory to work well for systems of slowly varying densities. Including gradient exchange and correlation corrections has not subsequently increased the domain of the theory to include the electronic structure of matter (which uses valency electrons). This is because the Thomas-Fermi theory is simply a rough approximation of the exact solution of the many body Schrodinger Equation [70].

The Hohenberg-Kohn theory which is primarily a generalization of the Thomas-Fermi theory covers electronic structure methods. The key concept that Hohenberg and Kohn carried forward from the Thomas-Fermi theory was the fact that the ground state density completely determines the system.

2.2 The Hohenberg-Kohn Theorem

The Hohenberg-Kohn theorem [60] is basically two fundamental statements, namely:

- i) there is a one-to-one correspondence between the ground state density $n(\mathbf{r})$ of a non-relativistic quantum system and its external potential $v(\mathbf{r})$, and
- ii) if one defines a universal energy functional (in terms of the density) that is valid for any external potential, then for a particular potential, the exact ground state energy of the system is the global minimum of this universal energy functional and the corresponding density that minimizes this functional is the ground state density of the system [104].

2.2.1 The density as the basic variable

Perhaps the most powerful meaning of the one-to-one correspondence between the density and the external potential of the system is that the density uniquely identifies the system. In other words, the density contains all the information about the system.

Proof: This proof is presented here for a non-degenerate ground state, but this condition can be lifted.

Now, consider a non-degenerate ground state density of N electrons, $n(\mathbf{r})$ in potential $v_1(\mathbf{r})$, corresponding to a ground state Ψ_1 and the energy E_1 given by

$$E_1 = \langle \Psi_1 | H | \Psi_1 \rangle = \int v_1(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \langle \Psi_1 | (T + U) | \Psi_1 \rangle \quad (2.3)$$

where H_1 is the total Hamiltonian corresponding to v_1 , while T and U are the kinetic and interaction energy operators, respectively.

Let us assume that there exists a second potential $v_2(\mathbf{r}) \neq v_1(\mathbf{r}) + \text{constant}$, with a corresponding ground state $\Psi_2 \neq e^{i\theta} \Psi_1$ that gives the same density $n(\mathbf{r})$. Then

$$E_2 = \int v_2(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \langle \Psi_2 | (T + U) | \Psi_2 \rangle. \quad (2.4)$$

Since Ψ_1 is degenerate (in our case), the Rayleigh-Ritz minimal principle for Ψ_1 gives

$$\begin{aligned} E_1 &< \langle \Psi_2 | H_1 | \Psi_2 \rangle = \int v_1(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \langle \Psi_2 | (T + U) | \Psi_2 \rangle \\ &= E_2 + \int [v_1(\mathbf{r}) - v_2(\mathbf{r})] n(\mathbf{r}) d\mathbf{r}. \end{aligned} \quad (2.5)$$

Similarly,

$$E_2 \leq \langle \Psi_1 | H | \Psi_1 \rangle = E_1 + \int [v_2(\mathbf{r}) - v_1(\mathbf{r})] n(\mathbf{r}) d\mathbf{r} \quad (2.6)$$

where $\leq$ emanates from the fact that we did not assume Ψ_2 to be degenerate.

Adding equations (2.5) and (2.6) leads to a contradiction that

$$E_1 + E_2 < E_2 + E_1,$$

which proves the one-to-one correspondence between the density $n(\mathbf{r})$ and the external potential $v(\mathbf{r})$ (up to an uninteresting constant) by reductio ad absurdum.

2.2.2 The variational principle

The below statement of the variational principle is the Rayleigh-Ritz minimal principle for the Hohenberg-Kohn theory. It basically means that the aforescribed functional (alone) is sufficient to determine the the ground state energy and density of the system.

However, excited state properties of electrons must be determined by other means.

To derive the Hohenberg-Kohn variational principle, we can employ the constrained search method due to Levy [77] and Lieb [78].

Now, we remember that the most important quantity of an electronic system in its ground state is its total energy E which can be computed using the Rayleigh-Ritz minimal principle:

$$E = \min_{\psi} \langle \psi | H | \psi \rangle \quad (2.7)$$

where ψ is a normalized trial wave-function for the given number of electrons N . This is the traditional Rayleigh-Ritz formula that Hohenberg and Kohn re-wrote in terms of a trial density $\tilde{n}(\mathbf{r})$.

Now, every trial wave function ψ corresponds to a trial density $\tilde{n}(\mathbf{r})$ obtained by integrating $\psi^* \psi$ over all variables except the first and multiplying by the N .

To minimize equation (2.7) we will make two major steps:

i) we fix a trial density $\tilde{n}(\mathbf{r})$ and denote by $\psi_{\tilde{n}}^{\alpha}$ the class of trial wave functions with this density $\tilde{n}(\mathbf{r})$. We define the constrained energy minimum (with fixed $\tilde{n}(\mathbf{r})$) as

$$E_v[\tilde{n}(\mathbf{r})] \equiv \min_{\alpha} (\psi_{\tilde{n}}^{\alpha}, H \psi_{\tilde{n}}^{\alpha}) = \int v(\mathbf{r}) \tilde{n}(\mathbf{r}) d\mathbf{r} + F[\tilde{n}(\mathbf{r})] \quad (2.8)$$

where the functional

$$F[\tilde{n}(\mathbf{r})] \equiv \min_{\alpha} [\psi_{\tilde{n}}^{\alpha}, (T + U) \psi_{\tilde{n}}^{\alpha}]. \quad (2.9)$$

At this point we note that $F[\tilde{n}(\mathbf{r})]$ requires explicit knowledge of the external potential $v(\mathbf{r})$. It is a universal functional of the trial density $\tilde{n}(\mathbf{r})$ irregardless of whether this density is v-representable or not.²

ii) we minimize equation (2.8) over all $\tilde{n}(\mathbf{r})$. This minimum is the ground state energy E , given by

$$E = \min_{\tilde{n}(\mathbf{r})} E_v[\tilde{n}(\mathbf{r})] = \min_{\tilde{n}(\mathbf{r})} \left\{ \int v(\mathbf{r}) \tilde{n}(\mathbf{r}) d\mathbf{r} + F[\tilde{n}(\mathbf{r})] \right\}. \quad (2.10)$$

For a non degenerate ground state, the minimum is attained when the trial density $\tilde{n}(\mathbf{r})$ is the ground state density. For a degenerate ground state, $\tilde{n}(\mathbf{r})$ must be one of the ground state densities.

² $\tilde{n}(\mathbf{r})$ is said to be v-representable if it is the ground state density corresponding to some potential $v(\mathbf{r})$.

Equation (2.10) is the Hohenberg-Kohn variational minimum principle. As pointed out earlier, it is a formal exactification of the Thomas-Fermi theory. Actually, the Thomas-Fermi theory can easily be derived from this generalization in the Hohenberg-Kohn theory by making the following substitutions:

$$T = \int n(\mathbf{r}) \frac{3}{10} k_F^2 [n(\mathbf{r})] d\mathbf{r} \quad (2.11)$$

and

$$U = \frac{1}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (2.12)$$

where k_F is the Fermi wave vector of a uniform electron gas of density n , and $\frac{3}{10} k_F^2 (n)$ is the mean kinetic energy of such a gas. U is written here in the classical (mean field) nomination.

The same goes for many of the generalizations of the Thomas-Fermi theory.

If the functional $F[\tilde{n}(\mathbf{r})]$ was known explicitly, then the Hohenberg-Kohn theorem would yield the exact ground state density and energy of the system.

Proof: The proof for the Hohenberg-Kohn theorem follows from the physical implications of the variational principle. Consider a non-degenerate system whose ground state density $n_0(\mathbf{r})$ corresponds to its ground state Ψ_0 corresponding to an external potential $v(\mathbf{r})$. The Hohenberg-Kohn functional is equal to an expectation value of the Hamiltonian in the unique ground state. The ground state energy will then be given by

$$E_0 = \langle \Psi_0 | H | \Psi_0 \rangle. \quad (2.13)$$

Now, if we consider another density $n'(\mathbf{r})$ corresponding to state Ψ' , then $E' > E_0$ since

$$E_0 = \langle \Psi_0 | H | \Psi_0 \rangle < \langle \Psi' | H | \Psi' \rangle = E'. \quad (2.14)$$

Therefore, the energy given by the ground state density is lower than the energy given by any other density which is not the ground state density. This sufficiently proves the Hohenberg-Kohn variational principle.

2.3 The Kohn-Sham Ansatz

While the Hohenberg-Kohn theorem [60] beautifully tells us that we can determine everything about a given system solely from its density, it does not tell us how to get

this very crucial density [83, 70]. This is where the Kohn-Sham ansatz [83] comes to our aid. What Kohn and Sham [71] did is that they proposed that the ground state density could be determined by mapping the fully interacting problem onto a fictitious non-interacting problem whose density is equal to that of the interacting problem. What this means is that the potential of the non-interacting problem should be chosen in such a way as to give the correct ground state density of the fully interacting problem [70].

2.3.1 The self-consistent Kohn-Sham equations

Following the publication of the Thomas-Fermi Theory [107, 39] on which the Hohenberg-Kohn Density Functional Theory was based, Hartree proposed a set of self-consistent single-particle equations in 1928, which approximately described the electronic structure of atoms [53]. In these equations, each electron was considered to be moving in an effective (fictitious) single-particle Hartree potential:

$$v_H = -\frac{Z}{r} + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (2.15)$$

where the first term represents the electrostatic potential due to a nucleus with atomic number Z and the second represents the potential due to the average electronic distribution $n(\mathbf{r}')$.

Here, each electron obeys the single-particle Schrodinger equation:

$$\left\{ -\frac{1}{2}\nabla^2 + v_H(\mathbf{r}) \right\} \varphi_j(\mathbf{r}) = \epsilon_j \varphi_j. \quad (2.16)$$

The mean density is given by

$$n(\mathbf{r}) = \sum_{j=1}^N |\varphi_j(\mathbf{r})|^2 \quad (2.17)$$

where the sum runs over N eigenvalues for the ground state, with respect to the Pauli-exclusion principle.

These three equations (2.15-2.17) are known as the self-consistent Hartree equations, which are solved numerically in a self consistent way.³ This is to say that one can start from some approximate initial value of the density $n(\mathbf{r})$, construct v_H , solve for

³A more detailed discussion of the Hartree and Hartree-Fock methods is presented in Appendix A. There, the transition from the many-particle Hamiltonian to the self-consistent approach is well presented.

φ_j in the single particle equation and then recalculate density $n(\mathbf{r})$ from the definition of the density and compare the new density with the previous one to some desired degree of accuracy. If the two values are the same within the required accuracy, then the calculation is over, otherwise one has to repeat this procedure until the required accuracy is achieved.

When Kohn and Sham worked out the so-called Kohn-Sham equations, Kohn had been inspired by the fact that the Hartree equations gave a much better description of atomic ground states, than the Thomas-Fermi theory. Comparing two theories, one can see that the difference between the two theories lies in their respective kinetic terms, equations (2.11) and (2.16), respectively. The potentials look similar – equations (2.2) and (2.15). Kohn’s quest therefore was to write down a generalization of the Hartree equations since a generalization of the Thomas-Theory had also been written down. These are now widely known as Kohn-Sham equations.⁴

In other words, the self-consistent Kohn-Sham equations are simply generalized Hartree equations [70].

The Hartree differential equation (2.16) looks like the Schrodinger equation for non-interacting electrons moving in an external potential v_{eff} . Now, for the Hohenberg-Kohn variational principle for a similar system moving in an external potential $v(\mathbf{r})$ takes the form

$$E_{v(r)}[\tilde{n}] \equiv \int v(\mathbf{r}) \tilde{n}(\mathbf{r}) d\mathbf{r} + T_s[\tilde{n}(\mathbf{r})] \geq E, \quad (2.18)$$

where $T_s[\tilde{n}(\mathbf{r})]$ is the kinetic energy of the ground state of non-interacting electrons whose density is $\tilde{n}(\mathbf{r})$ assumed to be v-representable. If we make the mean density $n(\mathbf{r})$ stationary with respect to variations of the trial density $\tilde{n}(\mathbf{r})$ so that the total number of electrons remains constant in the system under study, the Euler-Lagrange equation that follow is

$$\delta E_v[\tilde{n}(\mathbf{r})] \equiv \int \delta \tilde{n}(\mathbf{r}) \left\{ v(\mathbf{r}) + \frac{\delta}{\delta \tilde{n}(\mathbf{r})} T_s[\tilde{n}(\mathbf{r})] |_{\tilde{n} \equiv n} - \epsilon \right\} d\mathbf{r} = 0 \quad (2.19)$$

where $\tilde{n}(\mathbf{r})$ is now the ground state density for $v(\mathbf{r})$, ϵ is a Lagrange multiplier that ensures particle conservation. In this soluble non-interacting case, the ground state energy and density can be obtained by calculating the eigenfunctions $\varphi_j(\mathbf{r})$ and the corresponding eigenvalues ϵ_j of non-interacting single-particle Schrodinger-like equations:

⁴This paragraph is an indirect quotation of Walter Kohn in his 1998 Nobel lecture.

$$\left(-\frac{1}{2}\nabla^2 + v(\mathbf{r}) - \epsilon_j\right) \varphi_j(\mathbf{r}) = 0 \quad (2.20)$$

to get $E = \sum_{j=1}^N \epsilon_j$ and

$$n(\mathbf{r}) = \sum_{j=1}^N |\varphi_j(\mathbf{r})|^2 \quad (2.21)$$

with j labeling both orbital quantum numbers and spin indices, ± 1 .

At this point, the functional, equation (2.9) for the interacting case can be written as

$$F[\tilde{n}(\mathbf{r})] \equiv T_s[\tilde{n}(\mathbf{r})] + \frac{1}{2} \int \frac{\tilde{n}(\mathbf{r}) \tilde{n}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[\tilde{n}(\mathbf{r})] \quad (2.22)$$

where $T_s[\tilde{n}(\mathbf{r})]$ is the kinetic energy functional of the non-interacting electrons from equation (2.18), and $E_{xc}[\tilde{n}(\mathbf{r})]$ contains all the many body effects due to exchange and correlation and is therefore called the exchange-correlation energy functional. We can then write the Hohenberg-Kohn variational principle, equation (2.8), as

$$\begin{aligned} E_v[\tilde{n}(\mathbf{r})] &\equiv \int v(\mathbf{r}) \tilde{n}(\mathbf{r}) d\mathbf{r} + T_s[\tilde{n}(\mathbf{r})] + \frac{1}{2} \int \frac{\tilde{n}(\mathbf{r}) \tilde{n}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ &+ E_{xc}[\tilde{n}(\mathbf{r})] \geq E. \end{aligned} \quad (2.23)$$

The corresponding Euler-Lagrange equation then becomes

$$\delta E_v[\tilde{n}(\mathbf{r})] \equiv \int \delta \tilde{n}(\mathbf{r}) \left\{ v_{eff}(\mathbf{r}) + \frac{\delta}{\delta \tilde{n}(\mathbf{r})} T_s[\tilde{n}(\mathbf{r})] \Big|_{\tilde{n}(\mathbf{r})=n(\mathbf{r})} - \epsilon \right\} d\mathbf{r} = 0 \quad (2.24)$$

where

$$v_{eff}(\mathbf{r}) \equiv v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}) \quad (2.25)$$

and

$$v_{xc}(\mathbf{r}) \equiv \frac{\delta}{\delta \tilde{n}(\mathbf{r})} E_{xc}[\tilde{n}(\mathbf{r})] \Big|_{\tilde{n}(\mathbf{r})=n(\mathbf{r})}. \quad (2.26)$$

Now, the form of the Euler-Lagrange equation of the fully interacting problem, equation (2.24) looks very similar to that for the non-interacting system, equation (2.19) moving in an effective potential v_{eff} instead of $v(\mathbf{r})$. It therefore makes perfect sense to conclude that the minimizing density, $n(\mathbf{r})$, can be obtained by solving the single particle Schrodinger-like equation:

$$\left(-\frac{1}{2}\nabla^2 + v_{eff}(\mathbf{r}) - \epsilon_j\right) \varphi_j(\mathbf{r}) = 0 \quad (2.27)$$

where $v_{eff}(\mathbf{r})$ is given by equation (2.25) and

$$n(\mathbf{r}) = \sum_{j=1}^N |\varphi_j(\mathbf{r})|^2. \quad (2.28)$$

In this case, $v_{xc}(\mathbf{r})$ is the *local* exchange-correlation potential. It depends functionally on the entire density distribution $\tilde{n}(\mathbf{r})$ as presented in equation (2.26).

Finally, the ground state energy is given by

$$E = \sum_j \epsilon_j + E_{xc}[n(\mathbf{r})] - \int v_{xc}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} - \frac{1}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (2.29)$$

Equations (2.25-2.29) are the *self-consistent Kohn-Sham equations*, a complete generalization of the Hartree equations. Neglecting exchange-correlation terms, E_{xc} and v_{xc} reduces these Kohn-Sham equations to the self-consistent Hartree equations.

Note that all many body effects due to exchange and correlation are embedded in the two exchange-correlation terms, E_{xc} and v_{xc} . If these were known exactly, then the ground state energy of the interacting system would be calculated exactly.

However, since E_{xc} and v_{xc} are not known exactly, much attention is currently being given to their approximate solutions.

Comments:⁵ The exact single particle potential v_{eff} can be regarded as the *fictitious* potential that is needed to translate the non-interacting system to its equivalent fully interacting system moving in an external potential $v(\mathbf{r})$, with both systems sharing the same ground state density $n(\mathbf{r})$. Therefore, if this ground state density is independently known, say from experiment or some wavefunction-based calculation (for small systems), then the effective potential v_{eff} and subsequently, v_{xc} can be obtained directly from the density [118].

There is no known, directly observable meaning for the Kohn-Sham wave-functions φ_j and associated energies ϵ_j , except:

i) for the connection between these wave-functions φ_j and the true density of the system $n(\mathbf{r})$ as in equation (2.28), and

⁵All of these comments come from [70].

ii) the fact that the magnitude of the highest occupied eigenvalue (ϵ_j) relative to the vacuum equals the ionization energy [5].

Most practical calculations that employ Density Functional Theory use the Kohn-Sham equations rather than the generally less accurate Hohenberg-Kohn formulation.⁶

2.4 Exchange and Correlation Energy Functionals

The success and accuracy of modern Density Functional Theory hangs around good approximations of the unknown functionals, namely:

- i) $F[n(\mathbf{r})]$ for the Hohenberg-Kohn variational principle, and
- ii) $E_{xc}[n(\mathbf{r})]$ for the Kohn-Sham formulation of DFT.

As Walter Kohn put it his Nobel Lecture [70], “these approximations come from outside DFT. They reflect the physics of electronic structure.” In the interest of space, we will only look at some of the few ones employed in the Kohn-Sham system, i.e. those that approximate $E_{xc}[n(\mathbf{r})]$, which have a quasi-local form. As will be discussed later, the exchange-correlation energy functional $E_{xc}[n(\mathbf{r})]$ can be written as

$$E_{xc}[n(\mathbf{r})] = \int e_{xc}(\mathbf{r}; [n(\tilde{\mathbf{r}})] n(\mathbf{r})) d\mathbf{r} \quad (2.30)$$

where $e_{xc}(\mathbf{r}; [n(\tilde{\mathbf{r}})])$ is the exchange-correlation energy per particle at the point $\mathbf{r}$, which is a functional of the density $n(\tilde{\mathbf{r}})$. It depends primarily on the density $n(\tilde{\mathbf{r}})$ at points $\tilde{\mathbf{r}}$ near $\mathbf{r}$, where “near” refers to microscopic distances of the order of the Thomas-Fermi screening length or the local Fermi wavelength.

Equation (2.30) is somewhat similar to equation (2.11) in form.

All of the Kohn-Sham energy (apart from the long-range Coulomb potential) can be written in terms of one-particle and two-particle density matrices of the interacting and non-interacting system $G_1(\mathbf{r}_1; \mathbf{r}_1')$, $G_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1', \mathbf{r}_2')$ and $G_1^0(\mathbf{r}_1, \mathbf{r}_1')$, $G_2^0(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1', \mathbf{r}_2')$, all corresponding to and uniquely defined by the same physical density $n(\mathbf{r})$. Their calculation involves these Green’s functions for arguments that are primarily close to one another. Additionally, these Green’s functions depend only on the form of $n(\tilde{\mathbf{r}})$ for $\tilde{\mathbf{r}}$ near $\mathbf{r}_1$, for any given $\mathbf{r}_1$. This leads immediately to equation (2.30), where e_{xc} is a *nearsighted*⁷ functional of the density $n(\tilde{\mathbf{r}})$.

⁶The Hohenberg-Kohn formulation inherits the inaccuracies of the Rayleigh-Ritz variational principle, namely overestimation of the ground state energy.

⁷The concept of nearsightedness was originally presented by Walter Kohn in 1996 and is further referred to by the same author in his Nobel Lecture.

2.4.1 Local Density Approximation (LDA)⁸

The Local Density Approximation (LDA) is the “mother” of most of the approximations currently in use in DFT. It employs the quasi-local approach discussed in brief above. It is the simplest approximation to $E_{xc}[n(\mathbf{r})]$ and yet its accuracy and field of application is remarkable. It was originally designed for applications in which the density varies slowly, yet it has yielded very good results outside its domain, for instance in calculating work functions for metal surfaces: near metal surfaces, the density varies very rapidly. There are many other examples in which the LDA has given excellent results.

In the formulation of LDA,

$$E_{xc}^{LDA} \equiv \int e_{xc}(n(\mathbf{r})) n(\mathbf{r}) d\mathbf{r} \quad (2.31)$$

where $e_{xc}(n)$ is the exchange-correlation energy per particle of a uniform electron gas of density n .

Omitting the discussion of the exchange energy, the exchange part is given by

$$e_x(n) = -\frac{0.458}{r_s} \quad (2.32)$$

where we have introduced the Seitz radius r_s , which is the radius of a sphere containing one electron, given by $(\frac{4\pi}{3}) r_s^3 = n^{-1}$.

The correlation part was first estimated by E. P. Wigner in 1938 [120]:

$$e_c(n) = -\frac{0.44}{r_s + 7.8} \quad (2.33)$$

and then with a precision of about 1% by Ceperly and Alder in 1980, using Monte Carlo methods [30].

The accuracy of the LDA in solving the Kohn-Sham equations is typically within the order of 10% for the exchange part, the normally much smaller correlation energy is generally over-estimated by a factor of about 2. The two errors however, partially cancel one another.

LDA is known to give ionization energies of atoms, dissociation energies of molecules and cohesive energies with a fair accuracy of 10 – 20%. Interestingly though, it gives bond lengths, and thus the geometries of molecules and solids to within 1%. This is impressive.

⁸Based on [70] and [104].

In systems where electron-electron interaction effects dominate, the LDA is known to fail because they lack the resemblance of an electron gas for which it was originally designed. Such systems would include heavy fermion systems.

LDA was also known to fail in the description of van der Waals forces, but this has since been modified lately.

2.4.2 Generalized Gradient Approximation (GGA)⁹

To properly understand many other approximations, the Generalized Gradient Approximation (GGA) included, we must first discuss the concept of the *average exchange-correlation hole* around a given point $\mathbf{r}$. Talking of the *exchange-correlation hole*, an electron in space generally eliminates other electrons from a spherical region around it, following the Pauli exclusion principle. This spherical space around the electron where there is a depletion of electron density is known as the exchange-correlation hole. This concept can be formally derived from the exchange and correlation parts of exchange-correlation energy functional.

The physical exchange-correlation hole is given by

$$n_{xc}(\mathbf{r}, \mathbf{r}') = g(\mathbf{r}, \mathbf{r}') - n(\mathbf{r}') \quad (2.34)$$

where $g(\mathbf{r}, \mathbf{r}')$ is the conditional density at $\mathbf{r}'$ given that one electron is at $\mathbf{r}$. It describes the hole dug into the average density $n(\mathbf{r}')$ by the electron at $\mathbf{r}$.

The exchange-correlation hole density $n_{xc}(\mathbf{r}, \mathbf{r}')$ describes how the presence of an electron at $\mathbf{r}$ depletes the total density of the other electrons at the point $\mathbf{r}'$. This hole is normalized:

$$\int n_{xc}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = 1. \quad (2.35)$$

It is also a functional of the density distribution $n(\tilde{\mathbf{r}})$.

To define the *average exchange-correlation hole*, we need to introduce a fictitious Hamiltonian H_λ , where $0 \leq \lambda \leq 1$, which is different from the physical Hamiltonian $H_{\lambda=1}$ by replacing

$$\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \rightarrow \frac{\lambda e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (2.36)$$

⁹Also based on [70].

in the electron-electron potential, and

$$v(\mathbf{r}) \rightarrow v_\lambda(\mathbf{r}) \quad (2.37)$$

where the fictitious potential is chosen such that for all λ in the interval $(0,1)$ the corresponding density equals the physical density $n(\mathbf{r})$:

$$n_\lambda(\mathbf{r}) \equiv n_{\lambda=1}(\mathbf{r}) = n(\mathbf{r}). \quad (2.38)$$

The average exchange-correlation hole density is then defined as

$$\bar{n}_{xc}(\mathbf{r}, \mathbf{r}') = \int_0^1 d\lambda n_{xc}(\mathbf{r}, \mathbf{r}'; \lambda). \quad (2.39)$$

At this point, the exchange-correlation energy can then be written as

$$E_{xc} = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) \bar{n}_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (2.40)$$

This result was proved independently in three important publications [52, 76, 48]. It can also be written as

$$E_{xc} = -\frac{1}{2} \int d\mathbf{r} n(\mathbf{r}) \bar{R}_{xc}^{-1}(\mathbf{r}, [n(\tilde{\mathbf{r}})]) \quad (2.41)$$

where

$$\bar{R}_{xc}^{-1}(\mathbf{r}, n(\tilde{\mathbf{r}})) \equiv \int d\mathbf{r}' \frac{-\bar{n}_{xc}(\mathbf{r}, \mathbf{r}') [n(\tilde{\mathbf{r}})]}{|\mathbf{r} - \mathbf{r}'|} \quad (2.42)$$

is the moment of degree -1 of $-\bar{n}_{xc}(\mathbf{r}, \mathbf{r}')$, i.e. the inverse radius of the λ -averaged exchange-correlation hole.

Comparing equations (2.41) and (2.30) yields

$$e_{xc}(\mathbf{r}; [n(\tilde{\mathbf{r}})]) = -\frac{1}{2} R_{xc}^{-1}(\mathbf{r}, [n(\tilde{\mathbf{r}})]) \quad (2.43)$$

which is both physical and formally exact.

Since $R_{xc}^{-1}(\mathbf{r})$ is a functional of the density distribution $n(\tilde{\mathbf{r}})$ which is expected to be predominantly short-sighted, we can expand the density distribution $n(\tilde{\mathbf{r}})$ around the point $\mathbf{r}$ (taken as the origin) to get

$$n(\tilde{\mathbf{r}}) = n + n_i \tilde{r}_i + \frac{1}{2} \sum n_{ij} \tilde{r}_i \tilde{r}_j + \dots \quad (2.44)$$

where $n \equiv n(0)$, $n_i \equiv \nabla_i n(\mathbf{r})|_{\mathbf{r}=0}$ and so on, and we considered $R_{xc}(\mathbf{r})$ as a function of the coefficients n , n_i , n_{ij} , ... Ordering in powers of the differential operators and respecting the scalar nature of $R_{xc}(\mathbf{r})$ gives

$$\begin{aligned} R_{xc}^{-1}(\mathbf{r}) = & F_0(n(\mathbf{r})) + F_{21}(n(\mathbf{r})) \nabla^2 n(\mathbf{r}) \\ & + F_{22}(n(\mathbf{r})) \times \sum (\Delta_i n(\mathbf{r})) (\Delta_i n(\mathbf{r})) + \dots \end{aligned} \quad (2.45)$$

Substituting this into equation (2.41) and integrating by parts yields the following result to the gradient expansion:

$$E_{xc} = E_{xc}^{LDA} + \int G_2(n) (\nabla n)^2 d\mathbf{r} + \int [G_4(n) (\nabla^2 n)^2 + \dots] d\mathbf{r} + \dots \quad (2.46)$$

where $G_2(n)$ is a universal functional of n .

This expansion has worsened the results of LDA when applied to real systems.

However, the series, equation (2.44), can formally resume, resulting in the following sequence:

$$E_{xc}^0 = \int \epsilon(n(\mathbf{r})) n(\mathbf{r}) d\mathbf{r} \quad (2.47)$$

(LDA),

$$E_{xc}^{(1)} = \int f^{(1)}(n(\mathbf{r}), |\nabla n(\mathbf{r})|) n(\mathbf{r}) d\mathbf{r} \quad (2.48)$$

(GGA), and

$$E_{xc}^{(2)} = \int f^{(2)}(n(\mathbf{r}), |\nabla n(\mathbf{r})|) \nabla^2 n(\mathbf{r}) d\mathbf{r} \quad (2.49)$$

E_{xc}^0 is the LDA requiring the independently calculated function of one variable, $x \equiv n$. The next term $E_{xc}^{(1)}$ is the Generalized Gradient Approximation (GGA) and it requires the independently calculated function of two variables, $x \equiv n$ and $y \equiv |\nabla n|$.

The construction of GGA's of the form given in equation (2.48) has made use of sum rules, general scaling properties, asymptotic behavior of effective potentials and densities in the tail regions of atoms and their aggregates.

2.4.3 Orbital Dependent Functionals (OEP and EXX)¹⁰

The Kohn-Sham approach to electronic structure is a better than the older Thomas-Fermi approach primarily because it offers a better description of the kinetic energy, as discussed earlier. In the Kohn-Sham approach, the kinetic energy is explicitly expressed as a functional of the independent particle orbitals, ψ_i . It is a functional of the density, implicitly. This functional dependence on the density is highly non-trivial, non-analytic and certainly non-local. Derivatives of the Kohn-Sham kinetic energy with respect to the density are discontinuous at densities corresponding to filled shells, yielding shell structure in the Kohn-Sham approach.

It is also known that the true exchange-correlation energy functional E_{xc} is discontinuous at filled shells, which would yield correct descriptions of energy gaps between filled bands. Expressing E_{xc} in terms of the independent particle orbitals, ψ_i is to achieving this well favored description of energy bands. On the contrary, LDA and GGA (henceforth combinedly referred to as DFA, i.e. Density Functional Approximations) do not exhibit the orbital dependence of the exchange-correlation energy E_{xc} functional.

Sharp and Horton expressed this problem (in 1953, before DFT was formulated) [100] as the problem of finding “that potential, the same for all electrons, such that when ... given a small variation, the energy of the system remains stationary” [83]. This is known as the Optimized Effective Potential (OEP) method [29, 102, 24].

If one considers orbitals that are determined by the potential v_{eff} through the independent particle Schrodinger equation, it is possible to define (in principle) the energy functional of the potential v_{eff} as

$$E_{OEP}[v_{eff}] = E[\psi_i[v_{eff}]]. \quad (2.50)$$

This method is simply the optimization of the potential v_{eff} in the Kohn-Sham equation (2.27).

Equation (2.26) can be written in the OEP format as

$$v_{xc}^{OEP}(\mathbf{r}) = \frac{\delta E_{xc}^{OEP}}{\delta n(\mathbf{r})} \quad (2.51)$$

Applying the chain rule to equation (2.51) gives

¹⁰Mainly based on Richard Martin’s book [83].

$$\begin{aligned}
 v_{xc}^{OEP}(\mathbf{r}) &= \sum_{i=1}^N \int d\mathbf{r}' \frac{\delta E_{xc}}{\psi_i(\mathbf{r}) \delta n(\mathbf{r})} \psi_i(\mathbf{r}') + c.c. \\
 &= \sum_{i=1}^N \int d\mathbf{r}' \int d\mathbf{r}'' \left[\frac{\delta E_{xc}^{OEP}}{\delta \psi_i(\mathbf{r})} \frac{\delta \psi_i(\mathbf{r}')}{\delta v_{eff}(\mathbf{r}'')} + c.c. \right] \frac{\delta v_{eff}(\mathbf{r}'')}{\delta n(\mathbf{r})}
 \end{aligned} \tag{2.52}$$

where v_{eff} is the total potential in the independent-particle Kohn-Sham equations that determine the single particle orbitals ψ_i .

$$\frac{\delta E_{xc}^{OEP}}{\delta \psi_i(\mathbf{r}')} \equiv v_{i,xc}^{NL}(\mathbf{r}') \psi_i(\mathbf{r}') \tag{2.53}$$

is an orbital dependent non-local operator.

$$\frac{\delta \psi_i(\mathbf{r})}{\delta v_{eff}(\mathbf{r}'')} = G_0(\mathbf{r}', \mathbf{r}'') \psi_i(\mathbf{r}'') \tag{2.54}$$

in which the Green's function for the non-interacting Kohn-Sham system is given by

$$G_0(\mathbf{r}, \mathbf{r}') = \sum_{j \neq i}^{\infty} \frac{\psi_j(\mathbf{r}) \psi_j^*(\mathbf{r}')}{\varepsilon_i - \varepsilon_j} \tag{2.55}$$

This term can be evaluated by perturbation theory.

$\frac{\delta v_{eff}(\mathbf{r}'')}{\delta n(\mathbf{r})}$ is the inverse of a response function, χ_0 ¹¹, given by

$$\chi_0(\mathbf{r}, \mathbf{r}') = \frac{\delta n(\mathbf{r})}{\delta v_{eff}(\mathbf{r}'')} = \sum_i^N \psi_i^*(\mathbf{r}) G_0(\mathbf{r}, \mathbf{r}') \psi_i(\mathbf{r}') \tag{2.56}$$

where we have used the chain rule and the fact that the density is given by equation (2.28).

Multiplying equation (2.53) by $\chi_0(\mathbf{r}, \mathbf{r}')$ and integrating, we get

$$\sum_{i=1}^N \int d\mathbf{r}' \psi_i^*(\mathbf{r}') [v_{xc}^{OEP}(\mathbf{r}') - v_{i,xc}^{NL}(\mathbf{r}')] G_0(\mathbf{r}', \mathbf{r}) \psi_i(\mathbf{r}) + c.c. = 0 \tag{2.57}$$

which tells us that $v_{xc}^{OEP}(\mathbf{r})$ is physically a particular weighted average of the non-local orbital dependent potentials.

¹¹In general, the response function $\chi(r, r'; \omega)$ describes the change of total density at the point r due to a perturbing potential at the point r' , of frequency ω .

This integral form is the basis of for useful approximations for which the potential can be given explicitly. A good example is the exact exchange approximation (EXX) by Krieger, Li and Iafrate [102, 63, 64, 65], known as the KLI approximation. Although a complete derivation is available, a heuristic approach is to replace the energy denominator in the Green's function by $\Delta\varepsilon$ which then drops out of equation (2.57) and the Greens function (2.55) becomes

$$G_0(\mathbf{r}, \mathbf{r}') \rightarrow \sum_{j \neq i}^{\infty} \frac{\psi_j(\mathbf{r}) \psi_j^*(\mathbf{r}')}{\Delta\varepsilon} = \frac{\delta(\mathbf{r} - \mathbf{r}') - \psi_i(\mathbf{r}) \psi_i^*(\mathbf{r}')}{\Delta\varepsilon}. \quad (2.58)$$

Substituting equation (2.58) into equation (2.57) yields

$$v_{xc}^{KLI}(\mathbf{r}) = v_{xc}^S(\mathbf{r}) + \sum_{i=1}^N \frac{n_i(\mathbf{r})}{n(\mathbf{r})} [\bar{v}_{i,xc}^{KLI} - \bar{v}_{i,xc}^{NL}] \quad (2.59)$$

where $v_{xc}^S(\mathbf{r})$ is the density-weighted average proposed by Slater [101]:

$$v_{xc}^S(\mathbf{r}) = v_{xc}^S(\mathbf{r}) + \sum_{i=1}^N \frac{n_i(\mathbf{r})}{n(\mathbf{r})} v_{i,xc}^{NL}(\mathbf{r}). \quad (2.60)$$

and the $\bar{v}_{i,xc}$ are expectation values

$$\begin{aligned} \bar{v}_{i,xc}^{KLI} &= \langle \psi_i | \bar{v}_{i,xc}^{KLI} | \psi_i \rangle \\ \bar{v}_{i,xc}^{NL} &= \langle \psi_i | \bar{v}_{i,xc}^{NL} | \psi_i \rangle. \end{aligned} \quad (2.61)$$

Taking matrix elements of equation (2.59) yields a set of linear linear equations for the matrix elements $\bar{v}_{i,xc}^{KLI}$, which can be solved readily.

In the case of exchange only, the KLI approximation has been shown to be accurate in many cases [102].

2.4.4 Hybrid Functionals¹²

DFA and OEP functionals can and are successfully combined to give very accurate descriptions in electronic structure methods. This results in “hybrid” functionals [70]. They are generally more accurate than their parents functionals. The mixture emanates

¹²This sub-section is based on W. Kohn's Nobel lecture[70] and R. Martin's book [83].

from the effects of the coupling constant λ , introduced in section 2.4.2. The lower limit, $\lambda = 0$ corresponds to pure exchange. A. Becke [17] argues that the potential part of the LDA and the GGA functionals is most appropriate at full coupling, i.e. when $\lambda = 1$. He also suggests that the integral, equation (2.41), can be approximated assuming a linear dependence on λ . This leads to a “half-and-half” form

$$E_{xc} = \frac{1}{2} (E_x^{HF} + E_{xc}^{DFA}) \quad (2.62)$$

where DFA stands for either LDA or GGA as introduced in the previous section, and E_x^{HF} is exchange-only energy calculated from the exact Kohn-Sham wave-functions as has already been described.

Becke also introduced parametrized forms such as the B3P91 [17, 16] which is a three parameter functional that mixes Hartree-Fock exchange, the exchange functional of Becke (B88) and correlation from Perdew and Wang (PW91) [83]. These parametrized hybrid functionals are quite accurate for many molecules.

In the same language, we can also talk about the B3LYP which uses LYP correlation to give

$$E_{xc} = E_{xc}^{LDA} + \alpha_0 (E_x^{HF} - E_x^{DFA}) + \alpha_x E_x^{Becke} + \alpha_c E_c \quad (2.63)$$

where α_0 , α_x and α_c are fitting parameters that are empirically adjusted to fit molecular and atomic data.

There are many other hybrid functionals in use today from various contributors in the field of electronic structure methods. We have only described here, the few that will resurface in this work.

2.5 Applications of Density Functional Theory¹³

Ground state Density Functional Theory (DFT) has enjoyed many successes in the domain from which it was originally formulated, i.e. in calculating ground state energies and states [104]. We can also add to this list, quantities that can be derived from these two quantities. These include, but are not limited to (in addition to ground state energy and density)

- i) the electron localization functions (ELF) [6], which gives a visual description of the electron densities.

¹³Based mainly [104].

- ii) predictions of crystal structures at various macroscopic densities, which is achieved by calculating the ground state energies for all the possible unit cells for a given solid. The structure with the lowest energy is usually the most stable.
- iii) the bulk modulus which is determined by fitting the calculated total energies corresponding to various lattice parameters for a particular lattice structure, onto an equation of state.
- iv) predictions of phase transitions as a function of pressure can be deduced from the equations of state from (iii) above.
- v) unit cell volumes and bond distances can be deduced from lowest energy structure with very high accuracies.
- vi) surface physics is well studied using electronic structure methods.
- viii) phonon energies can be determined satisfactorily using “frozen-phonon” calculations, in which the lattice is given a static deformation corresponding to a phonon of a particular wave-vector q and polarization s . The total energy is then calculated and compared with the ground state energy.
- ix) ionization energies are also a good candidate for study as described earlier in this chapter.
- x) the band structures of solids are usually determined by interpreting the Kohn-Sham eigenvalues $\epsilon_{k,n}$ for Bloch states of wave-vector k in a band n as the band energies.

Despite all these successes, the ground state DFT in its original state does not describe systems with strong electron-electron correlations (such as in superconductors). It was not designed for that. Excitation energies require a reformulation of the whole theory as discussed in the next chapter.

Chapter 3

Excitations: Time Dependent Density Functional Theory¹

While the ground state Density Functional Theory (DFT) is a reformulation of the time-independent Schrodinger equation (which describes the ground state of a non-relativistic electronic system), Time Dependent Density Functional Theory (TDDFT) is a reformulation of the time-dependent Schrodinger equation

$$i \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \mathcal{H}(\mathbf{r}, t) \Psi(\mathbf{r}, t) \quad (3.1)$$

where $\Psi(\mathbf{r}, t)$ is the time-dependent many body wave-function. This equation describes the evolution of the non-relativistic electronic system placed in a time varying potential [3]. In both cases, the single particle density n must replace the many particle wave-function Ψ , with the difference that both n and Ψ are time-varying in the time-dependent case and time-independent in the ground state descriptions.

For N such particles, the time-dependent Hamiltonian can be written as

$$\mathcal{H}(\mathbf{r}, t) = T(\mathbf{r}) + W(\mathbf{r}) + V_{ext}(\mathbf{r}, t) \quad (3.2)$$

since it is only the external potential $V_{ext}(\mathbf{r}, t)$ that varies with time, while the kinetic energy $T(\mathbf{r})$ and the electron-electron interaction term $W(\mathbf{r})$ generally do not vary over the same time.

Employing the Hartree atomic units in which $\hbar = e = m = 1$, we can write out the first two terms in equation (3.2) as

¹This chapter is mainly based on [81].

$$T(\mathbf{r}) = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 \quad (3.3)$$

$$W(\mathbf{r}) = \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (3.4)$$

where $\mathbf{r}_i$ and $\mathbf{r}_j$ are the positions of the i^{th} and j^{th} electrons in the N -electron system.

Our interest will be to describe the retinal molecule inside a strong laser. Therefore the potential external to the i^{th} electron in the system can be written as

$$V_{ext}(\mathbf{r}, t) = U_{en}(\mathbf{r}, t) + V_{laser}(\mathbf{r}, t) \quad (3.5)$$

where the potential provided by all the nuclei in the system is

$$U_{ext}(\mathbf{r}, t) = - \sum_{v=1}^{N_n} \sum_{i=1}^N \frac{Z_v}{|\mathbf{r}_i - \mathbf{R}_v(t)|} \quad (3.6)$$

and the laser potential is

$$V_{laser}(\mathbf{r}, t) = E f(t) \sin(\omega t) \sum_{i=1}^N \mathbf{r}_i \cdot \alpha. \quad (3.7)$$

In equation (3.6), N_n is the total number of nuclei in the system, while Z_v and $\mathbf{R}_v$ are the charge and position of the v^{th} nucleus in the system. In this case, we have allowed $\mathbf{R}_v$ to depend on time to include the case in which the nuclei are allowed to move along a classical path. This will be useful in the study of the classical dynamics of the system.

In equation (3.7), E , ω and α are the amplitude, frequency and polarization of the laser whose pulse is shaped by an envelope (around the pulse) described by the function $f(t)$. In writing out this equation, two approximations were made, namely:

- i) the laser field is treated classically, which is a justified description for our case in which the density of photons is so large that their individual, i.e. quantum, nature can be ignored, and
- ii) we have used the dipole approximation.

The dipole approximation is valid when:

- a) the wavelength of the light is much larger than the size of the system, which is true for the retinal molecule and many other molecules that are smaller than very large proteins,
- b) the path that the particle travels in one period of the laser is small compared to the wavelength of the laser, and
- c) the total duration of the laser pulse should be short enough for the molecule not to leave the focus of the laser during the laser-molecule interaction time.

With these approximations, we can treat the laser pulse as a pure electric field, completely neglecting its magnetic component. Approximation (c) in particular only holds if the laser intensity is not strong enough to accelerate the electrons to relativistic velocities.

Now, the major steps in the ground state reformulation as described in Chapter 2 are:

- i) the Hohenberg-Kohn theorem that states the one-to-one correspondence of the density and the external potential, and
- ii) the mapping of the fully interacting system onto an auxiliary non-interacting one to derive the self-consistent Kohn-Sham equations.

We therefore expect a successful time-dependent reformulation (TDDFT) to have similar major steps in its formulation, except that:

- i) the density now described should be time-dependent, $n(\mathbf{r}, t)$, and
- ii) the Kohn-Sham equations must resemble the time-dependent single particle Schrodinger equation, rather than the time-independent one.

We will also need to reformulate or adjust the exchange-correlation functionals to suit the time-dependent description.

3.1 The Runge-Gross Theorem

Following the then still growing success of DFT, there were many attempts to write down the general TDDFT, which all fell short in one point or another until the work of Runge and Gross [98] in 1984. For this reason, the Hohenberg-Kohn theorem [60] for the time-dependent case is the now famous Runge-Gross theorem which we will prove.

The Runge-Gross theorem is the statement that given any two time-dependent potentials, $v(\mathbf{r}, t)$ and $v'(\mathbf{r}, t)$, that differ by more than a purely time-dependent function $c(t)$, they cannot produce the same time-dependent density $n(\mathbf{r}, t)$ when acting on the same system. If they differ only by a time-dependent function, they produce wave-functions

which are equal up to a purely time-dependent phase which will cancel when we calculate the density or any other observable of the system.

Before we prove the Runge-Gross theorem, it is probably important to note that the ground state Hohenberg-Kohn theorem was proved using the variational principle (conservation) of total energy, but we do not have such a total energy principle in excited states – the total energy is not a conserved quantity in this case. Maybe we can try the quantum mechanical action which is

$$A[\Phi] = \int_{t_0}^{t_1} dt \left\langle \Phi(t) \left| \left(i \frac{\partial}{\partial t} - \mathcal{H}(t) \right) \right| \Phi(t) \right\rangle \quad (3.8)$$

where $\Phi(t)$ is an N body function defined in some convenient space.

From equation (3.8), we can deduce the following properties of the quantum-mechanical action:

- i) setting the functional derivative of the action in terms of $\Phi^*(t)$ to zero leads to equation (3.1), the Schrodinger time-dependent equation. This means that we can therefore solve the time-dependent problem by calculating the stationary point of the functional $A[\Phi(t)]$. The function Ψ that yields this stationary point will be the solution of equation (3.1). {This is not a “minimum” principle, but rather, a “stationary” point principle}.
- ii) the action is always zero at the stationary point.

Because of these two observations, the quantum mechanical action is a lot less useful property of the system compared to the total energy in the ground state.

Well, this failure so far can be attributed to the fact that the time-dependent equation (3.1) is an *initial value* problem (being a first order partial differential equation in time), while the time-independent equation is a *boundary value* problem since it is a second order partial differential equation in space. Their solutions are therefore fundamentally different. The Runge-Gross theorem therefore, can hold only for a *fixed initial* state [81].

The correct proof: Our goal is to prove that given any two time-dependent potentials $v(\mathbf{r}, t)$ and $v'(\mathbf{r}, t)$, that differ by more than just a time-dependent potential $c(t)$, they cannot possibly produce the same time-dependent density, i.e.

$$v(\mathbf{r}, t) \neq v'(\mathbf{r}, t) + c(t) \Rightarrow \rho(\mathbf{r}, t) \neq \rho'(\mathbf{r}, t) \quad (3.9)$$

$\rho(\mathbf{r}, t)$ is the density produced by $v(\mathbf{r}, t)$ and $\rho'(\mathbf{r}, t)$ is the density produce by $v'(\mathbf{r}, t)$.

In this proof, we will restrict ourselves to external potentials that are Taylor series expandable with respect to the time coordinate around the initial time t_0 :

$$v(\mathbf{r}, t) = \sum_{k=0}^{\infty} c_k(\mathbf{r}) (t - t_0)^k \quad (3.10)$$

where the expansion coefficients

$$c_k(\mathbf{r}) = \frac{1}{k!} \frac{d^k}{dt^k} v(\mathbf{r}, t) \big|_{t=t_0}. \quad (3.11)$$

From now on, we will use primes to distinguish the quantities of the systems that are characterized by external potentials, v and v' .

We can therefore define the following function:

$$u_k(\mathbf{r}) = \frac{\partial^k}{\partial t^k} [v(\mathbf{r}, t) v'(\mathbf{r}, t)] \big|_{t=t_0}. \quad (3.12)$$

Equation (3.9) implies that at least one of the coefficients in equation (3.10) will differ by more than a constant, i.e.

$$\exists_{k \geq 0} : u_k(\mathbf{r}) \neq \text{const.} \quad (3.13)$$

Now, the proof will be in two major steps which will be proving that

- i) if $v(\mathbf{r}, t) \neq v'(\mathbf{r}, t) + c(t)$, then the current densities $j(\mathbf{r}, t)$ and $j'(\mathbf{r}, t)$ generated by $v(\mathbf{r}, t)$ and $v'(\mathbf{r}, t)$ (respectively) are also different, and
- ii) if the current densities $j(\mathbf{r}, t)$ and $j'(\mathbf{r}, t)$ are different, then the corresponding densities $n(\mathbf{r}, t)$ and $n'(\mathbf{r}, t)$ are also different.

Let us start by writing the current density as an expectation value of the current density operator:

$$j(\mathbf{r}, t) = \langle \Psi(t) | \hat{j}(\mathbf{r}) | \Psi(t) \rangle \quad (3.14)$$

where

$$\hat{j}(\mathbf{r}) \equiv -\frac{1}{2i} \left\{ \left[\nabla \psi^\dagger(\mathbf{r}) \right] \hat{\psi}(\mathbf{r}) - \hat{\psi}^\dagger(\mathbf{r}) \left[\nabla \hat{\psi}(\mathbf{r}) \right] \right\}. \quad (3.15)$$

Recall the quantum-mechanical equation of motion which is valid for any operator $\hat{O}(t)$:

$$i \frac{d}{dt} \langle \Psi(t) | \hat{O}(t) | \Psi(t) \rangle = \langle \Psi(t) | \left(i \frac{\partial}{\partial t} \hat{O}(t) + [\hat{O}(t), \hat{\mathcal{H}}(t)] \right) | \Psi(t) \rangle \quad (3.16)$$

Using equations (3.14) and (3.16) to write down the equation of motion of the current density in the primed and unprimed states yields the following two equations:

$$i \frac{d}{dt} j(\mathbf{r}, t) = \langle \Psi(t) | [\hat{j}(\mathbf{r}), \hat{\mathcal{H}}(t)] | \Psi(t) \rangle \quad (3.17)$$

$$i \frac{d}{dt} j'(\mathbf{r}, t) = \langle \Psi'(t) | [\hat{j}(\mathbf{r}), \hat{\mathcal{H}}'(t)] | \Psi'(t) \rangle. \quad (3.18)$$

At time $t = t_0$, the wave-functions as well as particle and current densities must be equal in both the primed and unprimed states since we start from the same initial many body state, i.e.

$$|\Psi(t_0)\rangle = |\Psi'(t_0)\rangle \equiv |\Psi_0\rangle \quad (3.19)$$

$$n(\mathbf{r}, t_0) = n'(\mathbf{r}, t_0) \equiv n_0(\mathbf{r}) \quad (3.20)$$

$$j(\mathbf{r}, t_0) = j'(\mathbf{r}, t_0) \equiv j_0(\mathbf{r}). \quad (3.21)$$

Taking the difference between equations (3.17) and (3.18) at time $t = t_0$, we obtain

$$\begin{aligned} i \frac{d}{dt} [j(\mathbf{r}, t) - j'(\mathbf{r}, t)]_{t=t_0} &= \langle \Psi_0 | [\hat{j}(\mathbf{r}), (\hat{\mathcal{H}}(t_0) - \hat{\mathcal{H}}'(t_0))] | \Psi_0 \rangle \\ &= \langle \Psi_0 | [\hat{j}(\mathbf{r}), (v(\mathbf{r}, t_0) - v'(\mathbf{r}, t_0))] | \Psi_0 \rangle \\ &= i n_0(r) \nabla [v(r, t) - v'(r, t)]. \end{aligned} \quad (3.22)$$

If the potentials differ already initially, i.e. when $k = 0$, then

$$i \frac{d}{dt} [j(\mathbf{r}, t) - j'(\mathbf{r}, t)]_{t=t_0} \neq 0 \quad (3.23)$$

The two current densities, $j(\mathbf{r}, t)$ and $j'(\mathbf{r}, t)$ will consequently deviate at later times $t > t_0$.

For $k > 0$, the equation is applied $k + 1$ times to yield

$$\frac{d^{k+1}}{dt^{k+1}} [j(\mathbf{r}, t) - j'(\mathbf{r}, t)]_{t=t_0} = n_0(\mathbf{r}) \nabla u_k(\mathbf{r}) \quad (3.24)$$

in which

$$\frac{d^{k+1}}{dt^{k+1}} [j(\mathbf{r}, t) - j'(\mathbf{r}, t)]_{t=t_0} \neq 0. \quad (3.25)$$

This implies that $j(\mathbf{r}, t) \neq j'(\mathbf{r}, t)$ for $t > t_0$.

Now we prove that if the current densities are different ($j(\mathbf{r}, t) \neq j'(\mathbf{r}, t)$), then the corresponding particle densities are also different ($n(\mathbf{r}, t) \neq n'(\mathbf{r}, t)$). One way is to make use of the continuity equation:

$$\frac{\partial}{\partial t} n(\mathbf{r}, t) = -\nabla \cdot j(\mathbf{r}, t). \quad (3.26)$$

Subtracting the two equations that evolve out of writing equation (3.26) in the primed and unprimed states yields

$$\frac{d}{dt} [n(\mathbf{r}, t) - n'(\mathbf{r}, t)] = -\nabla \cdot [j(\mathbf{r}, t) - j'(\mathbf{r}, t)]. \quad (3.27)$$

Taking the $(k+1)^{th}$ derivative at the initial time $t = t_0$ yields

$$\begin{aligned} \frac{d^{k+2}}{dt^{k+2}} [n(\mathbf{r}, t) - n'(\mathbf{r}, t)]_{t=t_0} &= -\nabla \cdot \frac{d^{k+1}}{dt^{k+1}} [j(\mathbf{r}, t) - j'(\mathbf{r}, t)]_{t=t_0} \\ &= -\nabla \cdot [n_0(\mathbf{r}) \nabla u_k(\mathbf{r})] \end{aligned} \quad (3.28)$$

where we have used equation (3.24).

Again, if equation (3.13) holds, then

$$\nabla \cdot [n_0(\mathbf{r}) \nabla u_k(\mathbf{r})] \neq 0 \quad (3.29)$$

which implies that the two densities $n(\mathbf{r}, t)$ and $n'(\mathbf{r}, t)$, generated by the two sufficiently different potentials $v(\mathbf{r}, t)$ and $v'(\mathbf{r}, t)$, are indeed different. This sufficiently proves the Runge-Gross theorem.

Maybe it is necessary to show the validity of equation (3.29) which we will do by *reductio ad absurdum*.

Let us start by assuming that

$$\nabla \cdot [n_0(\mathbf{r}) \nabla u_k(\mathbf{r})] = 0 \quad (3.30)$$

for $u_k(\mathbf{r}) \neq \text{const.}$

Next, let us look at the integral

$$\begin{aligned} \int d^3r n_0(\mathbf{r}) [\nabla u_k(\mathbf{r})]^2 &= - \int d^3r u_k(\mathbf{r}) \nabla \cdot [n_0(\mathbf{r}) \nabla u_k(\mathbf{r})] \\ &\quad + \int_S n_0(\mathbf{r}) u_k(\mathbf{r}) \nabla u_k(\mathbf{r}) \cdot dS \end{aligned} \quad (3.31)$$

in which we used Green's theorem.

Applying equation (3.30) leaves us with

$$\int d^3r n_0(\mathbf{r}) [\nabla u_k(\mathbf{r})]^2 = \int_S n_0(\mathbf{r}) u_k(\mathbf{r}) \nabla u_k(\mathbf{r}) \cdot dS. \quad (3.32)$$

Now, the right hand side vanishes for finite systems since the density $n_0(\mathbf{r})$ and the function u_k decay reasonably for $\mathbf{r} \rightarrow \infty$. On the other hand,

$$n_0(\mathbf{r}) [\nabla u_k(\mathbf{r})]^2 > 0 \quad (3.33)$$

which is a contradiction. Thus equation (3.29) is valid and this concludes the proof of the Runge-Gross theorem.

3.2 Time-Dependent Kohn-Sham Equations

Just like in the ground state theory, the Runge-Gross theorem asserts that all observables can be calculated with the knowledge of the single particle density only, but it does not tell us how to get this all-important density. However, just like in the ground state situation, we can map the interacting problem onto an auxiliary, fictitious non-interacting system, subject to the condition that the Kohn-Sham effective potential must be chosen such that the two systems share the same density. The non-interacting electrons must obey the time-dependent single particle Schrodinger equation

$$i \frac{\partial}{\partial t} \varphi_i(\mathbf{r}, t) = \left[-\frac{1}{2} \nabla^2 + v_{KS}(\mathbf{r}, t) \right] \varphi_i(\mathbf{r}, t) \quad (3.34)$$

where $v_{KS}(\mathbf{r}, t)$ is the effective time-dependent (Kohn-Sham) potential in which the non-interacting electrons move and $\varphi_i(\mathbf{r}, t)$ are the time-dependent Kohn-Sham orbitals.

The time-dependent density is then given by

$$n(\mathbf{r}, t) = \sum_{i=1}^{occ} |\varphi_i(\mathbf{r}, t)|^2. \quad (3.35)$$

If $v_{KS}(\mathbf{r}, t)$ was known explicitly, we would be able to get the exact density of the system from equations (3.34) and (3.35).

Now, the Kohn-Sham effective potential for the time-dependent case can be written as

$$v_{KS}(\mathbf{r}, t) = v_{ext}(\mathbf{r}, t) + v_{Hartree}(\mathbf{r}, t) + v_{xc}(\mathbf{r}, t) \quad (3.36)$$

where $v_{ext}(\mathbf{r}, t)$ is the time dependent external potential due to the ions in the system and any other external electromagnetic field such an external laser field,

$v_{Hartree}(\mathbf{r}, t) = \int d^3\mathbf{r}' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|}$ is the time dependent Hartree potential, and

$v_{xc}(\mathbf{r}, t)$ is the time-dependent exchange-correlation potential (bearing all the time-dependent many-body effects due to exchange and correlation as introduced in Appendix A). Owing to a problem related to causality, we cannot use the total energy functional of the system to write down the form of this term. According to van Leeuwen [110], we can use the Keldysh formalism to define a new action function $\tilde{A}$ to write

$$v_{xc}(\mathbf{r}, t) = \frac{\delta \tilde{A}}{\delta n(\mathbf{r}, \tau)} \Big|_{n(\mathbf{r}, t)} \quad (3.37)$$

where τ is the Keldysh pseudo-time.

3.3 Time-Dependent Exchange and Correlation Functionals

No fundamental time-dependent exchange-correlation functionals have been written down yet owing to our ignorance of the form of the time-dependent exchange-correlation potential in terms of the time-dependent density. Therefore, in order to make progress, we need to make some fundamental approximations that will allow us to use the exchange-correlation functional approximations from the ground state DFT.

3.3.1 Adiabatic approximations

The basic idea here is that the time-dependent system transforms adiabatically so that we can use the ground state exchange-correlation functionals evaluated at each quasi-stationary point in time. The functional that is thus constructed is local in time. In other words, if $\tilde{v}_{xc}[n]$ is an approximation to the ground state exchange-correlation functional, we can write down the adiabatic time-dependent exchange-correlation potential as

$$v_{xc}^{adiabatic}(\mathbf{r}, t) = \tilde{v}_{xc}[n](\mathbf{r})|_{n=n(t)}. \quad (3.38)$$

This (adiabatic approximation) is expected to work well only for slowly varying systems since it is only then that the adiabatic approximation makes sense. In the case of laser-matter interaction, this definitely is not the case.

If we use local density approximation (LDA), equation (3.38) becomes

$$v_{xc}^{ALDA}(\mathbf{r}, t) = v_{xc}^{HEG}(n)|_{n=n(\mathbf{r}, t)} \quad (3.39)$$

ALDA stands for Adiabatic Local Density Approximation and *HEG* is the Homogeneous (uniform) Electron Gas. This approximation obviously carries with it all the short falls of the ground state LDA functional (discussed in Chapter 2). Perhaps the most relevant one is the fact that the exact exchange-correlation potential falls off as $-\frac{1}{r}$, whereas LDA falls off exponentially. This follows for generalized gradient approximations (GGA) as well. This has a profound effect of giving wrong ionization yields – the ionization yield calculated using the ALDA approximation is usually too small. If the electrons are pushed far away from the nuclei by say a strong laser, they feel the incorrect tail of the ALDA or AGGA (Adiabatic GGA).

In spite of all this, the ALDA approximation yields remarkably good excitation energies, making it the most popular exchange-correlation functional in TDDFT.

3.3.2 Time Dependent Optimized Effective Potential²

While it is hard to express the time-dependent exchange-correlation functional in terms of the time-dependent density $n(\mathbf{r}, t)$, we can write it down explicitly in terms of the Kohn-Sham orbitals, $\varphi_i(\mathbf{r}, t)$. This yields the time-dependent orbital-dependent exchange-correlation functional(s). They are still implicit density functionals by virtue

²Though this particular discussion is based on [81], it was originally presented in [109] for time-dependent systems.

of the Runge-Gross theorem. As in the ground state, a typical member of this family of functionals is the exact exchange functional (EXX) written here in terms of terms of the Fock integral:

$$A_x^{EXX} = -\frac{1}{2} \sum_{j,k}^{occ} \int_{t_0}^{t_1} dt \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\varphi_j^*(\mathbf{r}', t) \varphi_k(\mathbf{r}', t) \varphi_j(\mathbf{r}, t) \varphi_k^*(\mathbf{r}, t)}{|\mathbf{r} - \mathbf{r}'|} \quad (3.40)$$

which is obtained by expanding A_{xc} in powers of e^2 (where e is the electronic charge) and retaining the lowest order (exchange) term. Applying the chain rule for functional derivatives as we did in the ground state case, yields the following equation that determines the EXX potential:

$$0 = \sum_j^{occ} \int_{-\infty}^{t_1} dt' \int d^3\mathbf{r}' [v_x(\mathbf{r}', t') - u_{x,j}(\mathbf{r}', t')] \times \varphi_j(\mathbf{r}, t) \varphi_j^*(\mathbf{r}', t') G_R(\mathbf{r}t, \mathbf{r}'t') + c.c. \quad (3.41)$$

where the kernel G_R is defined by

$$iG_R(\mathbf{r}t, \mathbf{r}'t') = \sum_{k=1}^{\infty} \varphi_k^*(\mathbf{r}, t) \varphi_k(\mathbf{r}', t') \theta(t - t'). \quad (3.42)$$

It is the retarded Green's function of the system.

$u_{x,j}(\mathbf{r}', t')$ in equation (3.41) is the functional derivative of the Kohn-Sham wave-functions:

$$u_{x,j}(\mathbf{r}', t') = \frac{1}{\varphi_j^*(\mathbf{r}', t')} \cdot \frac{\delta A_{xc}[\varphi_j(\mathbf{r}', t')]}{\delta \varphi_j(\mathbf{r}', t')}. \quad (3.43)$$

Although a non-local and non-linear equation was used to obtain this exchange-correlation potential, the EXX is still a local potential.

As in the ground state, the solution of equation (3.41) is quite difficult unless if we use an approximation such as the Krieger, Li and Iafrate (KLI) approximation [64]. In fact, the KLI approximation gives a semi-analytic solution [81].

Because EXX and its KLI approximation give the expected $-\frac{1}{r}$ asymptotic behavior for neutral finite systems, they are very good approximations of the exchange-correlation potential [81].

At this point, it is probably important to mention that there are other exchange-correlation functional approximations that we will not discuss here since they will not feature in this work. In fact, the development of good functionals in TDDFT is still a very live and vibrant subject as it is still in its infancy.

3.4 Propagators for the Time-Dependent Kohn-Sham Equations

Since the time-dependent problem we are trying to solve is an initial value problem, we start from some given (or previously determined) initial state, usually the ground state, and propagate the system through time for the required total time t . The most obvious question at this stage is how do we propagate the given system computationally? It turns out that there are many possible ways one can use and the best one is not yet known.

The single-particle time-dependent equations (3.34) may be written in integral form as

$$\varphi_i(\mathbf{r}, t_f) = \hat{U}(t_f, t_0) \varphi_i(\mathbf{r}, t_0) = T \exp \left\{ -i \int_0^t d\tau \hat{\mathcal{H}}_{KS}(\tau) \right\} \varphi_i(\mathbf{r}, t_0) \quad (3.44)$$

where $T \exp$ is the time-ordered exponential which is short for

$$\begin{aligned} \hat{U}(t_f, t_0) = & \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \int_{t_0}^{t_f} d\tau_1 \int_{t_0}^{t_f} d\tau_2 \dots \int_{t_0}^{t_f} d\tau_n \\ & \times T \left\{ \hat{H}(\tau_1) \hat{H}(\tau_2) \dots \hat{H}(\tau_n) \right\}. \end{aligned} \quad (3.45)$$

If the Hamiltonian commutes with itself, we can drop the time ordering product and if it is time independent, we would have

$$\varphi_i(\mathbf{r}, t) = \exp \left\{ -it\hat{\mathcal{H}} \right\} \varphi_i(\mathbf{r}, t_0) \quad (3.46)$$

which is definitely not the case for TDDFT (in any case).

As clearly spelt out in equation (3.45), the exponential in equation (3.44) is too complex to be applied in its original form and therefore needs to be approximate in a suitable manner. The time propagation from t_0 to t_f is too big to be considered wholly. It is

therefore split into smaller slices that reduce the error during propagation, each of length Δt .

The simplest approximation to the evolution operator is a direct expansion of the exponential in powers of Δt :

$$\hat{U}(t + \Delta t, t) \approx \sum_{l=0}^k \frac{\left[-i\hat{H}\left(t + \frac{\Delta t}{2}\right)\Delta t\right]^l}{l!} + \mathcal{O}\left(\Delta t^{k+1}\right). \quad (3.47)$$

Unfortunately, the approximation does not retain unitarity, which is one of the most important properties of the Kohn-Sham evolution operator. This means that the use of this approximation on a normalized wave-function (for instance) yields an unnormalized one, making the propagation unstable. We therefore discuss here, few of the many propagators that retain unitarity.

A modified Crank-Nicholson scheme We obtain this method by imposing time-reversal symmetry on an approximate time-evolution operator. This means we can obtain the same state at time $t + \frac{\Delta t}{2}$ either by propagating forward from $\varphi(\mathbf{r}, t)$ or backwards from state $\varphi(\mathbf{r}, t + \Delta t)$, i.e.

$$\varphi\left(t + \frac{\Delta t}{2}\right) = \hat{U}\left(t + \frac{\Delta t}{2}, t\right) \varphi(t) = \hat{U}\left(t - \frac{\Delta t}{2}, t + \Delta t\right) \varphi(t + \Delta t). \quad (3.48)$$

This leads to

$$\varphi(t + \Delta t) = \hat{U}\left(t + \frac{\Delta t}{2}, t + \Delta t\right) \hat{U}\left(t + \frac{\Delta t}{2}, t\right) \varphi(t) \quad (3.49)$$

where we used the property

$$\hat{U}^{-1}(t + \Delta t, t) = \hat{U}(t - \Delta t, t) \quad (3.50)$$

concerning the inverse of the time-evolution operator.

A propagation from $\varphi(t)$ to $\varphi(t + \Delta t)$ can be done in the following three steps:

- i) we obtain an estimate of $\varphi(t + \Delta t)$ by propagating from $\varphi(t)$ using a low quality formula for $\hat{U}(t + \Delta t, t)$, such as equation (3.47) expanded to the third or fourth order.
- ii) using the wave-functions obtained from step (i) above, we construct approximations to $\hat{H}(t + \Delta t)$ and $\hat{U}(t + \frac{\Delta t}{2}, t + \Delta t)$.

iii) apply equation (3.49).

The whole procedure leads to very stable propagation.

The split-operator method This method employs the fact that the kinetic term in the Kohn-Sham Hamiltonian is diagonal in momentum space, while the potential term is diagonal in real space.

Here, we start by neglecting the time-ordering in the exponent of equation (3.44) and then approximate the integral by a trapezoidal rule:

$$\begin{aligned}\hat{U}(t + \Delta t, t) &\approx \exp \left[-i\hat{\mathcal{H}}_{KS}(t) \Delta t \right] = \exp \left[-i \left(\hat{T} + \hat{V}_{KS} \right) \Delta t \right] \\ &= \exp \left(-i\hat{T}\Delta t \right) \exp \left(-i\hat{V}_{KS}\Delta t \right) + \mathcal{O}(\Delta t^2)\end{aligned}\quad (3.51)$$

where we have further split the Hamiltonian into the kinetic and potential terms.

To apply this method, we can start by applying the potential term to $\varphi(\mathbf{r}, t)$, followed by transforming the wave-function to momentum space and then applying the kinetic term. If we consider higher order terms in equation (3.51), we will have to transform the wave-function between real and momentum space alternatingly as necessary.

The efficiency of this method can be vastly improved by the use of Fast-Fourier Transforms (FFT).

An even better approximation to the time-evolution operator is the mid-point rule which yields

$$\hat{U}(t + \Delta t, t) \approx \exp \left[-i\hat{H}_{KS} \left(t + \frac{\Delta t}{2} \right) \Delta t \right]. \quad (3.52)$$

The procedure above can then be applied with a slight modification that the Kohn-Sham potential has to be updated each time a proceeding kinetic operator is applied (for higher order terms of the expansion).

3.5 Linear Response Theory³

Two regimes of solving the time-dependent Kohn-Sham equations exist. One is when the time-dependent potential is a very small perturbation. In this case, there is no need

³This section is based on [81] and [68].

(in principle) to solve the time-dependent Kohn-Sham equations explicitly. Instead, perturbation theory may be sufficient to determine the behavior of the system. The other case is when the external potential is so strong that perturbation theory fails as in the case of a strong laser field. This latter case will be discussed later. In this section, we focus on the weak perturbation case and consider the linear response of the density to the perturbing field. In fact, it turns out that this is all we need to study to determine the optical absorption spectrum of materials.

3.5.1 Basic theory

Recall that the external potential $v_{ext} = v^{(0)} + v^{(1)}$, where $v^{(0)}$ is the ionic potential and $v^{(1)}$ is any other external electromagnetic field, and write

$$v_{ext} = v^{(0)} + v^{(1)}\Theta(t) \quad (3.53)$$

where $\Theta(t) = 1$ for $t > t_0$ and zero otherwise (in which case the system is in its ground state with ground state density $n^{(0)}$). It should be clear that $v^{(1)}$ will introduce a change in the density. Assuming $v^{(1)}$ to be sufficiently well-behaved (which is usual in physics), we can expand the density in a perturbation series:

$$n(\mathbf{r}, t) = n^{(0)}(\mathbf{r}) + n^{(1)}(\mathbf{r}, t) + n^{(2)}(\mathbf{r}, t) + \dots \quad (3.54)$$

where $n^{(1)}$ is the component of $n(\mathbf{r}, t)$ that depends linearly on $v^{(1)}$, $n^{(2)}$ has quadratic dependence and so forth. Since the perturbation is weak, we may consider only the linear dependence which we write in frequency space as

$$n^{(1)}(\mathbf{r}, \omega) = \int d^3\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}'; \omega) v^{(1)}(\mathbf{r}', \omega) \quad (3.55)$$

where $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ is the linear response function, which tells us how the density at $\mathbf{r}$ changes due to a perturbing potential at $\mathbf{r}'$ with frequency ω .⁴

At this point, we make use of TDDFT to evaluate $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ as this is a daunting task in perturbation theory. In particular, we make use of the fact that the density $n^{(1)}(\mathbf{r}, \omega)$ can be evaluated from the Kohn-Sham system in which case the potential should equal the Kohn-Sham potential that yields this density and write

$$n^{(1)}(\mathbf{r}, \omega) = \int d^3\mathbf{r}' \chi_{KS}(\mathbf{r}, \mathbf{r}'; \omega) v_{KS}^{(1)}(\mathbf{r}', \omega) \quad (3.56)$$

⁴In many-body perturbation theory, it is called the reducible polarization function.

$\chi_{KS}(\mathbf{r}, \mathbf{r}'; \omega)$ measures the linear response of the non-interacting Kohn-Sham electrons, which is easier to calculate than the full function. In terms of the unperturbed, stationary orbitals

$$\chi_{KS}(\mathbf{r}, \mathbf{r}', \omega) = \lim_{\eta \rightarrow 0^+} \sum_{j,k}^{\infty} (f_k - f_j) \frac{\varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}') \varphi_k(\mathbf{r}') \varphi_k(\mathbf{r})}{\omega - (\epsilon_j - \epsilon_k) + i\eta} \quad (3.57)$$

where f_m is the occupation number (0 or 1) of the m^{th} Kohn-Sham ground state orbital. The summation therefore ranges over all orbitals, both the occupied and the unoccupied ones. It is important to note that though the Kohn-Sham potential, v_{KS} , includes all powers of the external perturbation due to its non-linear dependence on the density, it is only the linear term, $v_{KS}^{(1)}$, that enters equations (3.55) and (3.56), which can be calculated explicitly from the definition of the Kohn-Sham potential

$$v_{KS}^{(1)}(\mathbf{r}, t) = v^{(1)}(\mathbf{r}, t) + v_{Hartree}^{(1)}(\mathbf{r}, t) + v_{xc}^{(1)}(\mathbf{r}, t) \quad (3.58)$$

$v^{(1)}(\mathbf{r}, t)$ is the variation of the external potential,

$$v_{Hartree}^{(1)}(\mathbf{r}, t) = \int d^3\mathbf{r}' \frac{n^{(1)}(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} \quad (3.59)$$

is the variation of the Hartree potential, and

$$v_{xc}^{(1)}(\mathbf{r}, t) = \int dt' \int d^3\mathbf{r}' \frac{\delta v_{xc}(\mathbf{r}, t)}{\delta n(\mathbf{r}', t')} n^{(1)}(\mathbf{r}', t') \quad (3.60)$$

is the linear part in $n^{(1)}$ of the exchange-correlation functional $v_{xc}[n]$.

At this point, it is useful to introduce the exchange-correlation kernel f_{xc} ,⁵ which is defined by

$$f_{xc}(\mathbf{r}t, \mathbf{r}'t') = \frac{\delta v_{xc}(\mathbf{r}, t)}{\delta n(\mathbf{r}', t')}. \quad (3.61)$$

Combining the previous results and transforming to frequency space yields

⁵The Kernel common principle in Physics. For the electron gas, it is “local field correction” (up to a factor); in Landau’s Fermi-liquid theory, f_{xc} plus the bare Coulomb interaction is sometimes called the “effective interaction”, while in classical liquids it is the Ornstein-Zernicke function [68, 81].

$$n^{(1)}(\mathbf{r}, \omega) = \int d^3\mathbf{r}' \chi_{KS}(\mathbf{r}, \mathbf{r}'; \omega) v^{(1)}(\mathbf{r}', \omega) + \int d^3x \int d^3\mathbf{r}' \chi_{KS}(\mathbf{r}, x; \omega) \left[\frac{1}{|\mathbf{x} - \mathbf{x}'|} + f_{xc}(\mathbf{x}, \mathbf{x}'; \omega) \right] n^{(1)}(\mathbf{r}', \omega) \quad (3.62)$$

If we knew f_{xc} exactly from the exact v_{xc} , we would solve for the linear response function $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ of the interacting system. Therefore, equations (3.61) and (3.62) are formally exact.

3.5.2 The exchange-correlation kernel

Since we do not know the exact form of the exchange-correlation kernel in linear response theory, we need to approximate it. In fact, there are many approximations in this regard that have been proposed, of which the simplest is the ALDA kernel, written as

$$f_{xc}^{ALDA}(\mathbf{r}t, \mathbf{r}'t') = \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') f_{xc}^{HEG}(n) |_{n=n(\mathbf{r}, t)} \quad (3.63)$$

where

$$f_{xc}^{HEG}(n) = \frac{d}{dn} v_{xc}^{HEG}(n) \quad (3.64)$$

is the derivative of the exchange-correlation potential of the homogeneous electron gas. The ALDA kernel is local in both space and time coordinates.

Petersilka et al derived another commonly used exchange-correlation kernel in 1996, now known as the PGG kernel [80]. They used an analytic approximation (similar to the Slater approximation in Hartree-Fock theory discussed in Appendix A) for the exact exchange (EXX) potential and retained only the leading term in the expression for EXX, which reads

$$v_x^{PGG}(\mathbf{r}, t) = \sum_k^{occ} \frac{|\varphi_k(\mathbf{r}, t)|^2}{n(\mathbf{r}, t)} [u_{x,k}(\mathbf{r}, t) + c.c.]. \quad (3.65)$$

Using the definition of f_{xc} in equation (3.61), we can write the PGG kernel as

$$f_x^{PGG}(\mathbf{r}t, \mathbf{r}'t') = -\delta(t - t') \frac{1}{2|\mathbf{r} - \mathbf{r}'|} \frac{|\sum_k^{occ} \varphi_k(\mathbf{r}) \varphi_k^*(\mathbf{r}')|^2}{n(\mathbf{r}) n(\mathbf{r}')}. \quad (3.66)$$

The PGG kernel is also local in time.

Comments Though the ALDA kernel is crude and lacks frequency altogether, it still yields good results [81]. A detailed explanation for this lies in the properties of the kernel applied to the homogeneous electron gas [47]. Owing to space however, we will not indulge into this discussion here.

3.6 Solutions of the Time-Dependent Kohn-Sham Equations

In this section, we address the problem of solving the time-dependent Kohn-Sham equations [121]. As mentioned earlier, two regimes emerge:

- i) when the perturbing field is weak enough to be considered as a perturbation, linear response theory can be used to save us the burden of solving the equations explicitly.
- ii) the full solution which holds for all cases that can be solved by TDDFT.

3.6.1 The full solution

This is a very useful thing to do because it is the only way to treat cases such as laser-matter interaction. More broadly speaking though, these are cases in which the perturbing electromagnetic field is too strong to be treated using methods from perturbation theory. It is worthy noting that the full solution is also applicable to cases in which perturbation theory holds, such as the calculation of the photo-absorption spectra.

Now, let $\tilde{\varphi}_j(\mathbf{r})$ be the ground state Kohn-Sham wavefunction for the system under study. To prepare the initial state for the time-dependent propagation, we excite the system with an electric field potential

$$v(\mathbf{r}, t) = -k_0 x_v \delta(t) \quad (3.67)$$

where $x_v = x, y, z$ and the amplitude k_0 must be small in order to keep the response of the system linear and dipolar. This way, all frequencies of the system are excited with equal weight. At time $t = 0^+$, the initial state for the time evolution reads

$$\begin{aligned} \varphi_j(\mathbf{r}, t = 0^+) &= T \exp \left\{ -i \int_0^{0^+} dt \left[H_{KS} - \hat{k}_0 x_v \delta(t) \right] \right\} \tilde{\varphi}_j(r) \\ &= \exp [ik_0 x_v] \tilde{\varphi}_j(\mathbf{r}). \end{aligned} \quad (3.68)$$

The Kohn-Sham orbitals are then further propagated during a finite time.

The dynamical polarizability can be obtained from

$$\alpha_v(\omega) = -\frac{1}{k} \int d^3\mathbf{r} x_v \delta n(\mathbf{r}, \omega) \quad (3.69)$$

where $\delta n(\mathbf{r}, \omega)$ is the Fourier transform of $n(\mathbf{r}, t) - \tilde{n}(\mathbf{r})$ with $\tilde{n}(\mathbf{r})$ being the ground state density of the system.

Experiments usually measure the photo-absorption cross-section $\sigma(\omega)$ which is essentially proportional to the imaginary part of the dynamical polarizability averaged over x, y and z :

$$\sigma(\omega) = \frac{4\pi\omega}{c} \frac{1}{3} \Im \sum_v \alpha_v(\omega) \quad (3.70)$$

where c is the speed of light.

The other advantage of this method over the linear response theory is that it is easily expandable to include temperature effects. To use this method, one only requires an approximation of the exchange-correlation potential.

3.6.2 Excitations from linear response theory

Our aim here is to solve equation (3.62) for the linear response function. It is rather unfortunate that the full solution to this equation is still a numerical challenge – it is still an unsolved problem. To obtain the linear response function, it is usually necessary to perform a summation over all states – both occupied and unoccupied. These summations converge slowly and require a large number of unoccupied states. However, Petersilka et al [80] proposed an approximate framework that circumvents the full solution of equation (3.62) as has already been discussed.

They wrote the density response function in Lehmann representation as

$$\chi(\mathbf{r}, \mathbf{r}'; \omega) = \lim_{\eta \rightarrow 0^+} \sum_m \left[\frac{\langle 0 | \hat{\rho}(\mathbf{r}) | m \rangle \langle m | \hat{\rho}(\mathbf{r}') | 0 \rangle}{\omega - (E_m - E_0) + i\eta} - \frac{\langle 0 | \hat{\rho}(\mathbf{r}') | m \rangle \langle m | \hat{\rho}(\mathbf{r}) | 0 \rangle}{\omega + (E_m - E_0) + i\eta} \right] \quad (3.71)$$

where $|m\rangle$ is the complete set of many-body states with energies E_m . From this expansion, we notice that $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ has poles at frequencies that correspond to the excitation energies of the interacting system:

$$\Omega = E_m - E_0. \quad (3.72)$$

Since the external potential does not have any special pole structure as a function of ω , equation (3.55) also implies that $n^{(1)}(\mathbf{r}, \omega)$ has poles at the excitation energies Ω . In the same spirit, equation (3.56) has poles at the excitation energies of the non-interacting system, i.e. at the Kohn-Sham orbital energy differences $\epsilon_j - \epsilon_k$.

The terms in equation (3.62), we obtain

$$\int d^3\mathbf{r}' [\delta(\mathbf{r} - \mathbf{r}') - \Xi(\mathbf{r}, \mathbf{r}'; \omega)] n^1(\mathbf{r}', \omega) = \int d^3\mathbf{r}' \chi_{KS}(\mathbf{r}, \mathbf{r}'; \omega) v^{(1)}(\mathbf{r}', \omega) \quad (3.73)$$

where

$$\Xi(\mathbf{r}, \mathbf{r}'; \omega) = \int d^3\mathbf{r}'' \chi_{KS}(\mathbf{r}, \mathbf{r}''; \omega) \left[\frac{1}{|\mathbf{r}'' - \mathbf{r}'|} + f_{xc}(\mathbf{r}'', \mathbf{r}', \omega) \right]. \quad (3.74)$$

As has already been noted, in the limit $\omega \rightarrow \Omega$, the linear density $n^{(1)}$ has a pole, while the right hand side of equation (3.74) remains finite. If equation (3.74) holds, Ξ must have zero eigenvalues at the excitation energies Ω , i.e. $\lambda(\omega) \rightarrow 1$ when $\omega \rightarrow \Omega$, where $\lambda(\omega)$ is the solution of the eigenvalue equation

$$\int d^3\mathbf{r}' \Xi(\mathbf{r}, \mathbf{r}'; \omega) \xi(\mathbf{r}', \omega) = \lambda(\omega) \xi(\mathbf{r}, \omega). \quad (3.75)$$

This means we can determine the excitation energies of the system from the knowledge of χ_{KS} and f_{xc} .

We can still transform this equation into another eigenvalue equation that has the true excitation energies of the system, Ω , as eigenvalues. To do so, let us define

$$\zeta_{jk}(\omega) = \int d^3\mathbf{r}' \int d^3\mathbf{r}'' \varphi_j^*(\mathbf{r}'') \varphi_k(\mathbf{r}'') \left[\frac{1}{|\mathbf{r}'' - \mathbf{r}'|} + f_{xc}(\mathbf{r}'', \mathbf{r}', \omega) \right] \xi(\mathbf{r}', \omega). \quad (3.76)$$

Now equation (3.75) can be re-written as

$$\sum_{jk} \frac{(f_k - f_j) \varphi_i(\mathbf{r}) \varphi_k^*(\mathbf{r})}{\omega - (\epsilon_j - \epsilon_k) + i\eta} \zeta_{jk}(\omega) = \lambda(\omega) \xi(\mathbf{r}, \omega). \quad (3.77)$$

If we solve this equation for $\xi(\mathbf{r}, \omega)$ and insert the result into equation (3.76), we obtain

$$\sum_{j',k'} \frac{M_{jk,j'k'}}{\omega - (\epsilon_{j'} - \epsilon_{k'}) + i\eta} \zeta_{j'k'}(\omega) = \lambda(\omega) \zeta_{jk}(\omega) \quad (3.78)$$

where we have defined the matrix element

$$\begin{aligned} M_{jk,j'k'} &= (f_{k'} - f_{j'}) \int d^3\mathbf{r} \int d^3\mathbf{r}' \varphi_j^*(\mathbf{r}) \varphi_k(\mathbf{r}) \varphi_j(\mathbf{r}') \varphi_k^*(\mathbf{r}') \\ &\times \left[\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}(\mathbf{r}, \mathbf{r}'; \omega) \right]. \end{aligned} \quad (3.79)$$

Introducing the eigenvector

$$\beta_{jk} = \frac{\zeta_{jk}(\Omega)}{\Omega - (\epsilon_{j'} - \epsilon_{k'})} \quad (3.80)$$

taking the limit $\eta \rightarrow 0$ and using the condition that $\lambda(\Omega) = 1$, we can recast equation (3.78) into the eigenvalue equation

$$\sum_{j'k'} [\delta_{jj'} \delta_{kk'} (\epsilon_{j'} - \epsilon_{k'}) + M_{jk,j'k'}(\Omega)] \beta_{j'k'} = \Omega \beta_{jk}. \quad (3.81)$$

We can also derive an operator whose eigenvalues are the square of the true excitation energies, thereby reducing the dimension of the matrix equation (3.81) [29]. The oscillator strengths can be obtained from the eigenfunctions of the operator [81].

There are many ways of solving the eigenvalue equation (3.81). One way is to expand all quantities in a suitable basis and solve the resulting matrix eigenvalue equation numerically. Another way is to perform a Laurent expansion of the response function around the excitation energy

$$\chi_{KS}(\mathbf{r}, \mathbf{r}'; \omega) = \lim_{\eta \rightarrow 0^+} \frac{\varphi_{j_0}(\mathbf{r}) \varphi_{j_0}^*(\mathbf{r}') \varphi_{k_0}(\mathbf{r}') \varphi_{k_0}^*(\mathbf{r})}{\omega - (\epsilon_{j'} - \epsilon_{k'}) + i\eta} + \text{higher-order}. \quad (3.82)$$

If we neglect higher order terms, we can manipulate equation (3.75) to get the so called single-pole approximation (SPA) of the excitation energies

$$\Omega = \Delta\epsilon + K(\Delta\epsilon) \quad (3.83)$$

where

$$\Delta\epsilon = \epsilon_{j_0} - \epsilon_{k_0} \quad (3.84)$$

and K is a correction given by

$$K(\Delta\epsilon) = 2\Re \int d^3\mathbf{r} \int d^3\mathbf{r}' \varphi_{j_0}(\mathbf{r}) \varphi_{j_0}^*(\mathbf{r}') \varphi_{k_0}(\mathbf{r}') \varphi_{k_0}^*(\mathbf{r}) \\ \times \left[\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}(\mathbf{r}, \mathbf{r}', \Delta\epsilon) \right]. \quad (3.85)$$

Although this formula is not as precise as the direct solution of equation (3.81), it provides us with a quick way of calculating the excitation energies.

While Petersilka’s solution is a “single pole in frequency space”, Mark Casida proposed a solution of the full matrix equation(s) in momentum space. This will be referred to hereafter as Casida’s theory/formulation (<http://www.tddft.org/programs/octopus/wiki/index.php/Manual:O>

3.7 Applications of Time Dependent Density Functional Theory

Given that time dependent density functional theory is nothing but a reformulation of time dependent quantum mechanics, its applications should be those of the time dependent Schrodinger equation. These include scattering phenomena and excitations – non-relativistic time-dependent phenomena, in general. When molecular dynamics is included in the picture, TDDFT should describe photochemical reactions, chemical reactions and the interaction between matter and electromagnetic fields (weak and strong).

Quantities that are derived or calculated include – but are not limited to – the photo-absorption spectrum, the harmonic spectrum, time dependent occupation numbers, the probabilities of ionization.

To calculate the photo-absorption spectra, one can calculate the dynamic polarizability from which the photo-absorption cross section is derived. This is the quantity that is measured in experiments.

Calculating the induced dipole moment enables one to calculate the harmonic spectrum. The Fourier transform of the dipole moment, squared, is proportional to the harmonic spectrum. In turn, the harmonic spectrum is the intensity distribution of emitted photons as a function of their frequency.

Decreases in the norm of the single particle Kohn-Sham orbitals in a finite volume can be loosely equated to the probability of ionization of an electron from a given orbital.

Excitation energies are also a very good result of TDDFT.

The Kohn-Sham orbitals can also be used to calculate the Time-Dependent Electron Localization Function (TDELF) [23], which shows the electron clouds in space at any particular time. Combined with molecular dynamics, this provides a visual understanding of the many chemical, photochemical and biological processes in nature.

To date, no theory explains everything in nature. As such, TDDFT also has its own short-falls. First and foremost, it is expected to fail wherever time dependent quantum mechanics fails, since it is only a reformulation of the quantum mechanics. Such cases include relativistic phenomena and gravity cases. The rest of the failures and/or inaccuracies are related to any of the assumptions and approximations that we make when deriving the theory as well as our ignorance. Leading the list here is our ignorance of the true, explicit form of the exchange-correlation potential and kernel. If we use LDA to approximate any of these (in whichever appropriate form), for instance, we carry along the very limitations that LDA is known for. It is probably important to note that if we knew the explicit forms of these many body phenomena, we would accurately compute the exact quantities of interest.

If we use the local (LDA) or the gradient corrected (GGA) approximations to calculate the optical properties of long conjugated chains we can get over-estimations of several orders of magnitude. This is related to the non-local dependence of the exchange-correlation potential. If an external electric field is applied, the exact exchange-correlation potential develops a linear part that counteracts the applied field. LDA and GGA do not take this into consideration, though more non-local functionals like EXX do cater for this effect.

A somewhat similar problem occurs in solids. Here, TDDFT does not give good results in the calculation of excitations of non-metallic solids, especially in systems like wide band-gap semiconductors. For infinite systems, the Coulomb potential behaves like $\frac{4\pi}{q^2}$ in momentum space. Such asymptotic behavior is missing from the response equation (for $q \rightarrow 0$). Several attempts have been made to correct this problem though.

Despite all these short-falls, TDDFT works very well for the calculation of excitations in a large class of systems. In particular, LDA and GGA yield unexpectedly good results in spheres outside their normal use.

Chapter 4

The Molecule: A Biochromophore¹

In this chapter, we revisit the molecule under study in more detail and point out again, the goals of this study.

Figure 4.1² shows the retinal molecule in its *cis* and *trans* configurations.

The 11 – *cis* retinal molecule is a member of a large class of biological molecules, the biochromophores which are nothing but a class of molecules that absorb electromagnetic radiation (light) in its visible and ultraviolet regions [79]. Other members of this class include chlorophyll which is responsible for photosynthesis, DNA which is the chemical signature for all living organisms in the animal family and green fluorescent protein (GFP) which is a protein that is found in a jellyfish that lives in the cold waters of the north Pacific,³ among others. The optical absorption spectrum of chlorophyll was

¹Much of the generalized fundamental work discussed in this chapter is based on [79].

²Taken from http://edu.chem.tue.nl/6KM22/Downloads/cis%20trans_2005.pdf

³Since its discovery, GFP has played an important role in biotechnology as a marker to monitor gene expression and protein localization in living organisms.

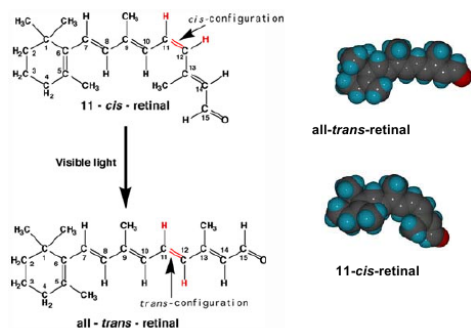


Figure 4.1: The molecular structure of 11 – *cis* retinal showing the “standard” atom numbering system 1.

studied theoretically in 2007 [115] and that of GFP in [82].⁴ In DNA, people study radiation induced damage [50, 49, 51].

As one may already tell, these molecules (the biochromophores) are the ones that are responsible for life as we know it, making them very important for the perpetuation of life. Without them, we would be blind and have no food, for instance.

As has already been highlighted in Chapter 1, the 11 – *cis* molecule is the primary transducer of light in our eyes – it is responsible for all the beauty that we see with our eyes. An obvious question that follows this statement is how then do we see all the various colours, which are basically different wavelengths, using the same molecule. Well, it turns out that the molecule is found in our eyes attached to different protein bases that affect its optical response to light. We discuss these variations below.⁵

Rhodopsin In rhodopsin, the 11 – *cis* molecule is attached to a lysine⁶ side chain, forming an imine⁷ fundamental chromophore that is responsible for vision in this case. In fact, the oxygen atom in the 11 – *cis* retinal is replaced by this lysine chain to form rhodopsin. By definition therefore, rhodopsin is a membrane-bound protein that contains a cavity for the retinal and a lysine side chain that can react with the aldehyde.⁸

The rhodopsins are housed in special cells called rods found in the retina at the back of the eye. Because the rhodopsin is too sensitive to light, it is normally dis-functional in bright daylight. It stays in the excited all-trans form most of the time. At night (or in dim light), the molecule functions just fine – well enough to distinguish black and white, dark and bright patches, which explains why it is hard to see and distinguish colour in dim light and at night. Rhodopsin has no colour in it, i.e. it cannot distinguish colour. As such, rhodopsin has a relatively broad spectrum with a peak wavelength of about 500 nm.

Absorption of a photon causes an isomerization (change of shape while preserving the chemical structure) to the all-trans form. The isomerization is quite rapid, occurring on the picosecond time scale. The reverse process (trans-to-cis isomerization) however, is much slower, being a thermal process. It is this cis-trans isomerization that is responsible for vision. Within the confines of the binding cavity, this structural change is sensed by

⁴Actually, the work on the GFP molecule [82] was one of the ground-breaking pieces that were done using the same code that was used in this very work (Octopus [84]).

⁵This particular part is mainly based on [10].

⁶Lysine is basically a protein/amino acid (<http://en.wikipedia.org/wiki/Lysine>) and [20].

⁷An imine is an organic compound with the substituent =NH [21].

⁸In organic chemistry, the 11 – *cis* molecule is viewed as an aldehyde, i.e. an organic compound whose functional group is $-CH = O$ [22].

the rest of the rhodopsin protein, launching a signaling cascade in the rod cell(s) that ultimately reaches the visual cortex of the brain.

Well, if rhodopsin sees no colour, what does?

In the other cells, cone cells, other variations of rhodopsin are sensitive to the three primary colours of light. In these cells, the primary aldehyde molecule, the 11 – *cis* retinal, is attached to a different protein base. It is these cone cells that are colour sensitive and therefore responsible for day-time vision. These variations of rhodopsin are less sensitive to light than the rhodopsin described above, so that the cone cells are just active enough in bright (but not too bright) light such as daylight, becoming inactive in dim light as at night.

The cone cells are specific RGB just like a computer monitor, i.e. they are specific Red, Green and Blue receptors. In other words, there are three different types of cone cells, with each type being sensitive only to one of the primary colours. The variation of the colour sensitivity is achieved by precisely attaching specific amino acid sequences. The most effective of these side chains have strong local dipoles. The absorption characteristics are perturbed to produce red ($\lambda = 560nm$), green ($\lambda = 530nm$) and blue ($\lambda = 410nm$) photoreceptors.

4.1 $\pi \rightarrow \pi^*$ transitions and biochromophores

At first sight, the 11 – *cis* retinal molecule appears to be too big, making it computationally demanding to study theoretically – with its chemical formula given by $C_{20}H_{28}O$, there are forty-nine atoms all in all. This number is even astronomically sky-rocketed by attaching a protein to the molecule. Why then does nature present us with such a large molecule for such an important process as vision? This is the question that we try to answer in this section.

It turns out that most organic molecules are completely transparent to visible light, starting to absorb only in the ultraviolet region of the electromagnetic spectrum. On the other hand, light emitted by the sun, after passing through the earth's atmosphere, has its maximum in the visible range.

Upon absorption of a photon, a molecule undergoes a transition between two molecular states. The most common of these transitions are $\sigma \rightarrow \sigma^{*9}$ and $n \rightarrow \sigma^*$ that absorb light only in the ultraviolet region. Because all chemically stable molecules have localized σ bonds, these processes are present in all molecules.

⁹ σ is the ground state σ -bond formed by *s*-wave electrons, while σ^* is the corresponding σ -anti-bonding (excited) state.

When π bonds¹⁰ are present however, a new transition occurs: $\pi \rightarrow \pi^*$. The simplest biological molecule containing a π bond is ethylene, C_2H_4 , which exhibits strong absorption at a wavelength of 163 nm which is still in the ultraviolet region. However, when one creates molecular chains that have alternate π bonds, the photo-absorption maximum is moved closer and closer to the visible region.¹¹ This is because in these so-called π -conjugate molecules, the π electrons are delocalized and the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) decreases, allowing less energetic photons (with longer wavelengths) to be absorbed by the π -electrons in their ground state. If the π system is long enough, optical absorption may lie in the visible spectrum.

For this reason, biochromophores, including the 11 - *cis* retinal, are usually organic molecules with long conjugated π bonds. The photo-absorption transition $\pi \rightarrow \pi^*$ therefore occurs in the visible or near ultraviolet range of the electromagnetic spectrum. Actually, some people with defects in their eyes have been reported to see images in the near ultraviolet region of the spectrum.

Another interesting observation is that most commonly occurring biochromophores are found attached to some protein bases. In the case of the 11 - *cis* retinal for example, the retinal is known to absorb at about $\lambda = 380\text{ nm}$, but when attached to the opsin protein, its photo-absorption peak is moved to the values quoted earlier, depending on the specific protein used.

Proteins on their own, are also unable to absorb electromagnetic radiation in the visible spectrum. Biological systems therefore can either

- i) incorporate prosthetic groups with large delocalized π systems inside the protein structure, or
- ii) chemically modify some of their amino acid chains to form chromopeptide structures.

Once the chromopeptide is inside the protein matrix, the protein structure can affect the optical response of the chromophore through a variety of effects:

- i) inducing a structural change on the chromophore that shifts the absorption spectrum,
- ii) polarizing the electron cloud differently in the ground and excited states, thereby producing a modification of the energy gap, and
- iii) effectively shielding the chromophore from the aqueous solvent environment.

All these effects act simultaneously.

¹⁰The π bond is formed by p sub-shell electrons.

¹¹It is only organic (C-based) molecules that have the ability to form long chains of molecules.

4.2 Laser-matter interaction¹²

In this section, we discuss the interaction between a strong laser field and a molecule or an atom.

4.2.1 What is a “strong” laser?

The electric field that an electron in a hydrogen atom feels at a distance of one Bohr from the nucleus is

$$E = \frac{1}{4\pi\epsilon_0} \frac{e}{a_0^2} = 5.1 \times 10^9 \text{V/m}. \quad (4.1)$$

The laser intensity that corresponds to this field is given by

$$I = \frac{1}{2} \epsilon_0 c E^2 = 3.51 \times 10^{16} \text{W/cm}^2. \quad (4.2)$$

We can therefore say a laser is strong when its intensity is comparable to equation (4.2), in which case perturbation theory fails to give a correct description of the interaction involved. We will be interested, in this work, in laser intensities that lie in the range $10^{13} - 10^{16} \text{W/cm}^2$ as this is the range in which perturbation theory fails. At larger intensities, the many body effects associated with electron-electron interaction become less important and density functional theory becomes inapplicable. This is because the much stronger external laser field becomes strongly dominant.

As one approaches these high intensities, a wealth of interesting phenomena occur. Examples of these phenomena include multi-photon ionization, above threshold ionization and high harmonic generation, to mention just a few.

Time dependent density functional theory is a tool particularly suited for the study of systems in strong laser fields within the range that we have just defined. We recall that the time-dependent Kohn-Sham equations yield the exact density of the system, including all non-linear effects. In a calculation that involves an external laser, one starts by calculating the ground state of the system, then propagating it under the influence of the laser field whose potential is given by

$$v_{TD}(\mathbf{r}, t) = E f(t) z \sin(\omega t) \quad (4.3)$$

¹²This section is based on [81].

where E is the amplitude of the laser, related to the laser intensity by equation (4.2), $f(t)$ is typically a Gaussian or the square of a sinus, that defines the temporal shape of the laser pulse, and ω is the frequency of the laser pulse.

From the photon absorption, one can then calculate the photon spectrum using

$$\sigma(\omega) \propto |d(\omega)|^2 \quad (4.4)$$

where

$$d(\omega) = \int d^3r z n(\mathbf{r}, t) \quad (4.5)$$

is the Fourier transform of the time-dependent dipole of the system.

Other observables such as the total ionization yield or the above threshold ionization spectrum are much harder to calculate within time-dependent density functional theory because their explicit functional dependence on the time-dependent density is unknown.

4.2.2 High harmonic generation

If a strong laser is shone onto an atom, molecule or the surface of a given material, a valence electron may absorb several photons, get excited to very high energy levels and then return to its ground state by emitting a single photon in a process known as high harmonic generation. The name comes about because the emitted photon may have a frequency that is an integer multiple of the external laser frequency.

Since the subsequently released photons maintain a fairly high coherence, they can be used as a source for soft X-ray lasers.

Examples of the practical spectrum, which is a plot of the squared mode of the Fourier transform of the time-dependent dipole, $|d(\omega)|^2$, against the harmonic order, consists of a series of peaks which first decrease in amplitude and then reach a plateau that extends to very high frequency. Any approach based on perturbation theory would yield a harmonic spectrum that decays exponentially, meaning that such a theory would never reproduce the experimentally measured peak intensities. On the contrary, time dependent density functional theory has been shown to give results that are satisfactory with experiments.

Time dependent density functional theory can be used to perform virtual experiments in a bid to optimize the laser parameters for maximal intensity harmonics. In this case, one fine tunes the laser frequency, its intensity and so forth for best (desired) results. This is much easier to do in a virtual experiment than it is in an optics laboratory. Practical results show that the intensity of the harmonic spectrum (soft X-ray) increases up to

a maximum value before starting a downward trend. This reflects the action of two competing processes which are

- i) ionization of the electrons and
- ii) the falling back of the electrons to their ground state after absorbing multiple photons.

If the excited electrons keep falling back to their ground state after absorbing the multiple photons, as the incident laser intensity is increased, it means ionization is over-powered by the latter process. After the peak intensity of soft X-rays is reached, the excited electrons get ionized and the emitted intensity falls.

4.2.3 Multi-photon ionization

There are three interesting ways of ionizing an atom as a function of the incident laser intensity. These three different regimes are governed by the Keldish parameter

$$\gamma = \frac{\omega}{E}. \quad (4.6)$$

At low laser intensities which are less than 10^{14}W/cm^2 , $\gamma \gg 1$, the valence electrons need to absorb multiple photons before acquiring enough energy to escape the nuclear potential and this is the multi-photon ionization regime. When the intensity is about 10^{15}W/cm^2 , $\gamma \approx 1$, then excited valence electrons can tunnel through the nuclear potential barrier in the so called tunneling regime. Finally, for frequencies higher than 10^{16}W/cm^2 , $\gamma \ll 1$, the electrons simply pass over the potential barrier.

The measured energy spectrum of the outgoing photo-electrons is the above threshold ionization (ATI) spectrum. Since any given electron can absorb more electrons than it really needs to escape the binding nuclear potential, the above threshold ionization spectrum usually consists of a sequence of equally spaced peaks at energies given by

$$E = (n + s) \omega - I_p \quad (4.7)$$

where n is a natural number, s is the minimum integer such that $s\omega - I_p > 0$, and I_p denotes the ionization potential of the system.

One can also observe the number of outgoing charged atoms as a function of the laser intensity. However, sequential ionization, which is the sequential removal of valence electrons from a given atom, for multi-ionized atoms yields wrong results for some intensities though.

For a variety of molecules, which are by definition complex systems, the coupling nuclear and electronic degrees of freedom gives rise to new interesting phenomena of which Coulomb explosion is a very good example. In this particular case, Coulomb explosion, the molecule practically explodes due to ionization.

4.2.4 Ionization yields from TDDFT

We have already highlighted that the sequential ionization mechanism cannot accurately describe multiple ionization¹³ in atoms. On the bright side, time dependent density functional theory can give accurate descriptions of multi-electron ionization. In fact, it is interesting to study how one can give this accurate description in TDDFT. To do so, we use the simplest many-body atomic system available in nature (that can be doubly ionized), the helium atom.

To start with, let us invoke a geometrical picture of ionization. Let us divide the three-dimensional space ($\mathbb{R}^3$) into a large box A that contains the neutral helium atom, and its complement $B = \mathbb{R}^3$. Normalization of the two-body wavefunction of the helium atom, $\Psi(\mathbf{r}_1, \mathbf{r}_2, t)$ then implies the following:

$$1 = \int_A \int_A d^3\mathbf{r}_1 d^3\mathbf{r}_2 |\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 + 2 \int_A \int_B d^3\mathbf{r}_1 d^3\mathbf{r}_2 |\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 + \int_B \int_B d^3\mathbf{r}_1 d^3\mathbf{r}_2 |\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2. \quad (4.8)$$

After long enough time following the passage of the laser, all ionized electrons are expected to be in region B . At that time, the first term on the right hand side of equation (4.8) would give the probability that an electron remains in region A , close to the nucleus and therefore unionized. The second term in the same equation would give the probability of finding an electron in region A (unionized), and the other in region B (ionized), simultaneously. This is single-electron ionization. Finally, the last term would give the probability of finding both electrons in region B (both ionized). This is double ionization. For convenience, let us label the three probabilities as $p^{(0)}(t)$, $p^{(1)}(t)$ and $p^{(2)}(t)$, respectively.

This far, we have been using the many-body wavefunction which we know is a problem computationally. Let us therefore write things in terms of the time dependent density, $n(\mathbf{r}, t)$. To do so, let us introduce the pair-correlation function

¹³Removal of many electrons such as double ionization.

$$g[n](\mathbf{r}_1, \mathbf{r}_2, t) = \frac{2|\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2}{n(\mathbf{r}_1, t)n(\mathbf{r}_2, t)} \quad (4.9)$$

and write

$$\begin{aligned} p^{(0)}(t) &= \frac{1}{2} \int_A \int_A d^3\mathbf{r}_1 d^3\mathbf{r}_2 n(\mathbf{r}_1, t) n(\mathbf{r}_2, t) g[n](\mathbf{r}_1, \mathbf{r}_2, t) \\ p^{(1)}(t) &= \int_A d^3\mathbf{r} n(\mathbf{r}, t) - 2p^{(0)}(t) \\ p^{(2)}(t) &= 1 - p^{(0)}(t) - p^{(1)}(t). \end{aligned} \quad (4.10)$$

We can separate the pair-correlation function, g , into an exchange part (which is just $\frac{1}{2}$ for helium) and a correlation part in this way

$$g[n](\mathbf{r}_1, \mathbf{r}_2, t) = \frac{1}{2} + g_c[n](\mathbf{r}_1, \mathbf{r}_2, t) \quad (4.11)$$

Now, we can recast equations (4.10) in the form

$$\begin{aligned} p^{(0)}(t) &= [N_{1s}(t)]^2 + K(t) \\ p^{(1)}(t) &= 2N_{1s}(t)[1 - N_{1s}(t)] - 2K(t) \\ p^{(2)}(t) &= [1 - N_{1s}(t)]^2 + K(t) \end{aligned} \quad (4.12)$$

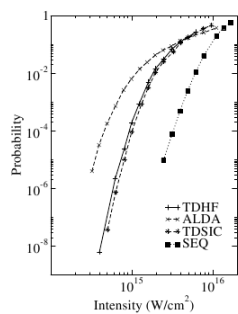
where

$$N_{1s}(t) = \frac{1}{2} \int_A d^3\mathbf{r} n(\mathbf{r}, t) = \int_A d^3\mathbf{r} |\varphi_{1s}(\mathbf{r}, t)|^2 \quad (4.13)$$

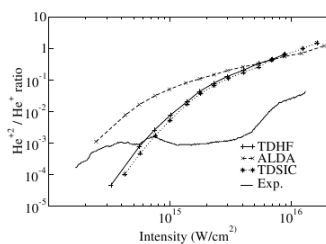
$$K(t) = \frac{1}{2} \int_A \int_A d^3\mathbf{r}_1 d^3\mathbf{r}_2 n(\mathbf{r}_1, t) n(\mathbf{r}_2, t) g_c[n](\mathbf{r}_1, \mathbf{r}_2, t) \quad (4.14)$$

In figure 4.2a [93], the probability of double ionization for helium is shown as a function of the incident laser intensity. These values were calculated using equation (4.12), neglecting the correlation part. Various methods of solving the many-body Schrodinger equation were used.

From these results, the sequential method is a far cry from the correct description, while the adiabatic LDA functional overestimates the ionization yields because of its incorrect behavior. The ALDA potential renders the outermost electron loosely bound and therefore it ionizes rather too easily. The time dependent Hartree-Fock (TDHF) method and TDDFT with self-interaction correction (TDSIC) kind of agree interestingly.



(a) Theoretical ionization probabilities.



(b) Ratios of double- to single-ionization compared (theory and experiment).

Figure 4.2: Calculated double ionization probabilities and ratios of double- to single-ionization probabilities from the ground state of helium irradiated by a 16fs, 760nm laser pulse 31.

We note also that all the time-dependent methods agree at intensities between 10^{15} and 10^{16}W/cm^2 . Experimental¹⁴ results are missing from this description.

To incorporate experimental results, one needs to look at the ratio of the double to single ionization yields as shown in figure 4.2b.

This way of analyzing the ionization yield eliminates the experimental error in determining the absolute yields. It should be clear from this figure that all the theoretical approximations used in this case are wrong. This largely owes to the incorrect approximation of the exchange-correlation functionals used in this case. To get better results from TDDFT, one needs to use the exact exchange functional (EXX), at least in its KLI approximation. The other error, of course, comes from the neglect of the correlation term in the pair-correlation function.

Using a one-dimensional helium model, Lappas and van Leeuwen proved that even the simplest approximation for the pair-correlation function is able to produce an interesting (expected) structure called the knee structure. Neither of the theoretical results show the knee structure obtained from experimental results, primarily because of the poor choice of the exchange-correlation functionals used in this case.

4.3 Methods

Given the known behavior of the 11-*cis* retinal in particular, it should be natural to use molecular dynamics (MD) and quantum-mechanical/molecular mechanics (QM/MM) methods, in conjunction with time-dependent density functional theory (TDDFT) to study the behavior of the molecule in different environments.

4.3.1 Molecular Dynamics

Molecular dynamics is one of the most widely used tools to study the structure and function(s) of molecules. It is such a vast subject in its own right, but we concentrate here on the little introductory part in the interest of space. The basic assumption of molecular dynamics is that molecular ions follow a classical path in their time evolution. In the language of statistical mechanics, the hypothesis states that significant averages can be obtained by averaging over the time evolution of a system:

$$\langle A \rangle_{ensemble} = \langle A \rangle_{time} \quad (4.15)$$

¹⁴It has become part of the norm for theorists to assume that experimental results are correct while experimentalists also assume that the theory is right.

The time evolution of the molecule is therefore given classically by Newton's equation of motion defined here for each i^{th} ion/atom in the system:

$$\mathbf{F}_i = m_i \mathbf{a}_i = m_i \frac{d^2 \mathbf{R}_i}{dt^2}. \quad (4.16)$$

Since our interest in molecular dynamics is to find the position of each i^{th} ion, $\mathbf{R}_i$, at a given time t , the force is an input that can be obtained from the potential¹⁵ in which the ion moves:

$$\mathbf{F}_i = -\frac{dV}{d\mathbf{R}_i}.$$

Now, there are several numerical methods that one can use to propagate these equations. One of the most widely used is the Verlet¹⁶ algorithm. This method is based on a Taylor expansion to second order of the trajectories of each atom:

$$\mathbf{R}(t + \Delta t) = \mathbf{R}(t) + \frac{d\mathbf{R}}{dt} \Big|_t \Delta t + \frac{1}{2} \frac{d^2 \mathbf{R}}{dt^2} \Big|_t (\Delta t)^2 + \dots \quad (4.17)$$

$$\mathbf{R}(t - \Delta t) = \mathbf{R}(t) - \frac{d\mathbf{R}}{dt} \Big|_t \Delta t + \frac{1}{2} \frac{d^2 \mathbf{R}}{dt^2} \Big|_t (\Delta t)^2 + \dots \quad (4.18)$$

Adding the two equations and rearranging slightly yields

$$\mathbf{R}(\mathbf{t} + \Delta \mathbf{t}) = 2\mathbf{R}(\mathbf{t}) - \mathbf{R}(t - \Delta t) + \frac{d^2 \mathbf{R}}{dt^2} \Big|_t (\Delta \mathbf{t})^2 + \dots \quad (4.19)$$

The starting positions of the ions can be obtained from the geometries obtained from experimental (X-ray diffraction) data. In the context of the 11-*cis* retinal molecule, the first experimental X-ray data appeared in 1972 [44], but this data lacked the coordinates of four of the hydrogen atoms present in the structure. It also stated the space group symmetry of the molecule as $P2_1/c$. A more detailed and complete report appeared in 1981 [36] and it stated the space group symmetry of the molecule as $P2_1/n$. These and the geometries of many other molecules obtained from X-ray crystallographic data is available from the Cambridge Crystallographic Database. For protein structures, the crystallographic data is available from the Protein Data Bank in standard .pdb files.

¹⁵At this point, it may be important to comment that the ions move in a potential defined by the electrons, other ions and any other classical external forces that may be acting on the system. A lot could be said about the potential and how we represent it, but there is not enough space to do so here.

¹⁶A similar procedure is the velocity Verlet which includes the velocity in its formulation.

4.3.2 Force fields

For most biological molecules that have large numbers of atoms in them, the molecular dynamics calculations are carried out using simple analytical forms of the potential energy, in which electrons are not treated explicitly. Two kinds of terms are usually distinguished in these molecular mechanics force fields, namely

- i) the bonded and
- ii) the non-bonded terms.

The bonded terms try to reproduce how the energy changes when atoms that are covalently bonded are geometrically distorted. These terms are usually written as harmonic potentials around the equilibrium molecular distances and angles. In addition, periodic potentials are added to account for changes in energy along torsional degrees of freedom.

On the other hand, the non-bonded terms simulate van der Waals and electrostatic attraction forces between atoms that are not covalently bound together.

Following this prescription, a typical force field takes the form

$$\begin{aligned}
 V_{MM} = & \sum_{bonds} \frac{1}{2} K_b (d - d_0)^2 + \sum_{angles} \frac{1}{2} K_\alpha (\theta - \theta_0)^2 + \sum_{dihedrals} K_d [1 + \cos(n\phi - \gamma)] \\
 & + \sum_{i=1}^N \sum_{j>i}^N 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{R_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{R_{ij}} \right)^6 \right] + \sum_{i=1}^N \sum_{j>i}^N \frac{q_i q_j}{\epsilon R_{ij}}
 \end{aligned} \tag{4.20}$$

where d measures the bond distances, θ is the angle formed by three atoms, ϕ is dihedral angle formed by four atoms and R_{ij} is the distance between atoms i and j . All other quantities are carefully chosen constants. The first three summations correspond to bonded terms while the last two correspond to the non-bonded van der Waals and electrostatic terms, respectively. There are various force fields available, but the most common are the CHARMM [14], AMBER [33] and OPLS-AA [117].

4.3.3 QM/MM techniques

When studying molecules that have no parametrization available, or when studying chemical reactions in which bonds are broken and formed, the force field approximation is insufficient. In such cases, we use a mixed quantum mechanical/molecular mechanical (QM/MM) approach. In this formulation, the system is divided into a small region that is treated quantum mechanically and a big region that is handled by the force field. The resulting Hamiltonian is a sum of the force field, the quantum mechanical energy

and a Hamiltonian describing the interaction between the quantum mechanical (QM) and molecular mechanical (MM) parts:

$$H = H_{QM} + H_{MM} + H_{QM/MM} \quad (4.21)$$

where

$$H_{QM/MM} = H_{QM/MM}^{elect} + H_{QM/MM}^{vdW} + H_{QM/MM}^{bonded}. \quad (4.22)$$

Here,

$$H_{QM/MM}^{elect} = -\sum_{i,M} \frac{q_M}{r_{i,M}} + \sum_{\alpha,M} \frac{Z_{\alpha} q_M}{R_{\alpha M}} \quad (4.23)$$

accounts for the electrostatic interaction between the quantum mechanical region and the set of point charges q_M representing that part of the molecule that is in the molecular mechanics zone. $r_{i,M}$ is the distance between the quantum mechanical nucleus α and the molecular mechanical nucleus M . This is the part that enters the self consistent equations, requiring the evaluation of extra one-electron integrals.

Special must be taken with the QM/MM boundary. One option is to introduce a hydrogen atom whenever the frontier between the QM and MM regions passes through a chemical bond, the so called H-link. During the minimization, this H-link is forcibly aligned to the frontier bond and does not interact with the MM atoms. Other techniques are more sophisticated. In these techniques, the self-consistent equations are solved in the presence of frozen orbitals located at the QM-MM atom interfaces.

4.4 The dynamics of the visual process

Molecular dynamics calculations of the evolution of the 11 – *cis* retinal molecule were performed in 1996 [7, 41], even though the geometry of the molecule had been fully known from experiment since 1981. This can be heavily accredited to the size of the 49 – *atom* molecule which is quite heavy on computers.

4.5 What has been done in this work

While there are numerous quantities and properties that one can calculate in principle for any molecule as interesting as the 11 – *cis* retinal molecule, practical considerations limit one's plight to a few equally interesting quantities. This is mainly because the molecule is quite big, having 49 atoms. As such, the current computational resources

would not allow one to carry out all the calculations in real time. For this and many other reasons that will be highlighted as we go, the spectrum of calculations performed has been limited to the ones listed below.

4.5.1 Why the 11 – cis retinal molecule?

One might be curious and ambitious enough to perform calculations on the 11 – *cis* retinal molecule attached to some protein base as has become the norm in the latest research papers, but the available computational resources do not allow for such expensive calculations in reasonable time. In any case, we have an extra added advantage of learning how the basic chromophore works, rather than studying every single variation of the molecule attached to the protein base. The protein base primarily fine tunes the already known optical properties of the basic chromophore. For these main reasons, the calculations were performed on the primary chromophore, the 11 – *cis* retinal molecule.

4.5.2 The ground state

Any excited state calculation typically begins with a ground state calculation, since it is this ground state calculation that is evolved to the excited state. For this reason, the ground state calculation was performed within the Kohn-Sham density functional theory. Because the LDA approximation to the exchange-correlation functional is quite fast and accurate enough for our purposes, it was the functional of natural choice. In calculating optical response spectra, this functional yields results that are in good agreement with experiment. Exemplary cases include the spectrum of the green fluorescent protein (GFP), which was calculated using the very code which we used in our case.

Exact exchange functional (in its KLI approximation) was also used to compute the ground state properties of the system. This is a much heavier calculation that does not converge easily. Just to give a taste of what it's really like, a ground state calculation for benzene (C_6H_6) that converges in about ten LDA iterations would take more than seventy iterations to converge using the KLI approximation combined with a GGA approximation in the `hyb_gga_xc_x3lyp` hybrid functional on the same computer. An only calculation using the KLI approximation is even worse. For benzene, it cramps down the machine heavily, while for the 11 – *cis* retinal molecule it fails to set up the Hamiltonian (which is a primary step in the calculation). One can imagine what would happen for the time-dependent calculation, which is usually more involved than its ground state counterpart.

4.5.3 Optical response spectra

The optical response spectrum was calculated using the adiabatic LDA (ALDA) approximation. The two basic ways of solving the time-dependent Kohn-Sham equations were employed.

One involves a full solution of the time-dependent Kohn-Sham equations, which is unnecessarily involved for small to medium molecules. While the 11-*cis* retinal molecule is quite big in comparison to many other simple molecules that we know, it can be classified as medium-sized in comparison to other biochromophores like chlorophyll. In practice, big biological molecules involve atoms to the order of 200 atoms.

The other is linear response theory that was also used to compute the optical spectrum of the molecule, using both the Petersilka and the Casida formulation of the theory. In this case, the code that was used did not make room for the use of any other functional approximation, save LDA or ALDA.

All the results were compared to experimental experimental results [96].

4.5.4 Classical dynamics of the molecule in normal light

A classical dynamics of the molecule in normal light was partly performed. A proper complete calculation promised to take an unignominably long time, eating up so much disk space that no room would be left for the other calculations. It was a very slow and memory consuming calculation. To drive the point home, 50 iterations were performed out of the required 1000000 that would yield total evolution times of the few picoseconds required to isomerize the molecule completely.

4.5.5 Strong laser interaction

The bulk of the results of this report come from the interaction of the 11-*cis* retinal molecule with a strong laser. Unfortunately, the size of the molecule coupled to the current computational resources prohibits the accurate calculation that uses the KLI exact exchange functional. The results that presented are from the use of the inaccurate LDA/ALDA calculation, unfortunately.

For this and a few other reasons, many interesting quantities that one would naturally compute in this case were not calculated. Examples include the ionization yield, among others. In fact, the spectrum of quantities reported here is disappointingly small.

The few calculations that were performed in this regime include a molecular dynamics calculation combined with a time-dependent calculation of the phenomena. two extreme

intensities were used, $10^{13}W/cm^2$ and $10^{16}W/cm^2$. the expectation was that $10^{16}W/cm^2$ would yield a Coulomb explosion while $10^{13}W/cm^2$ would yield high harmonic generation of soft X-ray lasers, say.

More details on all the above mentioned calculations will be discussed later.

Chapter 5

Apparatus: The Code¹

The results presented here were performed on an eight-core computer using a real-space computer code called Octopus [4].² This code is still under active development which partly explains the narrowed spectrum of properties that were investigated in this work. A good example for explaining this is that the long-standing *ab-initio* Car-Parrinello Molecular Dynamics [28] calculations were only incorporated into the code recently.

Octopus was written particularly for the calculation of time-dependent density functional (TDDFT) phenomena, with one of its authors being the very founder of modern day TDDFT, E.K.U. Gross. Its target problems are

- i) linear optical/electronic response of molecules and clusters to external electromagnetic fields,
- ii) non-linear response to classical high-intensity electromagnetic fields, which takes into account both the ionic and electronic degrees of freedom,
- iii) ground state and excited state electronic properties of systems with “low dimensions” such as quantum dots,
- iv) photo-induced reactions of molecules such as photo-isomerization, and
- v) electronic transport properties.

Work is in progress to accurately extend these procedures to infinite and periodic systems like polymers, slabs, nanotubes and solids.

The underlying theories that the code solves are the ground state DFT and excited state TDDFT. In addition, by considering a point-particle classical approximation for the

¹This chapter is mainly based on [4] and the Octopus manual.

²The work was first done on a South African supercomputer, the CHPC, but little progress was made using that machine.

nuclei, the code can also perform classical dynamics of the nuclei. The dynamics may be non-adiabatic because the system evolves along an Ehrenfest path. Recent developments have seen Born-Oppenheimer and Car-Parrinello dynamics become a reality to perform with the code. In solving TDDFT, the code performs both linear response and full, explicit calculations of the time-dependent Kohn-Sham equations. The latter approach allows us to place the molecules/materials into strong external potentials that cannot be handled using perturbation theory, for instance, into strong laser fields.

Because the code performs real space calculations, it does not depend on any basis set. Instead, it uses numerical meshes. However, when necessary, auxiliary basis sets (plane waves and atomic orbitals) are used when necessary.

For most calculations, the code relies on the use of pseudopotentials discussed in Appendix B. Of these, the Troullier-Martins [108] and Hartwigsen-Goedecker-Hutter [45] pseudopotentials are readily available for use in the code.

The code also performs calculations in two and one dimensions, in addition to the default three dimensions.

FORTRAN 90 is the main programming language that was used to write the code, with an ever-growing large number lines of code (50 000 in the year 2006 [4]). A number of its modules are also written in other languages like C and Perl. Because of its high portability, the code runs on virtually any Unix-like environment.

Octopus is a free code licensed under the GNU General Public License (GPL). For that reason, its development version bears the marks of many developers besides its original developers.

5.1 Ground state DFT calculations

In this case, the code simply solves the ground state Kohn-Sham equations [71] (self-consistently) for an auxiliary non-interacting electron system to obtain the ground state density $n(\mathbf{r})$ which contains all the information about the system [70, 60]. The kinetic term in the Kohn-Sham Hamiltonian is approximated by a finite difference formula. The potential generated by all the nuclei combined, uses projectors that are well-localized in real space, making the calculation of their effect feasible and much faster in real space than in a plane wave formulation. In relation to this potential, the code also allows for the use of user-defined external potentials so that QM/MM [75] calculations are possible.

The Hartree (electron-electron interaction) potential is quite time consuming. Some of the various ways of calculating this term [1] include

- i) conjugate gradients which use a conjugate gradient algorithm,
- ii) multi-grids which is a linear scaling iterative method to solve elliptic problems. In this case, a group of different grids that have less points than the original real space grid is used where possible.
- iii) Fourier space which thrives on the fact that the Hartree potential is simply a multiplicative function in Fourier space, thereby making its computation faster in this space. Fast Fourier Transforms make it even faster.

To approximate the exchange-correlation functional, Octopus employs many different approximations that range from the local density approximation (LDA) [30, 87] through generalized gradient approximations (GGAs) [88, 91, 92, 15, 89, 90] to the state of the art orbital dependent functionals [100, 103, 62]. The orbital dependent functionals require the use of the optimized effective potential (OEP) method. Of these, both the Krieger, Li and Iafrate (KLI) [62] approximation and the full solution of the OEP equation [74, 73] are implemented in Octopus.

The set of functionals is being extended to cater for current-density functionals [113, 114, 97, 27].

5.1.1 Eigensolvers

Given the Kohn-Sham Hamiltonian for a trial density n , one solves the Kohn-Sham equations for the lowest occupied³ states. In real space, the problem is simply the solution of an eigen-problem for large sparse matrices [99]. In Octopus, several schemes are tried, including

- i) conjugate gradients based schemes [105, 86],
- ii) Lanczos-based algorithms [66], and
- iii) the Jacobi-Davidson procedure [43].

5.1.2 Mixing

To converge the self-consistent calculations, it is essential to mix the density. If $n^{(i)}$ is a series of densities that converge to the true/solution density n , then each new density is generated using a prescription of the form

$$n^{(i+1)} = G \left[\tilde{n}^{(i+1)}, n^{(i)}, \dots, n^{(i-s)} \right] \quad (5.1)$$

³This assumes the use of pseudopotentials discussed in Appendix B.

where $\tilde{n}^{(i+1)}$ is the density obtained from the definition of the density

$$n(\mathbf{r}) = \sum_{i=1}^N |\varphi_i(\mathbf{r})|^2 \quad (5.2)$$

in terms of the Kohn-Sham orbitals $\varphi_i(\mathbf{r})$.⁴ However, in obtaining $\tilde{n}^{(i+1)}$, one uses Kohn-Sham orbitals of the $(i+1)^{th}$ iteration.

The simplest example of this kind of mixing is the so-called linear mixing [35], in which equation (5.1) takes the form

$$n^{(i+1)} = (1 - \alpha) \tilde{n}^{(i+1)} + \alpha n^{(i)}. \quad (5.3)$$

In addition to this type of mixing, Octopus also allows for the use of other types of mixing like the generalized Broyden algorithm of Johnson [67] and the guaranteed reduction Pulay algorithm [19].

5.1.3 Spin

Octopus is well capable of performing calculations that incorporate spin using spin density functional theory, either considering complete spin alignment throughout the system or not. The latter case requires the use of generalized local spin density theory [116]. The wavefunctions are then described as two-component spinors

$$\Phi(\mathbf{r}) = (\varphi_1(\mathbf{r}), \varphi_2(\mathbf{r})) \quad (5.4)$$

where the components are complex wavefunctions.

In the same vein, Octopus is also able to perform calculations for systems in external magnetic fields since purely magnetic fields can be viewed as electromagnetic fields whose electric field component is always zero.

⁴By virtue of the Kohn-Sham ansatz, the Kohn-Sham density equals the true density of the fully interacting problem.

5.2 Response calculations

The goal here is to solve the corresponding time-dependent Kohn-Sham (Runge-Gross) equations:

$$i \frac{\partial}{\partial t} \varphi_i(\mathbf{r}, t) = H_{KS}(t) \varphi_i(\mathbf{r}), \quad (i = 1, \dots, N) \quad (5.5)$$

and

$$n(\mathbf{r}, t) = \sum_{i=1}^N |\varphi_i(\mathbf{r}, t)|^2 \quad (5.6)$$

where the time-dependent Kohn-Sham Hamiltonian is given by

$$H_{KS}(t) = -\frac{1}{2} \nabla^2 + v(\mathbf{r}, t) + v_{Hartree}[n](\mathbf{r}, t) + v_{xc}[n](\mathbf{r}, t) \quad (5.7)$$

since the density (equation 5.6) contains all the information about the system.

The external potential is written in its explicit time-dependent form $v(\mathbf{r}, t)$ to allow for time varying potentials. The exchange-correlation potential is a functional of both the time-dependent density and the initial state of the system, usually the ground state. Applying TDDFT relies on the adiabatic approximation

$$v_{xc}[n](\mathbf{r}, t) = v_{xc}^{gs}[\rho] |_{\rho=n(\mathbf{r}, t)} \quad (5.8)$$

where v_{xc}^{gs} is the ground state exchange-correlation potential functional.

This way, all the approximations implemented in the code for the ground state calculation translate immediately to the time-dependent formalism. Orbital functionals are also implemented in Octopus for time-dependent calculations within the time-dependent KLI scheme [109].

While most other codes are restricted to linear applications of TDDFT, Octopus allows for the solution of the theory in both perturbative regions and beyond, i.e. in cases where the external perturbing potential is small enough to be handled by perturbation (linear response) theory and cases where the potential is too strong for perturbation to treat properly. In other words, while linear response theory is implemented in Octopus, a full solution of the time-dependent Kohn-Sham equations (5.5) and (5.6) is also well implemented. The latter allows for the computation of linear response properties as well as other properties beyond the linear response, such as molecules in strong laser fields. The full solution of equations also allow for the computation of combine electron-ion response dynamical simulations.

In Octopus, various approximations to the time evolution operator have been implemented. Among them are polynomial expansions (in the standard base or in the Chebyshev base), Krylov subspace projections, the split-operator method, higher order split-operator like schemes, the implicit midpoint rule, the exponential mid-point rule and Magnus expansions [3].

5.2.1 Coupled electron-ion response

In order to study the dynamics of molecules exposed to external electromagnetic fields, a mixed classical/quantum mechanical approach is used in Octopus. This is the QM/MM approach introduced in the previous chapter. Particularly, the electronic system is treated quantum mechanically while the ions are treated classically.

In this case, the Hellman-Feynman theorem is no longer valid and therefore the Erhenfest theorem can be used.

The ionic (classical) system obeys Newton's laws of motion:

$$m_{\alpha} = \frac{d\mathbf{R}_{\alpha}}{dt} = \mathbf{P}_{\alpha} \quad (5.9)$$

$$\frac{d\mathbf{P}_{\alpha}}{dt} = -\sum_j \langle \varphi_j(t) | \nabla_{\mathbf{R}_{\alpha}} v_{KS}[n] | \varphi_j(t) \rangle + \sum_{\beta \neq \alpha} \mathbf{F}_{\beta \rightarrow \alpha} \quad (5.10)$$

where m_{α} is the mass of the nucleus tagged by α , $\mathbf{R}_{\alpha}$ and $\mathbf{P}_{\alpha}$ are the corresponding position and momentum respectively. $\mathbf{F}_{\beta \rightarrow \alpha}$ is the classical electrostatic force exerted by nucleus β on nucleus α . Equation 5.10 is just a reformulation of Erhenfest's theorem.

5.2.2 Sternheimer's equations

Octopus is also able to calculate response properties using density functional perturbation theory, which has not been described in this report since we will not use it in this work. It is possible to calculate static polarizabilities and first hyperpolarizabilities.

5.3 Units

There are many possible unit conventions that can be used, but Octopus uses two different types, namely

i) atomic and

ii) convenient units.

5.3.1 Atomic units

This is the default unit type used in Octopus. Atomic units are a Gaussian⁵ system of units in which the numerical values of the Bohr radius, the mass and charge of an electron as well as the reduced Planck's constant are set to unity:

$$a_0 = m_e = e^2 = \hbar = 1. \quad (5.11)$$

Subsequently, the atomic units of length and mass become

i) $au_{length} = a_0 = 5.2917721 \times 10^{-11}m$, and

ii) $au_{mass} = m_e = 9.1093819 \times 10^{-31}kg$.

Since e^2 must have units of energy times length, the atomic units of energy read $au_{energy} = \frac{e^2}{a_0} = 4.3597438 \times 10^{-18}J$ which is called the Hartree (Ha).

The atomic unit of time can thus be derived as follows:

$$\begin{aligned} Ha = m_e \frac{a_0^2}{au_{time}^2} &\Rightarrow au_{time} = a_0 \sqrt{\frac{m_e}{Ha}} = \frac{a_0}{e} \sqrt{m_e a_0} \\ &= 2.4188843 \times 10^{-17}s. \end{aligned} \quad (5.12)$$

5.3.2 Convenient units

It is very common to find the energy and length expressed in electron volts (eV) and Angstroms (Å) respectively. For that reason, we call these units the convenient units. In this case, while the unit of mass does not change, that of time becomes $\hbar/eV$, where $\hbar = 6.5821220(20) \times 10^{-16}eVs$. Octopus allows the user to switch from the default atomic units to the convenient system by simply including the line following in one's input file:

Units = eVA

The user can actually set the input units to be different output units quite easily.

5.3.3 Mass units

In all this discourse, the units of mass remain unchanged in Octopus, i.e. atomic mass units (amu) are used always, when dealing with masses of ions.

⁵In the Gaussian system, the vacuum dielectric constant is dimensionless and therefore set to $\epsilon_0 = \frac{1}{4\pi}$.

$1amu = \frac{1}{12}$ of the mass of the mass of a ^{12}C atom.

5.4 Utilities

Octopus has an ever-growing number of utilities, short programs, that make post-processing of data easy and fast. Some notable examples include:

- i) oct-center-geom which centers the ions in the simulation box,
- ii) oct-cross-section which calculates the absorption cross-section tensor, and
- iii) oct-broad which broadens the linear response spectra.

5.5 Discretization

It is worthy noting that we have so far been describing continuous systems that no present day computer can solve. It therefore becomes imperative to discretize the equations one way or the other. In this light, Octopus uses a grid in real space to solve the Kohn-Sham equations. In this computational procedure, functions are represented by their value over a set of points in real space. Normally, these points (grid) are equally spaced, but non-uniform grids can be used.

In addition, one can adapt the shape of the simulation box/region to suit the geometric configuration of the system. Various shapes of the simulation box are supported in Octopus. They include the sphere, cylinder, parallel-piped and user-defined box shapes. The default box shape is a set of spheres around each ion in the molecule. This cuts down on computer time since it does not waste time performing calculations over empty space.

It should follow from this discourse that there are two very important discrete parameters that must be specified, namely

- i) the spacing between the grid points in the simulation box, and
- ii) the size of the box (typically the radius of the spheres in the case of the default or general spherical box shapes).

Octopus, by default, assumes zero boundary conditions, i.e. it sets the wavefunctions and density to zero over the boundary of the simulation box. This point reinforces the importance of a good/optimal box size. If the box is too big, computer time is escalated unnecessarily. On the other hand, if the box is too small, the wavefunctions and density will be forced to go to zero unnaturally (prematurely).

5.6 Visualization

The ultimate aim of performing a computational condensed matter simulation is to view pictorially the atomic processes. Octopus writes its output data in form that are readable by many other visualization programs. The primary and most beautiful one is Data Explorer (OpenDx).⁶ It produces beautiful 3-dimensional pictures and animations of any appropriate data fed to it. However, because OpenDx is a general purpose data-visualization package, an extra layer of software (Chemistry Extensions) must be included to translate the data from Octopus into a format that OpenDx understands and can manipulate. One very good program that serves that purpose exactly was written by Richard Gillian from Cornell Theory Center.⁷

To run the data visualization, OpenDx needs two programs, one .net and the other .cfg. While getting OpenDx to work properly is not trivial, the work is well paid off by the beautiful visualizations.

Data Explorer can also generate two dimensional images of the data.

Other visualization programs supported by Octopus include Xcrysden [72], Matlab (www.mathworks.com) and Gnuplot (www.Gnuplot.info). Matlab and Gnuplot in particular, cannot generate three dimensional pictures as does OpenDx.

⁶OpenDx is found on www.OpenDx.org.

⁷However, the Octopus team had to update these. They now provide an updated version of the Chemistry Extensions.

Chapter 6

Calculation Procedure

In this chapter, we give a somewhat detailed outline of how the calculations were carried out.

Coordinates of all the atoms in the system are an essential part in the real space code, Octopus. As such, the initial coordinates were obtained from the Cambridge Structural Database (www.ccdc.cam.ac.uk).¹The coordinates that were used were from [36].

The Cambridge Structural Database gave the coordinates in fractional coordinates which are not orthogonal, yet Octopus expects the input xyz coordinates to be orthogonal.² Using a spreadsheet, these coordinates were then converted to their cartesian values before use.

Both input and output units were conveniently set to eV for energy and $\text{\AA}$ for length.

6.1 The Simulation Box

The default simulation box (spheres around each atom) was used throughout in this work, i.e. each atom in the molecule was surrounded by a sphere of a particular radius. The accuracy and convergence of the calculations depended heavily on the simulation box, which, in turn, is characterized by the following two parameters:

- i) the grid spacing, and
- ii) the box size.

¹This was done through Prof. Demetrius Levendis of the University of Witwatersrand (Chemistry Department) who is the contact person for the database in South Africa.

²A further discussion on this issue can be found in [25].

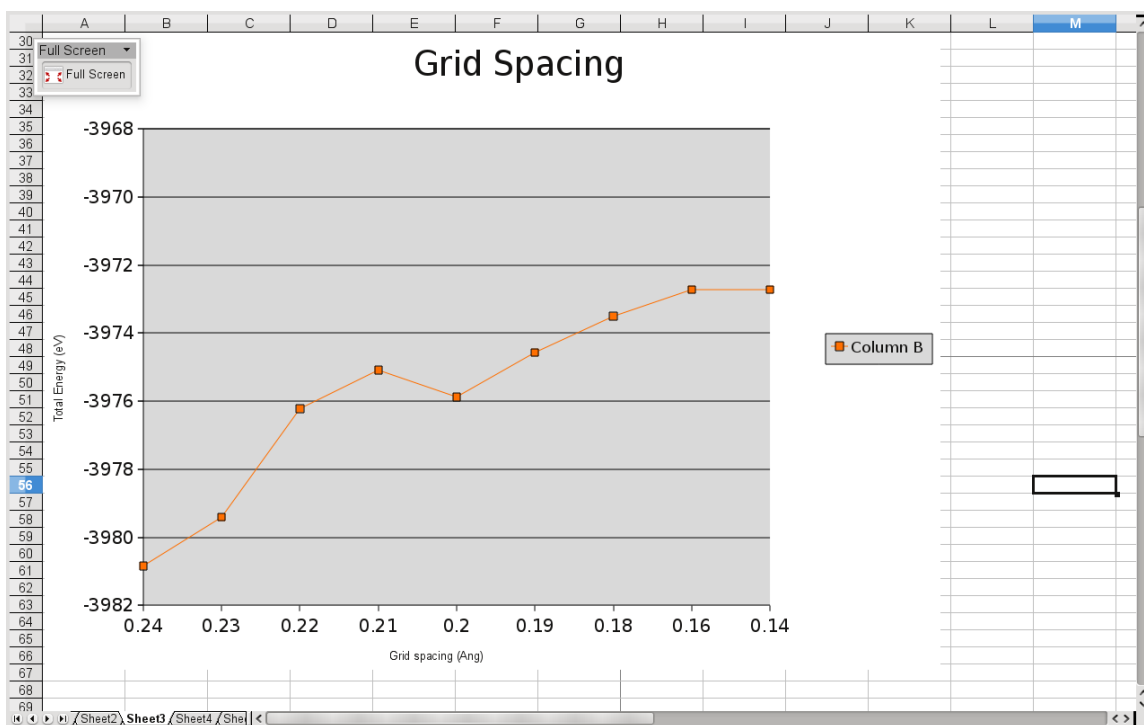


Figure 6.1: Grid spacing convergence study.

6.1.1 Spacing

To start with, the box size was kept constant, as well as every other variable in the input file. A series of ground state calculations were then performed for various grid spacings, each time recording the total energy of the system against the particular grid spacing. The spacing was varied from $0.14\text{\AA}$ to $0.26\text{\AA}$ and a graph of the total energy plotted against the grid spacing (figure 6.1).

The best grid spacing to use in this case was found to be $0.20\text{\AA}$ because of its apparently local minimum value. Within the sensible range of the spacing values, there is no global minimum.

6.1.2 Box size

The grid spacing was then held constant at $0.20\text{\AA}$ while the radius of the spheres were varied from $1.5\text{\AA}$ to $6.5\text{\AA}$. A similar plot of the total energy against the box size was made to determine the most stable radius (figure 6.2).

As can be seen in figure 6.2, the most sensible box size to use for the spheres had a radius of $5.5\text{\AA}$. This is where the global minimum (within the physically sensible data

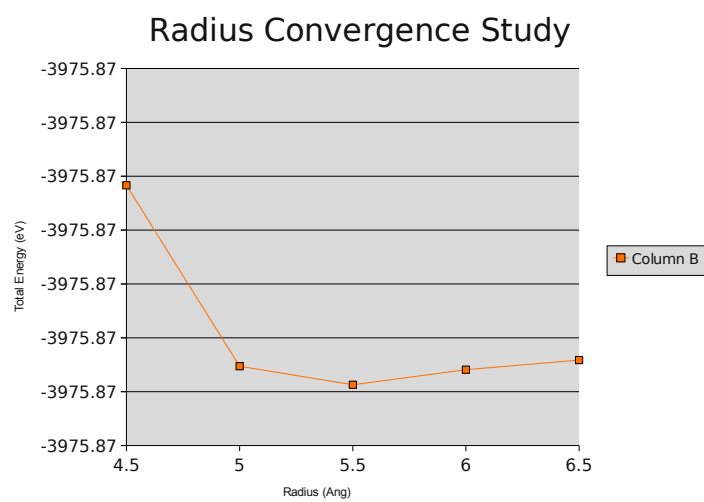


Figure 6.2: Box size (radius of spheres).

range studied) appears to be.

6.2 Geometry Optimization

Up to this point, cartesian coordinates derived from experiment were being unused. Unfortunately, the experimental data contain inherited experimental errors which make it needful to optimize the geometry in a geometric optimization calculation. In other words, the cartesian coordinates obtained from experiment were used as input to generate a new set of coordinates.

The optimized cartesian coordinates were then centered using the Octopus utility “oct-center-geom” for two reasons. One was to align the molecule to an orthogonal set of axes, the cartesian system. The other reason was to get the ions to the centers of their simulation boxes so that the corresponding densities for each of the atoms would be fully contained in the simulation box.

LDA was used for this part of the calculations mainly because it gives excellent results with little computational effort.

6.3 The Ground State Calculation

The first few procedures above set the stage for the ground state calculations that would be used as a starting point for the time dependent calculations.

Both LDA and KLI ground state calculations were performed, with no self-interaction correction (SIC). In each case, we endeavored to converge the absolute density rather than the total energy, which is a harder thing to do. This is especially necessary in our case since we would evolve the density later. If the total energy is converged here, the time dependent run requires a very small time step (to be described below). This would then greatly slow down the evolution calculation. The convergence criterion for the density was intentionally set to 1×10^{-9} in order to achieve very high convergence of the density.

No relativistic corrections were included in the calculations. We mixed the density using the Broyden type of mixing. The conjugate gradients (cg) eigensolver was used.

For the KLI calculation, a hybrid exchange-correlation functional (hyb_gga_xc_x3lyp) was used, primarily because it was labeled as the best hybrid functional. An explicit OEP calculation was too complex for the machine to handle as evidenced by the fact that

with four processors running, the computer was still trying to set up the Hamiltonian after twelve hours.

Various ground state quantities were extracted and written in a OpenDx friendly format.

6.4 Optical Absorption Spectrum

The optical absorption spectrum was calculated using two different methods, which are the linear response theory and the full, explicit solution of the Kohn-Sham equations. In both cases, only LDA calculations were performed.

6.4.1 Linear response theory

Because Casida and Petersilka's formulation of linear response theory requires a prior knowledge of the unoccupied states, an unoccupied states calculation was first launched for the first thirty low-lying unoccupied states. The calculation usually has serious convergence problems. Likewise, this calculation also did not converge. In fact, none of the unoccupied states converged.

Next, the calculation mode was set to Casida to calculate the linear response spectrum which was then broadened using the utility "oct-broad." Both the Petersilka and Casida spectra were written to the working directory as output information.

It is probably important to state here that linear response theory as implemented in Octopus only works with LDA and not KLI.

6.4.2 Explicit solution

To perform the time dependent calculation, one needs to get a good time step and check all the other input variables before applying any external electromagnetic field. If everything is correct, the total energy should remain constant as one propagates the system in time. The maximum time step that conserved the total energy in the absence of an external electromagnetic field was found to be 0.002 units.

A delta kick with a time dependent delta strength of 0.01 was applied in the x -direction and the system evolved using time reversal symmetry to achieve a total of 5000 iterations which translate to $6.5821fs$. These should be enough to resolve a meaningful optical absorption spectrum. Among other things, multipoles were written to the working directory as output which were then labeled as multipoles1 for the x -direction.

Two other similar calculations were made for the y and z directions, each time renaming the multipoles file to *multipoles2* and *multipoles3* respectively. If the molecule were symmetric in more than one direction, there would be no need of calculating the multipoles for all the equivalent directions. In the input file, one would just specify how many directions are equivalent.

Running the utility “oct-cross-section” then yields the *cross_section_tensor* file from which the whole optical absorption spectrum can be plotted. Depending on the number of equivalent axes, other files named *cross_section_vector.1*, *cross_section_vector.2* and *cross_section_vector.3* are also generated.

The ions were not allowed to move in this calculation.

6.5 Laser-Molecule Interaction

A different propagation calculation was performed for the molecule in a strong laser field. Only one laser pulse was introduced in each of these calculations. The laser frequency was set and fixed to 18.0 eV. The rest of the laser parameters were as follows:

***** Time-dependent external fields *****

1: Electric Field.

Polarization: (0.0000, 0.0000)(0.0000, 0.0000)(1.0000, 0.0000)

Carrier frequency = 18.00000000 [eV]

Envelope:

Mode: cosinoidal envelope.

Amplitude: 0.0194 [a.u.]

Width: 0.5000 [$\hbar$ bar/eV]

Middle t: 0.5000 [$\hbar$ bar/eV]

Peak intensity = 2.050515E-03 [a.u.] = 1.319795E+13 [W/cm^2]

Int. intensity = 1.403994E-02 [a.u.]

Fluence=2.574942E-03[a.u.] *****

This was for the $10^{13} W/cm^2$ laser intensity. The other peak intensity was 1.351471E+16 [W/cm^2].

For each of the two intensities, the laser field was polarized in the x , y , z and the negative x -directions.

The state of the molecule was projected to the ground state every 1000 iterations during the 5000 iterations for each direction.

A QM/MM approach was adopted, in which the electrons were treated quantum mechanically while the ions were treated classically. The motion of the ions was described

by Erhenfest dynamics. The velocity verlet algorithm was used. The 40% faster Approximated Enforced Time-Reversal Symmetry (aetrs) evolution method was used to get accurate and very fast time evolution of the system.

The boundaries of the simulation box were set to absorb the wavefunctions outside the simulation box using the $\sin^2$ function.

Chapter 7

Results and Discussion

In this chapter, we present and discuss the results of the ground and excited states calculations.

It makes sense to start by presenting the ground state geometry of the molecule that was finally used in the calculations, after the geometrical optimization procedure. It is shown here in three orthogonal directions (on three orthonormal planes), x , y and z .¹ The most natural way of looking at the molecule is in the z -direction, i.e. on the $x-y$ plane shown in figure 7.1a on the following page since the very interesting cis-trans isomerization of the molecule is most easily seen in this direction. For this reason, we will be sticking to this natural viewpoint of the molecule and only switching to the other views where necessary to clarify any points. Since the isomerization process is profound around the 11th and 12th carbon atoms, we will be studying in great detail, the behavior of this region of the molecule. In particular, we will be monitoring the distances and angles between the 10th and 13th carbon atoms, the 10th and 12th, and between the 11th and 13th carbon atoms. Just to sum it all up, we will also look at the general length of the molecule, i.e. the distance between the 3rd and 15th carbon atoms.²

The starting (ground state) values of these quantities are given in table 7.1.

The $C_{10} - C_{13}$ distance agrees with experimentally measured length of 3.18Å to within 0.4%. The bond angle (2.95°) is also in excellent agreement with what R. D. Gilardi et al reported in [44]. Their observed value was 2.1° with an error of 0.9° .³ Since there are two other atoms between the C_{10} and C_{13} atoms, we measure here the dihedral angle

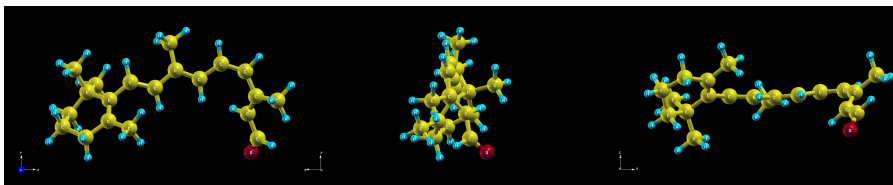
¹The choice of this coordinate system is completely arbitrary. Renaming the axes does not change any of the physical properties of the molecule.

²We have adopted here, the standard numbering system used by R. D. Gilardi et al in 1972 [44] also shown in figure 4.1.

³Unfortunately, these are the only quantities considered here that were also investigated experimentally in the seminal paper of 1972 [44].

Table 7.1: Initial (ground state) distances and angles of interest on the molecule

Species	Distance (Å)	Angle ($^{\circ}$)
$C_{10} - C_{13}$	3.166	2.95 (dihedral)
$C_{10} - C_{12}$	2.503	128.17
$C_{11} - C_{13}$	2.536	130.12
$C_3 - C_{15}$	10.541	-



(a) Viewed in the natural z-direction (b) Viewed in the x-direction (c) Viewed in the y-direction

Figure 7.1: Ground state geometrical structure of the 11 – *cis* retinal molecule after geometry optimization

instead. A measurement of the angle between the C_3 and C_{15} atoms makes no great deal of scientific sense and is therefore ignored.

A close look at figure 7.1c suggests the well-known fact that the carbon backbone structure of the molecule lies on at least three distinct, but non-orthonormal planes. The first accommodates the benzyl ring, the second stretches from the benzene ring to the thirteenth carbon atom in the main carbon structure, and the last spans the atoms from the twelfth carbon atom in the main frame to the end of the molecule. This should convince one that structure was minimized correctly.

It is probably worthy mentioning that figure 7.1 and every other pictorial diagram of the molecular structure of the 11 – *cis* retinal molecule presented in this work does not show whether the chemical bonds are single or double bonds. This is probably because these structures are drawn simply from some *xyz* coordinates file that has no information whatsoever about the nature of bonds involved. This is good because when we manipulate the electron numbers, for example by ionizing the molecule using a laser beam, the correct information about the electronic structure of the molecule ceases to be encoded in the molecular structure. In other words, in such cases, the molecular structure contains no information at all about the nature of the bonds involved.

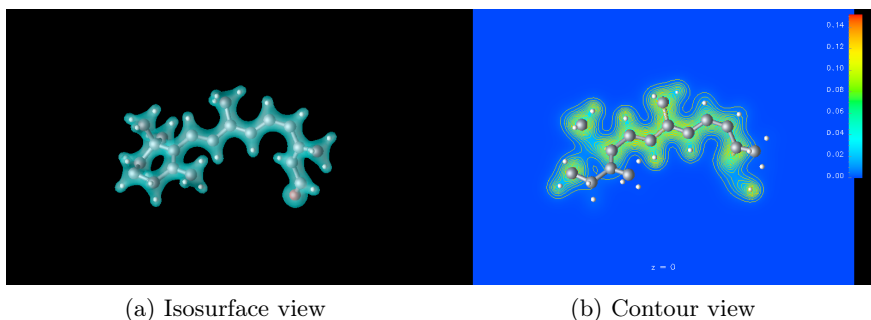


Figure 7.2: Ground state electron density.

7.1 Ground State

The ground state calculation gave the total ground state energy of the molecule to be $-3.98460971 \times 10^3 eV$.

The ground state electronic density distribution of the molecule is shown in figure 7.2. Figure 7.2 is an isosurface view of the particle density, showing pictorially how the electron density is distributed along the molecule. Figure 7.2 is a contour plot of the same density distribution about the origin, taken on the $x-y$ plane. Not all the atoms are visible in this diagram because the molecule is not planar as has already been discussed above. A colour scale showing the probability distribution of finding the electrons in any given spatial region is also shown, in which blue corresponds to null probability and red to the highest density distribution. While this is the best contour picture (of the ground state density distribution) that could be obtained for the molecule in this work, it is rather disappointing that the density distribution does not seem to indicate this very high density probability. Even though the density contains everything about the electronic structure of the molecule, it appears here to be uninterestingly deficient of finer details about the molecule. This is a known fact that led to the invention of the Electron Localization Function (ELF) [6].

Embedded into both diagrams is the crystal structure of the molecule generated using OpenDx. One might note here that the hydrogen atoms appear to be detached from the backbone carbon structure, i.e. there are no covalent bonds between the hydrogen atoms and their corresponding carbon atoms. Well, in all similar pictures presented in this work, this should not be taken to mean that the bonds are broken, unless otherwise stated. In each case, the electron density or the electron localization function (ELF) should help clarify any such ambiguities.

Figure 7.3 shows two plots of the electron localization function, an isosurface representation and its corresponding contour representation taken about the origin on the $x-y$

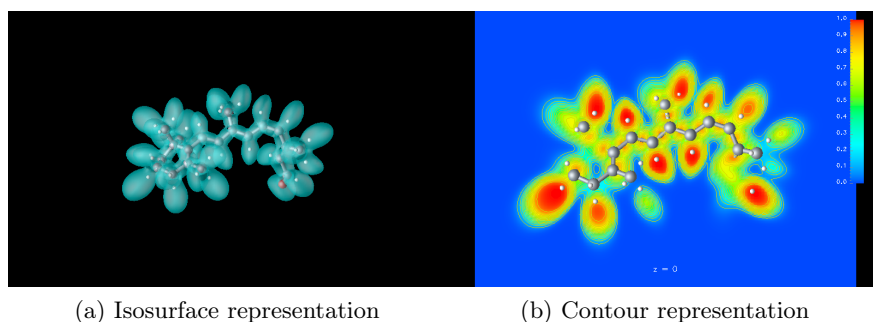


Figure 7.3: Ground state electron localization function (ELF)

plane (the area as the density discussed above).

It should be evident that the electron localization function gives finer details than the electron density distribution. Notably, the ELF [6] gives a beautiful, well-detailed representation of the particle density around each ion/atom. The delocalized π -bonds are quite well spelt out. Actually, judging from this simple comparison, one can readily conclude that the ELF is an ideal candidate for studying bond behavior. When combined with molecular dynamics, the ELF gives interestingly detailed visual insight into the quantum mechanical/molecular mechanical behavior of substances.

Looking at the contour representation in figure 7.3a, the expected red patches are very visible. Additional features are also profound, for instance the isolated contour plot below the rest of the figure, which shows that if one observes the molecule on the x-y plane about the origin, one should be able to see the electron(s) popping in and out of the plane below the rest of the structure, detached from it. This electron is sensibly due to one of the carbon atoms located below the plane we are considering at the moment. At least one of its valence electrons moves onto or above the surface of interest. While this is readily visible from the electron localization function, the all-knowing density does not say so.

From this argument, it makes sense to follow only the ELF at the expense of the density in subsequent studies, but since the density contains all the information about the electronic structure of the molecule, we will continue to present both the ELF and the density distribution in the subsequent studies.

Other quantities of possible interest that were also calculated for the ground state are shown in figure 7.4. Only the isosurfaces are presented here.

Maybe with the exception of the nuclear potential, all the other potentials are associated with the fictitious Kohn-Sham system of non-interacting electrons. As such, they should have no well-known physical meaning in a non-fictitious world. For that reason, they

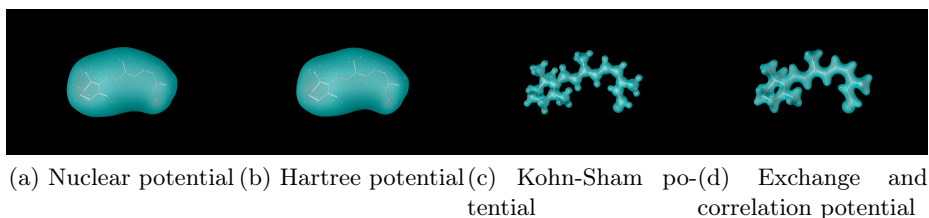


Figure 7.4: Other properties of the ground state system

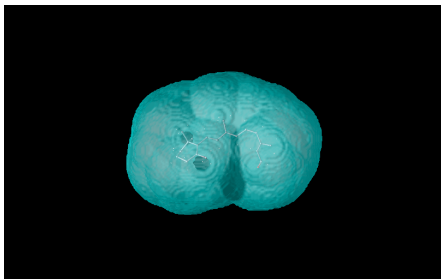


Figure 7.5: Electron pressure

will be not followed.

The electron pressure shown in figure 7.5 might be an interesting quantity to follow, but in the interest of brevity, we shall not study it in this work. For our purposes, the ELF and the electron density, combined with the physical geometry of the molecule should suffice our quest of understanding the visual processes we tasked ourselves to understand.

Therefore, from this point on, we will follow the evolution of the physical geometry of the molecule, the electron localization function and the electron density only.

7.2 Optical Absorption Spectrum

The optical absorption spectra from both linear response theory and the explicit solution of the Kohn-Sham equations is presented. First, we present the result from experiment [96] in figure 7.6.

Let the main point from this graph extract be that the molecule has two notable peaks at wavelengths of 400 nm and 250 nm , respectively. These two peaks are separated by an optically sensitive region as shown. In other words, the molecule is sensitive to a wide optical spectrum, but it is most sensitive to light of wavelengths close to 400 nm ($\sim 3.1\text{ eV}$) which is the shortest visible blue, and 250 nm ($\sim 4.96\text{ eV}$) which is in the ultraviolet region.

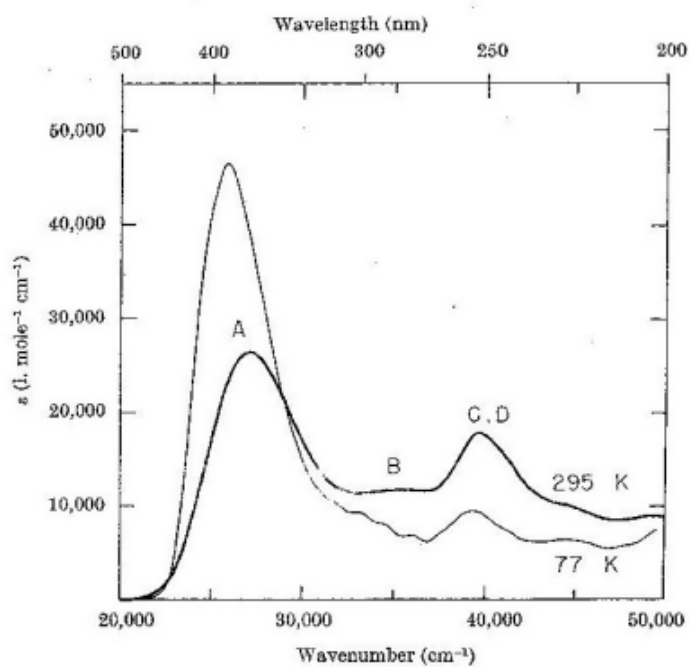


Fig. 2. Absorption spectrum of 11-*cis*-retinal in EPA at 295° C (heavy line) and liquid nitrogen (light line) temperature. Optical path length, 1 mm; concentration, 2.69×10^{-4} M at 295° C. Contraction factor of EPA for cooling from 295 K to 77 K, 0.771.

Figure 7.6: Optical absorption spectrum from experiment

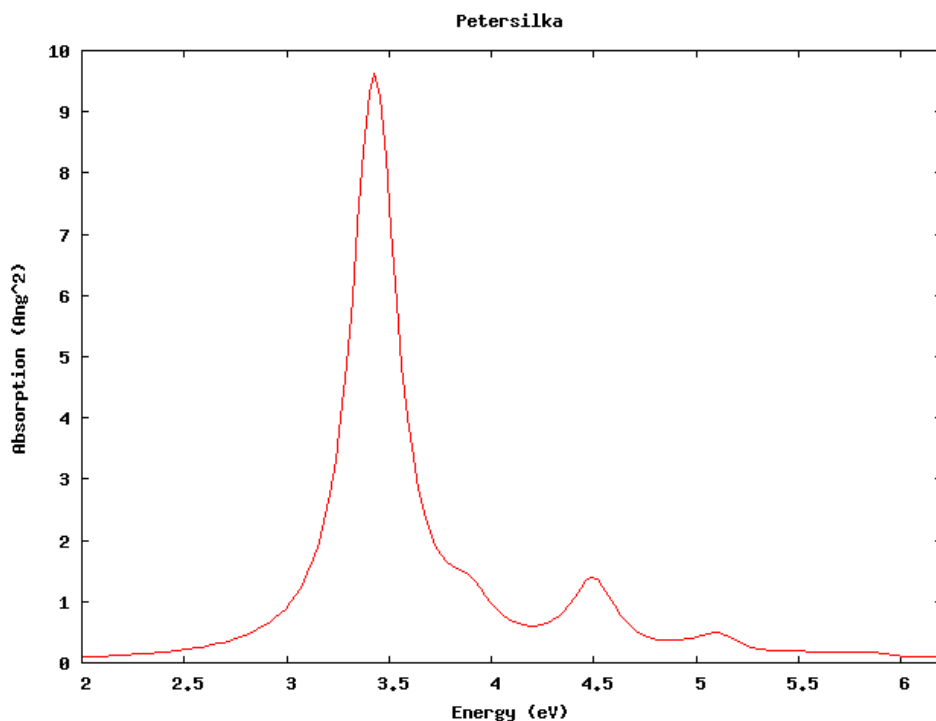


Figure 7.7: The photo-absorption spectrum from linear response theory (Petersilka)

Of course, lowering the temperature makes the molecule more sensitive to the lower energy wavelength and one would expect to see this kind of behavior in our case in which the absorption spectrum is calculated at $0K$. However, the value/height of the peaks in our calculations have no known physical meaning. It is the area under the peaks that really matters.

Please note well that the molecule was in a vacuum in all the calculations conducted in this work.

7.2.1 Linear response theory

Figure 7.8 shows the linear photo-absorption spectrum calculated using Petersilka's formulation of linear response theory. It remarkably reproduces the two major peaks at 3.44 eV ($\lambda \approx 360\text{ nm}$) and 4.51 eV ($\lambda \approx 275\text{ nm}$) respectively. If one considers experimental error coupled with the exchange-correlation error, this is a very good agreement between theory and experiment. In addition, theory also reproduces the little peak at about 225 nm (from experiment) at about 5.13 eV ($\lambda \approx 242\text{ nm}$). The agreement is just spectacular.

It is interesting that the Casida spectrum shown in figure 7.8 does not only reproduce the

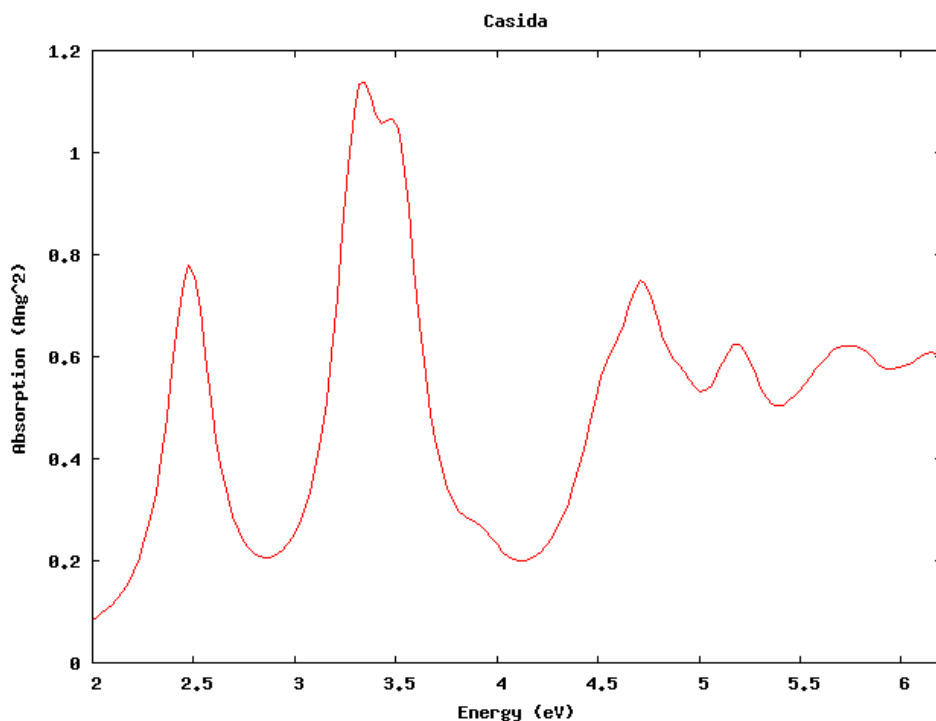


Figure 7.8: The photo-absorption spectrum from Casida's equations

peaks from experiment, but that it also shows a few other peaks that do not appear in experimental results. The second of the two land-mark peaks appears at about 4.72 eV ($\lambda \approx 263 \text{ nm}$) while the first is actually split into two sub-peaks – the higher at 3.35 eV ($\lambda \approx 370 \text{ nm}$) and the lower of the two at 3.49 eV ($\lambda \approx 355 \text{ nm}$). The 3.35 eV ($\lambda \approx 370 \text{ nm}$) of these two is even closer to experiment.

Now, in addition to the two major peaks, the Casida calculation predicts that the molecule is also sensitive to blue-green visible light ($energy = 2.48 \text{ eV}$ and $\lambda = 500 \text{ nm}$) in its vacuo state at $0K$, while experiment suggests that the molecule becomes totally insensitive to electromagnetic radiation in this energy region. The third peak also appears here at 5.18 eV ($\lambda \approx 239 \text{ nm}$). Besides these, the Casida spectrum also amplifies a few other peaks in the ultraviolet region.⁴

7.2.2 Explicit solution

Figure 7.9 shows a plot of the average absorption coefficient against the photon energy from the full solution of the time-dependent Kohn-Sham equations. The explicit time

⁴Actually, in the full spectrum obtained from these calculations (not shown here), the Casida equations suggest that the molecule is much more sensitive to UV radiation, which is expected.

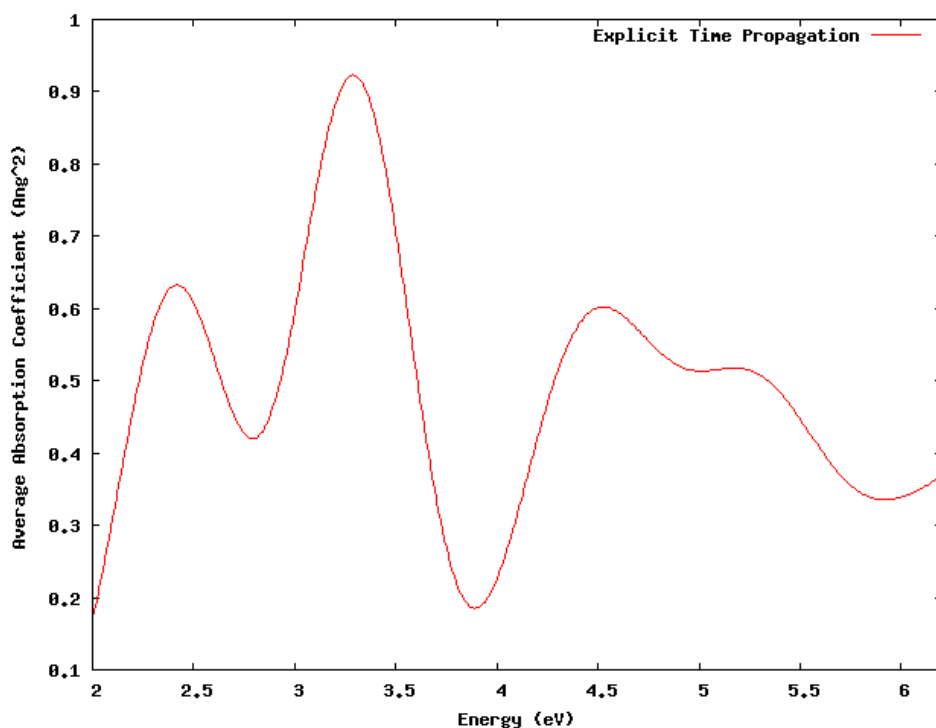


Figure 7.9: Optical absorption spectrum from the full solution of TDKS equations

propagation also predicts the low energy green-blue peak that was also predicted by Casida's solution, but not by experiment. The Petersilka solution also missed this interesting peak. If this peak is true, this means that the 11 - *cis* retinal molecule is very sensitive to the green wavelength of the electromagnetic spectrum. Of course, the protein (opsin) attached to the molecule should shift the peaks to lower energies, but we still might have some peak moved from higher energies to the green wavelength. This transition would be very interesting to study theoretically.

In line with the trend set out by both Casida and Petersilka solutions, the explicit solution also reproduces the other land-mark peaks, one at 3.29 eV ($\lambda \approx 377\text{ nm}$) and the other at 4.53 eV ($\lambda \approx 274\text{ nm}$). It also reproduces the small UV peak at 5.22 eV ($\lambda \approx 238\text{ nm}$). In this case though, the 5.22 eV peak lies on the edge of the 3.29 eV one. This is because the peaks in the time-dependent spectrum are somewhat too broad, a condition that one should be able to correct by running the propagation for uncomfortably much longer times. The widths of the peaks are completely artificial anyway, though the area under them gives the oscillator strength of the transition.

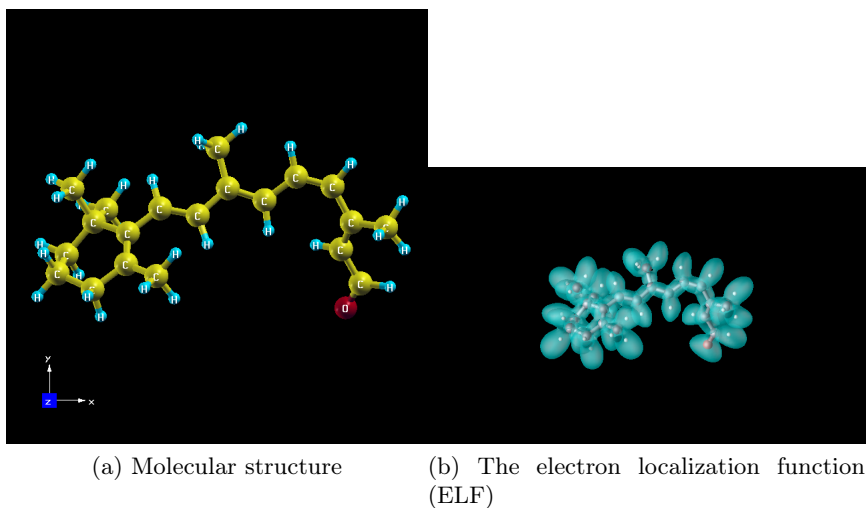


Figure 7.10: The final structure of the molecule after the first 65.821fs

7.3 Molecular Dynamics in Normal Light

Because the behavior of the molecule in a strong laser field is very interesting, it is insightful to start by presenting the results for the classical dynamics of the molecular ions when the molecule is placed in normal light, at least for comparison reasons. The molecule behaves so differently in a strong laser field that this first portion is really worth mentioning.

Comparing ?? with the ground state geometry (figure 7.1a) and ELF (figure 7.3a), the first impression one gets is that the molecule has hardly evolved from its ground state, especially when told that the cis-trans isomerization has not been completed yet, i.e. figure ?? is not a return to the ground state of the molecule. The irony of the observation is that it is nearly true. Well, when one views a video of the molecular motion up to this (65^{th} fs) moment in time, nothing seems to be happening if the video is slowly moving. However, at high enough a speed of the video, a very interesting process seems to be happening. The structure shown in figure ?? is definitely not the ground state of the molecule, though it appears like it. One then remembers that the cis-trans isomerization takes a few pico-seconds (i.e. a few thousand femto-seconds) to complete.

Noteworthy from the video (which cannot be presented here) is that it is **not** only the cis bond that moves. In fact, the whole structure appears to move in very interesting way, most notably the methyl sub-group hanging directly below the 7^{th} carbon atom in the main chain. Table ?? shows the distances between the carbon atoms around the cis bond(s) as well as the length of the whole molecule for the first 50 000 iterations (65 femto-seconds). The first six time steps (six columns) are equally spaced, 1000 iterations

Table 7.2: Distances between atoms for the molecule in normal light

Species	Lengths/Distances (Å)						
time (fs)	0.00000	1.31642	2.63284	3.94926	5.26568	6.58210	65.82100
$C_{10} - C_{13}$	3.166	3.166	3.166	3.166	3.166	3.167	3.218
$C_{10} - C_{12}$	2.503	2.503	2.503	2.503	2.503	2.503	2.512
$C_{11} - C_{13}$	2.536	2.536	2.536	2.536	2.536	2.536	2.556
$C_3 - C_{15}$	10.541	10.541	10.542	10.543	10.546	10.549	10.865

Table 7.3: Angles between atoms for the molecule in normal light

Species	Angles ($^\circ$)						
time (fs)	0.00000	1.31642	2.63284	3.94926	5.26568	6.58210	65.82100
$C_{10} - C_{13}$	2.952	2.963	2.994	3.050	3.136	3.256	17.603
$C_{10} - C_{12}$	128.17	128.17	128.19	128.21	128.25	128.29	129.06
$C_{11} - C_{13}$	130.12	130.12	130.11	130.10	130.08	130.04	130.71
$C_3 - C_{15}$	—	—	—	—	—	—	—

(1.31642 fs) apart while the last one is the 50000th iteration whose output is shown in figure ??.

Comparing the values for ground state ($t = 0.00000 fs$) with those of ($t = 65.821 fs$), to three decimal places (3d.p.), the atomic distances around the cis bonds appear to be stagnant for the first 6.5821 fs , with only a very small change in the $C_{10} - C_{13}$ distance. Interestingly, when one looks at the overall length of the molecule, the $C_3 - C_{15}$ distance, there is an exponentiating rate of increase of the atomic distance, which is not evident in shorter, local distances. This should serve as proof that the stretching of the molecule is not localized around the cis bond region.

Table ?? shows the bond angles for the same cis bond region in degrees for the same time periods.

The bond angles change much more notably, with the dihedral angle mapped by $C_{10} - C_{11} - C_{12} - C_{13}$ atoms and the $C_{10} - C_{11} - C_{12}$ increasing at a steadily increasing rate. In a rather very interesting manner that is best projected by the video, the $C_{11} - C_{12} - C_{13}$ bond angle first decreases before increasing. This suggests a very interesting and complex phenomenon in the dynamics of the molecule, whose causal agent is a very interesting problem to investigate. Unfortunately, such an investigation, which may involve a careful study of the evolution of the electron potential in which the ions live, is somewhat beyond the scope of this work.

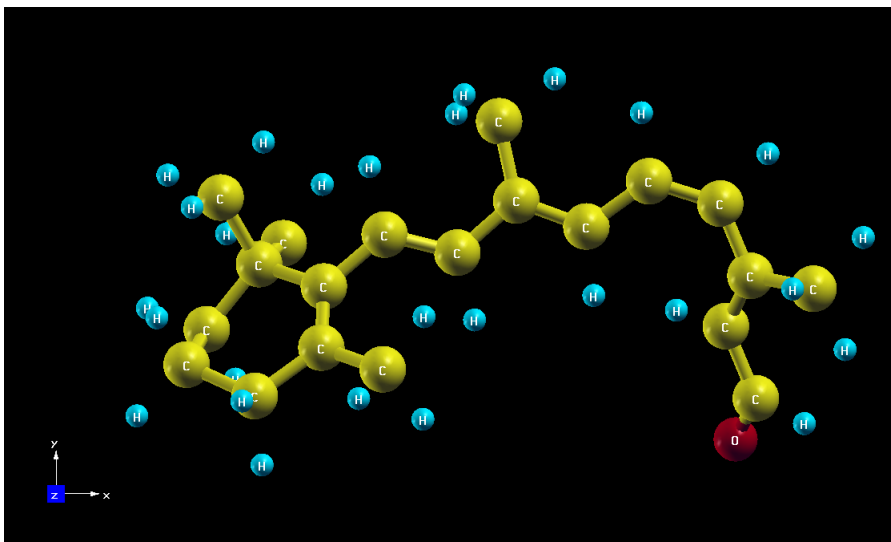


Figure 7.11: The molecular structure at time $t = 1.31642 \text{ fs}$ in a laser intensity of 10^{16} W/cm^2 .

7.4 Laser-Molecule Interaction

We recall at this point that one expects the molecule to explode (Coulomb explosion) when a laser pulse of intensity $I = 10^{16} \text{ W/cm}^2$ is shot through the molecule, and harmonic generation of a very intense (possibly gamma) photon for $I = 10^{13} \text{ W/cm}^2$. However, it should be taken into account that the exchange-correlation potential used (LDA) has been shown to over-estimate ionization in other studies as has already been discussed. As such, the results of this very interesting session should be treated with great caution. They are only intended to show what can be achieved as well as paint a “vague” picture of the very interesting interaction of the molecule and the laser pulse which is well-known to cause blindness.

In all the results presented here, the laser goes through the molecule in the first 500 iterations ($t = 0.65821 \text{ fs}$). The results presented here therefore show what happens after the laser pulse has gone through the molecule completely.

7.4.1 $I = 10^{16} \text{ W/cm}^2$

We present first the results from the intensity of 10^{16} W/cm^2 , with laser pulse short in the z-direction, i.e. perpendicular to the plane of the paper in figure 7.12.

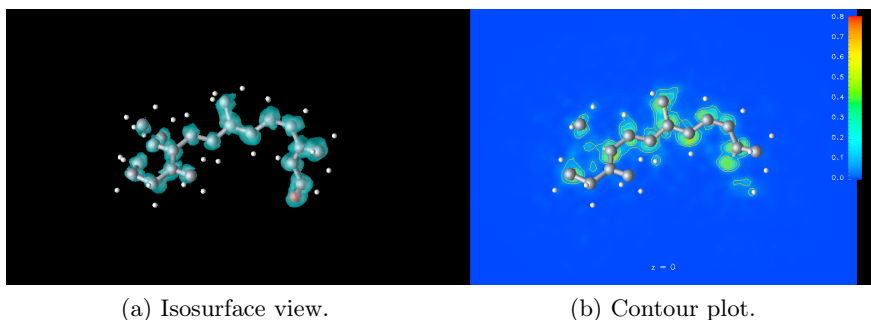


Figure 7.12: ELF at $t = 1.31642 \text{ fs}$ for $I = 10^{16} \text{ W/cm}^2$.

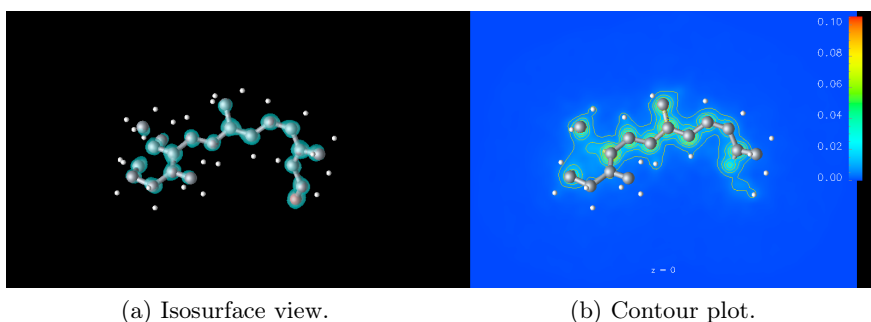


Figure 7.13: Electron density for $I = 10^{16} \text{ W/cm}^2$ at time $t = 1.31642 \text{ fs}$.

7.4.1.1 At time $t = 1.31642 \text{ fs}$

Figure 7.12 shows the molecular structure of the molecule after the first 1.31642 fs , as generated by XCrysden. At this moment in time, all the C-H bonds in the molecule are broken, while the back-bone carbon structure remains in tact. This further reinforced by the electron localization function shown in figure 7.12. The isosurface presentation suggests that there are no electrons at all around the hydrogen atoms, while the contour plot shows the presence of some isolated charge around some of the hydrogen atoms. Nonetheless, nearly all the C-H bonds appear to be broken in this (contour) plot as well.

The electron density at the same instant, shown in figure 7.13 suggests that some hydrogen atoms – shown by the ELF as detached – are still bound to the main structure. Interestingly, these atoms are not the same ones suggested to be still attached by the ELF contour plot. Which description is correct is paradox that may be solved possibly by the use of the exact exchange (EXX) functional. From this point on though, we stick to the well-trusted electron localization function (ELF).

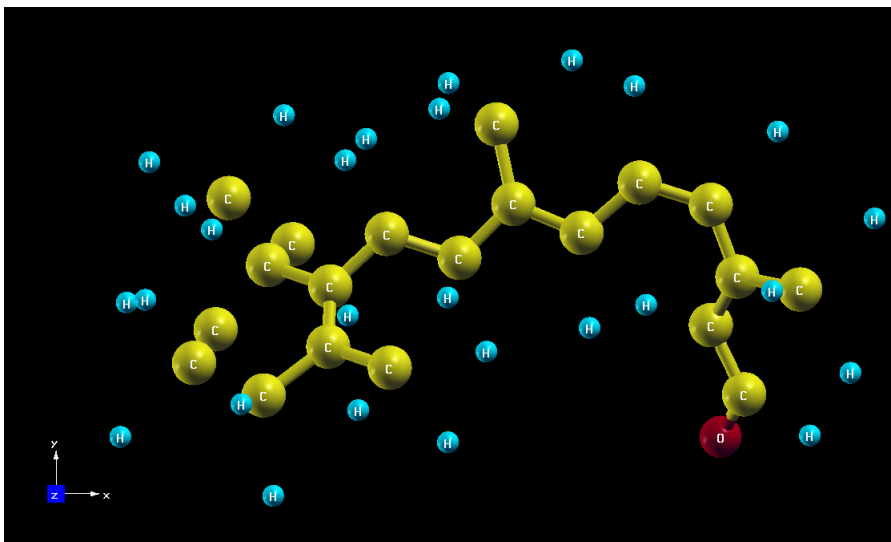
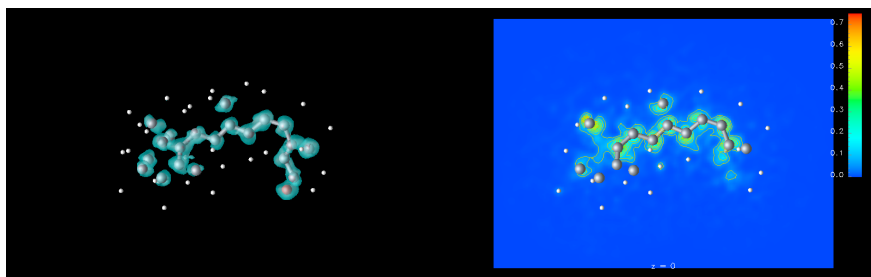


Figure 7.14: Molecular structure at time $t = 2.63284 \text{ fs}$ and laser intensity $I = 10^{16} \text{ W/cm}^2$.



(a) Isosurface view.

(b) Contour plot.

Figure 7.15: ELF at $t = 2.63284 \text{ fs}$ for $I = 10^{16} \text{ W/cm}^2$.

7.4.1.2 At time $t = 2.63284 \text{ fs}$

Figure 7.14 suggests that the backbone structure of the 11 – *cis* retinal molecule placed in a strong laser of intensity $I = 10^{16} \text{ W/cm}^2$ begins to break from the extreme end of the aryl (benzene) ring, detaching the two upper methyl carbons along the way. The rest of the structure is still in tact at this moment.

The ELF corresponding to this time, shown in figure 7.15 suggests that after 2.63284 fs , nearly all the methyl carbon atoms are now detached, save the one to the extreme right of the molecule (near the oxygen atom). While this seems inconsistent with the molecular structure shown in figure 7.14, remembering that the molecular structure shown in figure 7.14 depends only on the inter-atomic distances plotted from some .xyz geometry file comes to our rescue. Conclusively, the bonds that are depicted as broken in figure 7.14

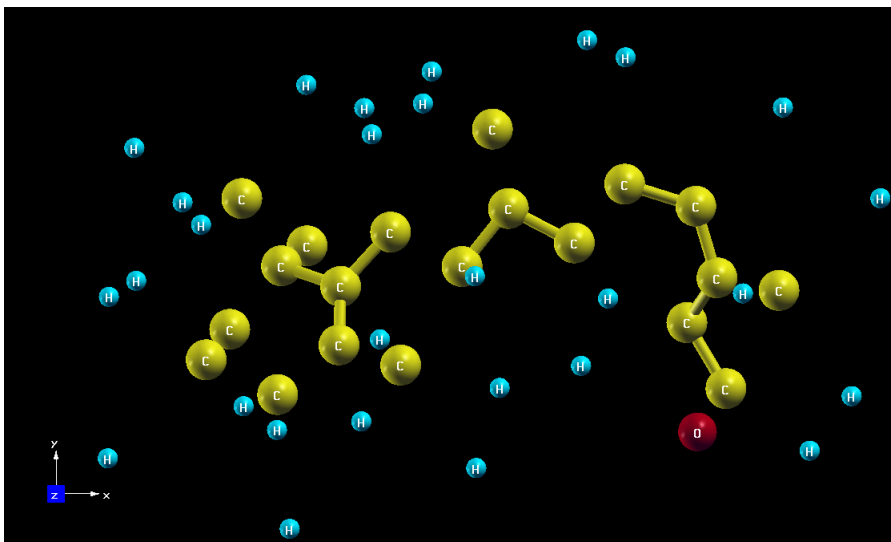


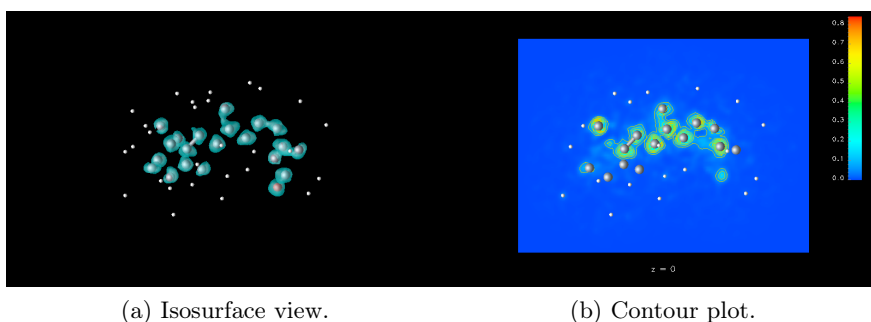
Figure 7.16: Molecular structure at time $t = 3.94926 \text{ fs}$ for $I = 10^{16} \text{ W/cm}^2$.

are the ones that have moved sufficiently far away from their bonding partners to be expressed as such. From this, one would probably expect the next molecular structure (for $t = 3.94926 \text{ fs}$) to show the other methyl group carbons as detached from the rest of the molecule and it indeed does (figure 7.16).

7.4.1.3 At time $t = 3.94926 \text{ fs}$

At time $t = 3.94926 \text{ fs}$, the molecular structure shown in figure 7.16 suggests that all the methyl groups/carbons are detached from the back-bone structure of the molecule. Not only that, but also that an interesting bond breaking pattern appears in the main structure. To the left hand side of the 11-*cis* bond, the bonds that survive have a double C-C bond adjacent to a single C-C bond on the other side, where the central carbon in the single-double (C-C-C) bond has a single bond on one side and a double bond on the other. This suggests that such bonds are quite strong, with the single C-C bonds of this nature being much stronger than their simple C-C single bonds. From the 11th carbon in the main structure (the pivot of the 11-*cis* bend) to the only oxygen atom, we have such alternating single-double bonds, which explain why that part of the molecule is still in tact at this moment in time. The double C-O bond is already broken at this moment though, suggesting that this C-O double bond is relatively weak in this molecule, though much stronger than the C-H and isolated/pure C-C single bonds (with no double C-C bond in their proximity).

Figure 7.17 shows the corresponding ELF at time $t = 3.94926 \text{ fs}$. The contour plot



(a) Isosurface view.

(b) Contour plot.

Figure 7.17: ELF at $t = 3.94926 \text{ fs}$ for $I = 10^{16} \text{ W/cm}^2$.

still suggests finite probabilities of finding electrons in regions that are forbidden by the isosurface view, particularly within the borders of $C_{10}-C_{11}-C_{12}-C_{13}$ atoms. However, this somewhat agrees with the molecular structure shown in figure 7.16, although there are other serious anomalies. As an example, the C-C single bond between C_9 and the neighboring methyl carbon are still in tact according to the ELF (both isosurface and contour versions). A few other single bonds are still in tact as well according to the ELF, although the atoms concerned are so far apart that no bond show be present at this stage.

The correct interpretation (were the calculation correct) would be that the broken bonds in figure 7.16 simply show that the atoms involved are drifting away from each other with some bonds surprisingly still in tact according to figure 7.17.

7.4.1.4 At time $t = 5.26568 \text{ fs}$

The hydrogen atoms at this time are still flying away from the center of the Coulomb explosion at such a high speed that two of them bump into each other's way as shown in figure 7.18. All the other heavy carbon atoms are still drifting away from each other at a slower speed, and at this moment, only two of them (from the aryl ring) are still close enough to one another to be assumed as bonded. Interestingly, the bond between them in the ground state was a double bond.

The ELF diagrams, figure 7.19 show the presence of some weak bonds where the carbon atoms have separated to distances infeasible for meaningful covalent bonding. Maybe the electrons still tunnel between the ions in an interesting fashion. It also interesting that that the oxygen atom, together with some carbon atoms, remains fairly concentrated with valence electrons even after 5.26568 fs . This counter-intuitively suggests that the oxygen atom is not as easy to ionize as one would initially guess. This may also be because the oxygen atom only felt the weaker edge of the laser potential.

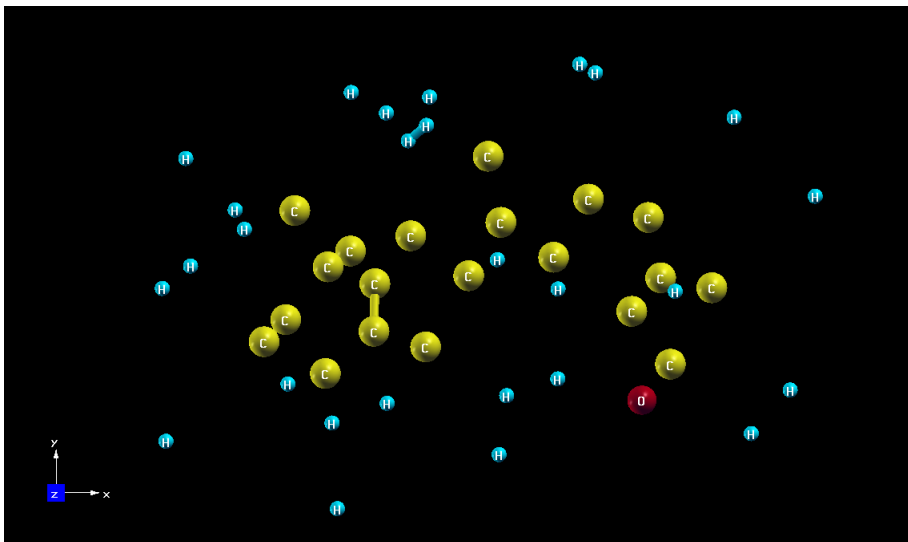
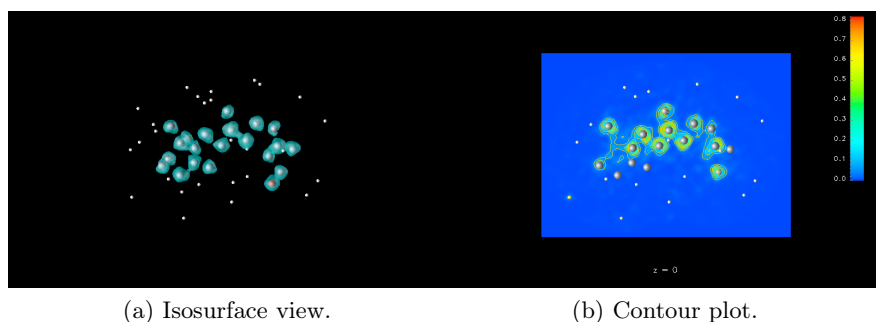


Figure 7.18: Molecular structure at time $t = 5.26568 \text{ fs}$ for $I = 10^{16} \text{ W/cm}^2$.



(a) Isosurface view.

(b) Contour plot.

Figure 7.19: ELF at $t = 5.26568 \text{ fs}$ for $I = 10^{16} \text{ W/cm}^2$.

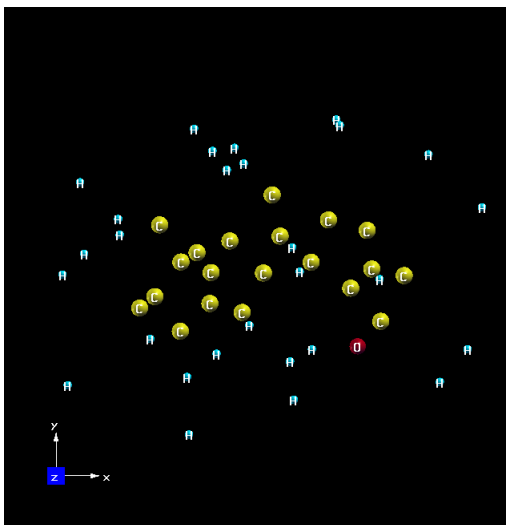
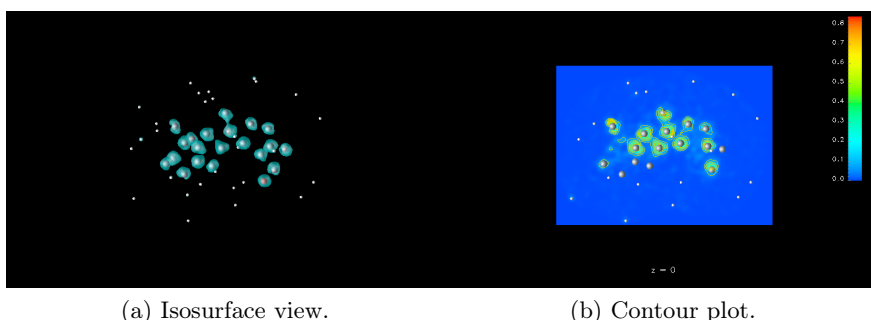


Figure 7.20: Molecular structure at time $t = 6.58210 \text{ fs}$ for $I = 10^{16} \text{ W/cm}^2$.



(a) Isosurface view.

(b) Contour plot.

Figure 7.21: ELF at $t = 6.58210 \text{ fs}$ for $I = 10^{16} \text{ W/cm}^2$.

7.4.1.5 At time $t = 6.58210 \text{ fs}$

The final structure of the totally annihilated 11 – *cis* retinal molecule is shown in figure 7.20 after the total 5000 iterations ($t = 6.58210 \text{ fs}$). At this moment, everything looks chaotic, with the light protons (hydrogen ions) flying away at interesting rates and the heavier carbon (and possibly oxygen) atoms slowly following suit. The protons that appear to be mingled with the carbon atoms are actually scattering perpendicular to the $x - y$ plane of the molecule shown here – they are not inside, but very far away from the molecule.

The ELF, figure 7.21 still suggests that a weird mixture of double and single C-C bonds still survive this intense ionization even up to this moment. Amongst some of the most notable victims, the C-O double bond definitely did not survive the single laser pulse shot in the z -direction.

Table 7.4: Distances between atoms for the molecule in the laser of intensity $I = 10^{16} \text{ W/cm}^2$.

Species	Lengths/Distances (Å)					
time (fs)	0.00000	1.31642	2.63284	3.94926	5.26568	6.58210
$C_{10} - C_{13}$	3.166	3.158	3.135	3.104	3.072	3.067
$C_{10} - C_{12}$	2.503	2.508	2.563	2.691	2.910	3.225
$C_{11} - C_{13}$	2.536	2.544	2.607	2.748	2.967	3.254
$C_3 - C_{15}$	10.541	10.576	10.753	11.078	11.525	12.065

Table 7.5: Angles between atoms for the molecule in the laser of intensity $I = 10^{16} \text{ W/cm}^2$.

Species	Angles ($^\circ$)					
time (fs)	0.00000	1.31642	2.63284	3.94926	5.26568	6.58210
$C_{10} - C_{13}$	2.952	2.734	1.926	0.757	0.538	1.694
$C_{10} - C_{12}$	128.17	127.36	122.62	114.50	105.34	97.49
$C_{11} - C_{13}$	130.12	129.74	127.56	123.34	117.73	111.72
$C_3 - C_{15}$	—	—	—	—	—	—

7.4.2 Other comments

It is interesting that the molecule simply exploded in the face of the single laser pulse of intensity $I = 10^{16} \text{ W/cm}^2$. It never got the chance to stretch (isomerize) as in the presence of normal sunlight only. The explosion was so heavy that in the time period in which almost nothing seems to happen for the case normal sunlight ($t = 6.58210 \text{ fs}$), the molecule has almost completely disintegrated in the case of this very strong laser pulse. As noticed, some C-C bonds still survive up this time though.

Table 7.22 shows the evolution of the atomic distances with time of the molecule when placed in the strong laser ($I = 10^{16} \text{ W/cm}^2$).

Figure 7.22 shows the evolution of the inter-atomic distances of interest with time for the laser pulse incident in the x-direction as well as the opposite direction. The other two direction not shown here yield results somewhat similar to those of the x -direction, with minor differences. In these graphs, the $C_{10} - C_{13}$ distance is shown in red, $C_{10} - C_{12}$ in green and the $C_{11} - C_{13}$ variation in blue. While the 10th and the 13th carbon atoms (ions) come close together, the other couples drift from each other at nearly similar rates.

As is clearly shown in figure 7.23, shooting the same laser pulse in different directions towards the molecule does not yield the same results. In this case, the rate of expansion

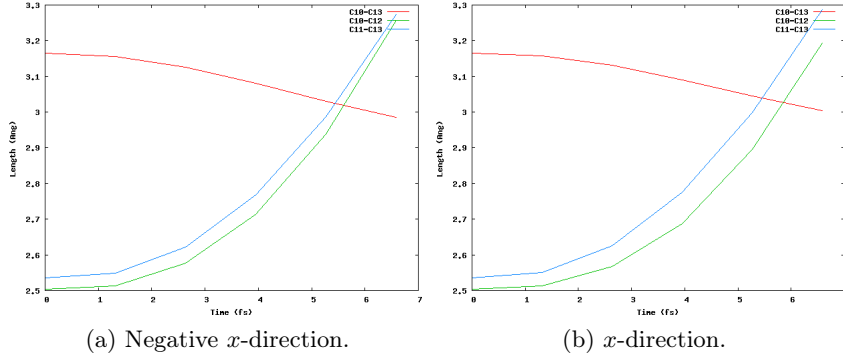


Figure 7.22: Variation of some inter-atomic distances with time for $I = 10^{16} \text{ W/cm}^2$.

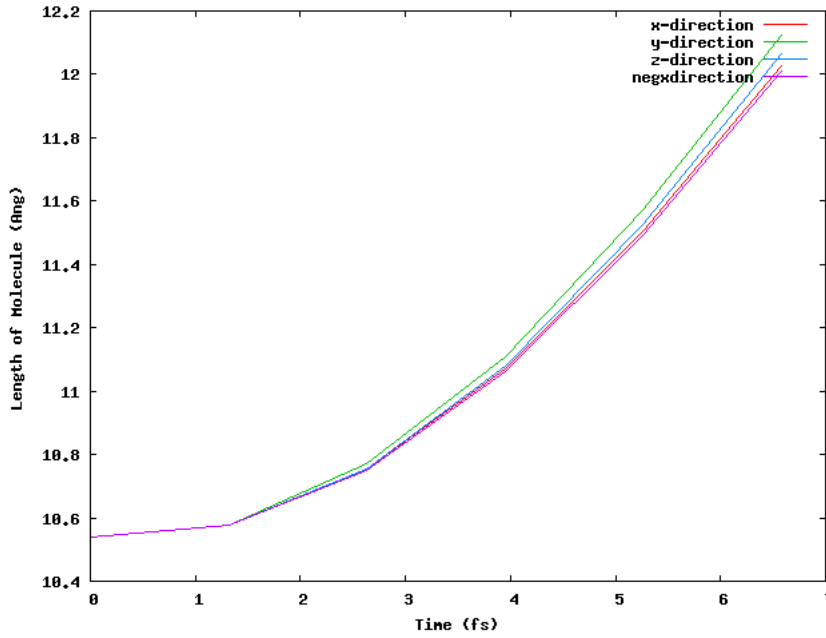


Figure 7.23: Change of the overall length of the molecule with time.

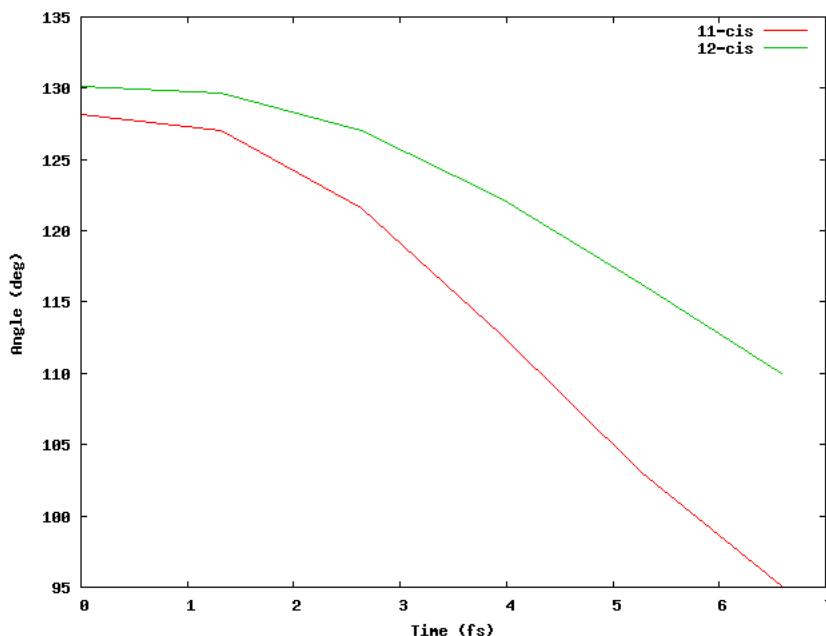


Figure 7.24: Rate of change of the 11 – *cis* bond angle against the 12-*cis* bond for the pulse incident in the *y*-direction.

of the molecule⁵ for the four different directions in which the simulation was done is clearly shown to be different for each case. Even simply reversing the direction in which the laser pulse is shot has notable effects in long run. In this case, the molecule explodes much faster if the pulse is incident in the *y*-direction (green), followed by the *z*-direction (blue) and lastly the *x* and negative *x*-direction in that order.

From figure 7.24, it appears the 11 – *cis* ($C_{10} - C_{11} - C_{12}$) bond is by far more sensitive to the laser pulse than the 12-*cis* ($C_{11} - C_{12} - C_{13}$) bond.⁶ The 11 – *cis* bond angle is much decreasing faster than that of the 12-*cis* bond. The decrease in magnitude of either bond angle is surprising because in normal cis-trans isomerization, the bond angles generally increase over time, especially the 11 – *cis* one. This only shows how pregnant the Coulomb explosion is with surprises and information. Surprising enough, it does not appear to be random at all.

The dihedral angle ($C_{10} - C_{11} - C_{12} - C_{13}$) appears to first decrease before increasing, as shown in figure 7.25. Interestingly, irregardless of the direction of incidence of the laser pulse, the change in the dihedral angle shows a notable turn around 5.2 – 5.3 *fs*. Such an observation, together with many others, may be important in molecular switching

⁵In this case, the length of the molecule is conveniently measured between the 3rd and 15th carbon atoms in backbone structure of the molecule.

⁶Although the *y*-incidence is shown here, the other directions yield very similar trends.

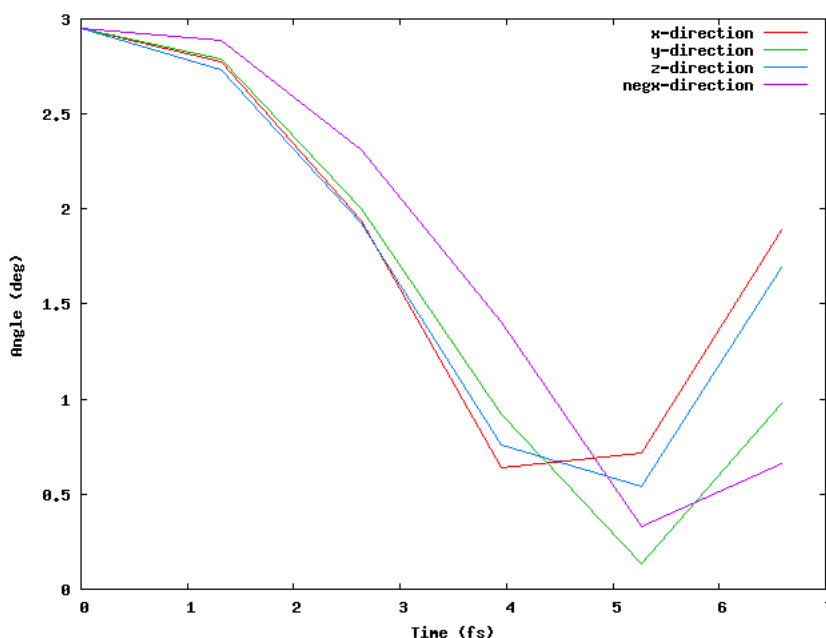


Figure 7.25: Dihedral angle.

(electronics).⁷ Once again, the sharpest turn comes about if the laser pulse is incident in the y -direction.

The evolution of the 11-*cis* bond angle ($C_{10}-C_{11}-C_{12}$) and the 12-*cis* bond angle ($C_{11}-C_{12}-C_{13}$) for all the four different directions of the incidence of the laser pulse are shown independently in figures 7.26 and 7.27 respectively. The 11-*cis* angle decreases more orderly than the 12-*cis* angle. Notably, the laser pulse incident in the z -direction causes the slowest decrease, while the y and positive x -directions cause the fastest decreases. The 12-*cis* angle bears signs of chaotic behavior as spelt out by the entanglement that is clearly visible. This is not altogether to surprising though since the molecule is exploding.

Of all the observations made in this case ($I = 10^{16} \text{ W/cm}^2$), perhaps the most striking one is that the molecule does not get the chance to isomerize before exploding. There is no doubt that such a laser intensity will definitely cause blindness in a human being.

7.4.3 $I = 10^{13} \text{ W/cm}^2$

With the laser pulse of intensity $I = 10^{13} \text{ W/cm}^2$ shot in the z -direction, the molecular structure at time $t = 1.31642 \text{ fs}$ and the final structure at time $t = 6.58210 \text{ fs}$ are shown

⁷One such switch was recently (August 2009) reported on <http://nanobugle.wordpress.com/page/5>.

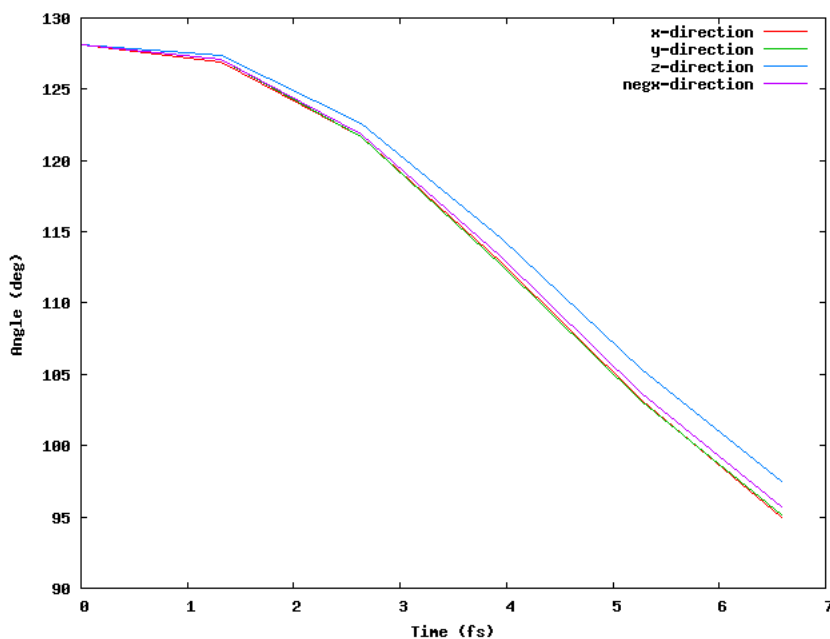


Figure 7.26: Evolution of the 11 – *cis* bond angle for the various directions of incidence of the laser pulse.

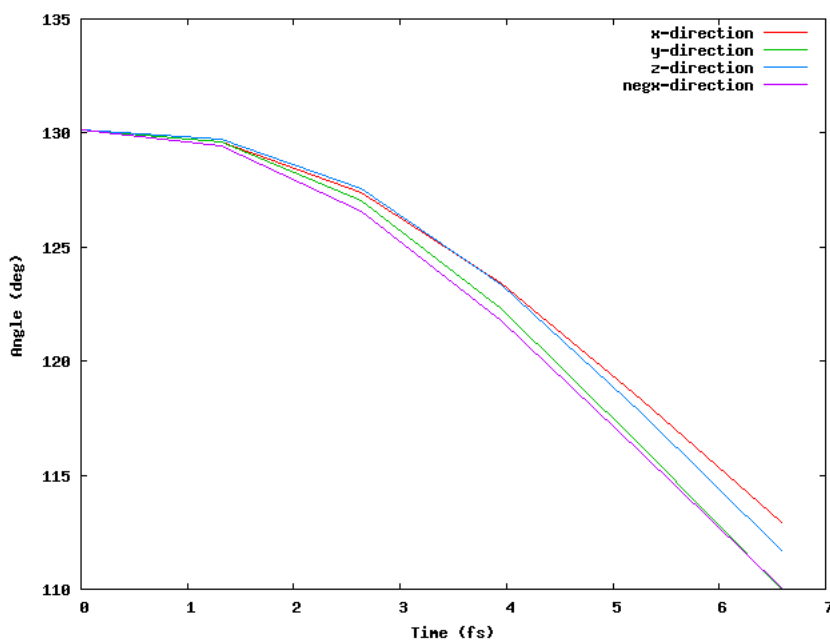
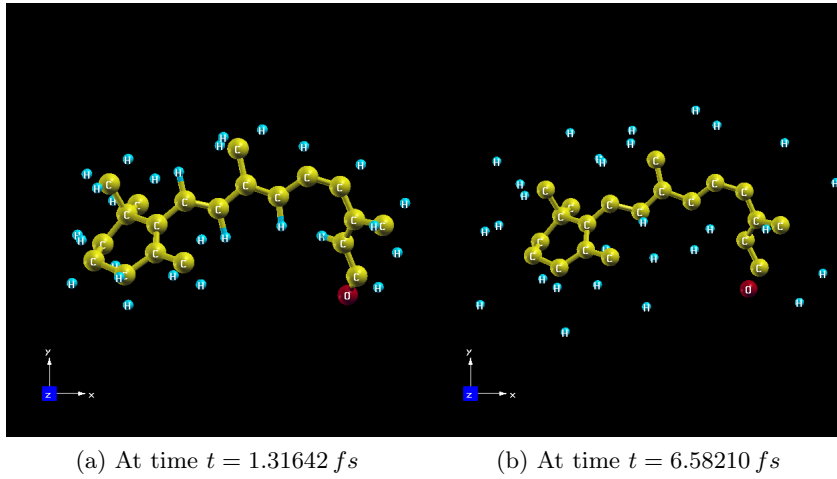
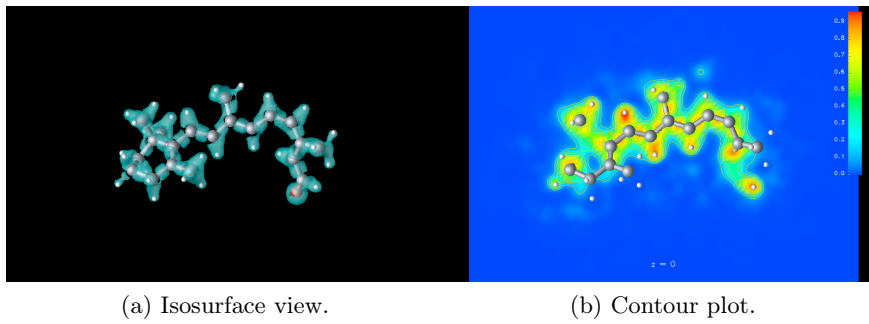
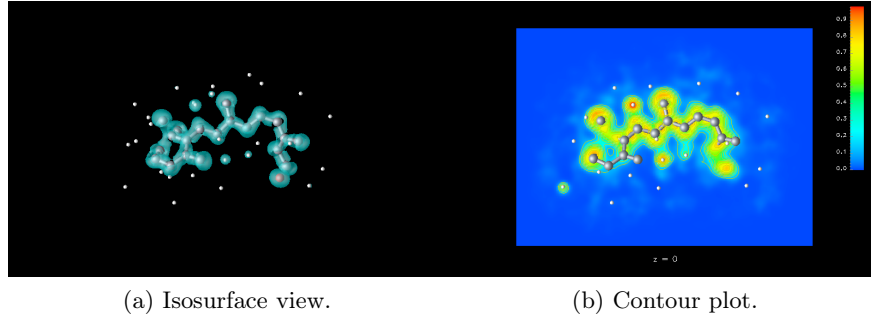


Figure 7.27: Evolution of the 12-cis bond angle for the various incidence directions of the laser pulse.

Figure 7.28: Molecular structure for $I = 10^{13} \text{ W/cm}^2$ Figure 7.29: ELF at time $t = 1.31642 \text{ fs}$ for laser intensity $I = 10^{13} \text{ W/cm}^2$.

in figure 7.28. It is interesting to note that the carbon atoms making up the backbone structure do not drift from each other notably for the whole duration of the observation time, even though the oxygen atom does. Probably because the LDA approximation overestimates ionization, the hydrogen atoms easily get ionized and move away from the rest of the molecule (though more slowly than for $I = 10^{16} \text{ W/cm}^2$).

In figures 7.29 and 7.30, the ELF shows that the molecule is not too heavily ionized since there are still many electrons around the carbon and oxygen ions. Some of the hydrogen atoms still retain their charge (electrons) even at the end of the simulation time, although their bonds with their carbon parents have been broken. It appears the C-O double bond still lives, though extended. Of course, there are traces of anti-bonding appearing throughout the whole molecule. All these interesting phenomena are only visible in the ELF pictures. The density does not seem to have changed much from its ground state configuration.

Figure 7.30: ELF at time $t = 6.58210 \text{ fs}$ for $I = 10^{13} \text{ W/cm}^2$.Table 7.6: Distances between atoms for the molecule in the laser of intensity $I = 10^{13} \text{ W/cm}^2$.

Species	Lengths/Distances ($\text{\AA}$)					
time (fs)	0.00000	1.31642	2.63284	3.94926	5.26568	6.58210
$C_{10} - C_{13}$	3.166	3.166	3.167	3.165	3.159	3.152
$C_{10} - C_{12}$	2.503	2.497	2.489	2.487	2.491	2.503
$C_{11} - C_{13}$	2.536	2.534	2.536	2.544	2.558	2.578
$C_3 - C_{15}$	10.541	10.536	10.536	10.548	10.571	10.606

Table 7.7: Angles between atoms for the molecule in the laser of intensity $I = 10^{13} \text{ W/cm}^2$.

Species	Angles ($^\circ$)					
time (fs)	0.00000	1.31642	2.63284	3.94926	5.26568	6.58210
$C_{10} - C_{13}$	2.952	2.760	2.141	1.155	0.231	0.661
$C_{10} - C_{12}$	128.17	128.40	128.58	128.21	127.23	125.80
$C_{11} - C_{13}$	130.12	130.31	130.53	130.84	130.39	129.91
$C_3 - C_{15}$	—	—	—	—	—	—

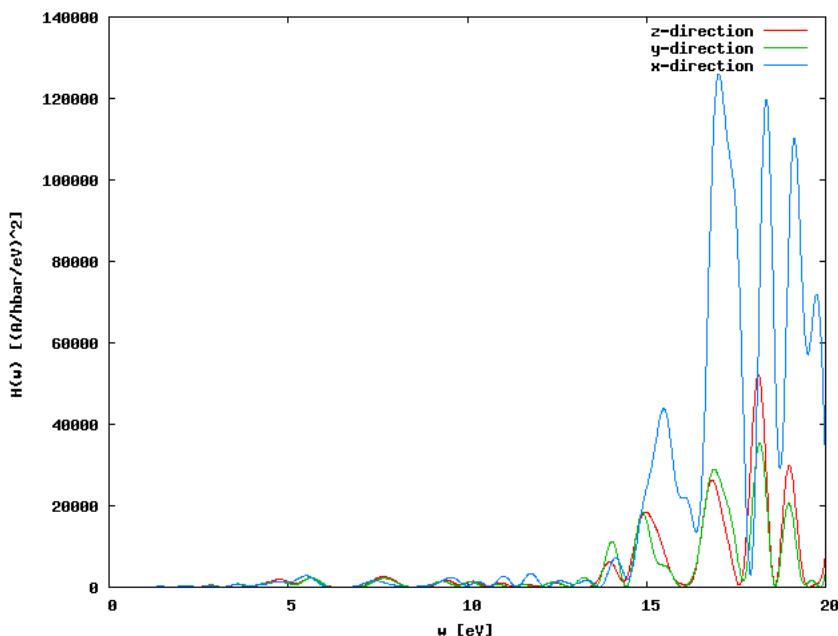


Figure 7.31: The Harmonic spectra for an incident laser of intensity $I = 1.319795 \times 10^{13} \text{ W/cm}^2$ shot in the x , y and z directions.

Tables 7.6 and 7.7 show the evolution of the inter-atomic distances and the bond angles respectively. Because no drastic change seems to occur in this case, we will only present here the results for the laser pulse shot in the z -direction though results from the other directions are also available.

It appears it is a general rule that these distances decrease before increasing steadily. The dihedral angle mapped by $C_{10} - C_{11} - C_{12} - C_{13}$ is decreasing, suggesting that the molecule is probably flattening. The $11 - cis$ bond angle ($C_{10} - C_{11} - C_{12}$) leaps first, then decreases steadily – an observation that is a bit surprising, though in agreement with the normal light case.

Figure 7.31 is a plot of the harmonic spectra of the molecule with the laser of intensity $1.319795 \times 10^{13} \text{ W/cm}^2$ incident in three different directions. In all three cases, high energy photons are produced, but this technique of producing higher energy photons using the $11 - cis$ retinal molecule seems to be most effective (at this intensity) if the laser pulse is shot in the x -direction. Again, since this is an LDA approximation, care should be taken in considering these results. One then wonders what happens if the exact exchange (EXX) functional is used in the calculation, instead of the the LDA approximation.

Chapter 8

Conclusion and Outlook

All the goals of this study were met, though some of the observations made, particularly in the laser-molecule interaction, must be treated with great care since the LDA approximation was used in this case. Of course, the more computationally expensive exact exchange (EXX) even in its KLI approximation would have yielded much better results, had the computational resources permitted.

The molecular geometry was well optimized using the LDA approximation, reproducing some of the key-note observations from experiment. The ground state calculation was quite accurate, though it did not really converge since we were trying to converge the absolute density, which is much harder to converge than the total energy. Such a trade off was important since the time-dependent would evolve the density and not exactly the total energy which is not conserved in time-dependent calculations.

Taking the good ground state results as a starting point, tremendous time dependent calculations were made. In the linear response and perturbation theory, the optical response spectrum of the molecule was calculated with great accuracy – judging from the previous work experimental published on the same molecule. As if that was not enough, the full calculations of the spectrum both by solving Casida’s equations and explicit evolution of the Schrodinger-like equations also predicted that the molecule is also sensitive to the green-blue light in the electromagnetic spectrum. This result was not observed in [96]. Maybe modern experiments can pick this up today.

The ambitious laser simulation whose results should be taken with caution, beautifully reproduced the theoretically expected harmonic spectrum for laser intensities of about 10^{13} W/cm^2 and the mind-blowing Coulomb explosion in which some properties of the molecule surprisingly change in an orderly manner – too orderly for an explosion. Most of the work in the very strong intensity of $I = 10^{16} \text{ W/cm}^2$ concentrated around the

11 – *cis* and 12 – *cis* bond area. The information gathered there, though not altogether very accurate, is quite interesting. Most notably, the molecule does not by any means get the chance to isomerize to its famous trans excited state before it explodes.

Needless to mention is the most beautiful result of the molecular dynamics in normal light. Though a somewhat similar calculation was done in 1996 [7, 41], the intermediate behavior of the molecule (between its *cis* and *trans* configurations) appears to be very interesting. As an example, while many scientists concentrate on the 11 – *cis* and less popularly on the 12 – *cis* bonds, other interesting dynamics of the molecule seems to happen elsewhere in the molecule. Unfortunately, because the *cis-trans* isomerization takes much time and computational memory, only the first few (65.821 *fs* out of some pico-seconds) were successfully simulated in this particular work.

The work that remains to be done includes an accurate recalculation of the laser-molecule interaction using the exact exchange (EXX) at least in its KLI approximation, and a complete molecular dynamics of the molecule, among other things. There is reason to think that the laser-molecule interaction holds the key great technological developments such as biological molecule switches which may be used in electronics and telecommunications.

Since it is very hard to say what is totally impossible in science, it makes logical sense to expect that further studies of the molecule's behavior may help humanity solve blindness in an amicable way some day. Currently, teams of physicists, engineers and medical personnel have made notable developments in this direction by inventing cameras that help blind persons distinguish between bright and dark surfaces [119]. A solution that re-constructs the eye or uses more natural ways may someday be in sight.

It is amazing what Quantum Mechanics, and physics in general, can do!!!

Appendix A

From Many Particle Hamiltonian to Self-Consistent Field Approach¹

Density Functional Theory (DFT) is a reformulation of the Schrodinger Quantum Mechanics in terms of the single particle density $n(r)$ instead of the many body wavefunction Ψ_i . Its development in the Kohn-Sham taste, however, hinges on the the self-consistent methods that had been developed way before its ushering in. It is the purpose of this appendix to shed some light on the inadequately discussed area between the Schrodinger equation and the Kohn-Sham equations. This means that we will discuss here, the **Hartree** and **Hartree-Fock** approximations to many body Quantum Mechanics along with other approximations that made DFT possible.

A.0.4 Many Particle Hamiltonians

We start by recalling that all condensed matter systems behaving non-relativistically are precisely described by the Schrodinger equation:

$$i\hbar \frac{\partial}{\partial t} \Psi = \mathcal{H} \Psi \tag{A.1}$$

where Ψ is the many body wavefunction.

One mole of the condensed matter typically contains at least 10^{24} atoms and a much bigger number of electrons. That is a very huge number of particles at play. It is currently impossible to solve the corresponding Schrodinger equation in its original state for big systems. To proceed, we resort to approximations which in turn give approximate descriptions of nature.

¹Based on the comprehensible discussion of the topic in [37].

The first assumption to make is to think of the many electrons in a piece of condensed matter (adequately described the Schrodinger equation) as free particles with each moving in a static potential $v(r_i)$, i.e. they do not interact. In this case, the Hamiltonian $\mathcal{H}$ becomes the sum of the Hamiltonians for each electron,

$$\mathcal{H} = \sum_i \mathcal{H}_i = \sum_i \left[-\frac{\hbar^2}{2m} \nabla_i^2 + v(\mathbf{r}_i) \right], \quad (\text{A.2})$$

where $-\frac{\hbar^2}{2m} \nabla_i^2$ is the kinetic energy of the i^{th} electron in the material. The independent particle eigenstate ψ_n for each $\mathcal{H}_i$ satisfies

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + v(r) \right] \psi_n = \varepsilon_n \psi_n. \quad (\text{A.3})$$

These wavefunctions can be combined to form a total wavefunction for the system according to the well-known fermion rules.

Now we can turn on the previously ignored interaction and observe what happens. Well, the motion of any of the particles is now correlated with all the other particles present in system such that the Hamiltonian that now describes the whole system is

$$\mathcal{H} = \sum_i \frac{p_i^2}{2m} + \sum_\alpha \frac{P_\alpha^2}{2M_\alpha} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{\alpha \neq \beta} \frac{Z_\alpha Z_\beta e^2}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|} - \sum_{i\alpha} \frac{Z_\alpha e^2}{|\mathbf{r}_i - \mathbf{R}_\alpha|} \quad (\text{A.4})$$

where $\mathbf{r}_i$, p_i , m and $-e$ label the electron coordinates, momenta, mass and charge, respectively. $\mathbf{R}_\alpha$, P_α , M_α and $Z_\alpha e$ are the corresponding quantities for the nuclei. To move between the coordinate and momentum space in a full Quantum Mechanical approach, we can use the following hand-waving replacements:

$$\begin{aligned} p_i &\rightarrow -i\hbar \nabla_i \\ P_\alpha &\rightarrow -i\hbar \nabla_\alpha. \end{aligned} \quad (\text{A.5})$$

Here, we are deliberately omitting the spin labels for brevity and clarity. However, when studying magnetic properties, we will need to include the spin labels.

A.0.5 Valence Electrons and the Adiabatic Approximations

In this subsection we discuss two further approximations, namely:

- i) the valency electron approximation and
- ii) the adiabatic (Born-Oppenheimer) approximation.

A.0.5.1 The valency electron approximation

To reduce the number of electrons that we have to treat in the interacting system, we assume that it is only the valency electrons that take part in bonding while all the core electrons do not – they are tightly bound to the nucleus creating an ion around which the valency electrons move. We therefore treat the core electrons as part of the nucleus. Their sole purpose is to shield the valency electrons partly from the positive potential of the nucleus. This assumption makes sense for most of the cases that we describe in nature because the core electrons are highly localized while the valency electrons are delocalized. For this reason, the electrical and optical properties of materials are determined by these valency electrons.

The valency electron assumption is not always valid though. In transition metals and rare earth elements for instance, there appears to be a mixed valency-core electron phenomenon.

If we further assume that there is (on average) only one valency electron per ion in an identical particle system, then the Hamiltonian reduces to

$$\begin{aligned} \mathcal{H} = & -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 - \frac{\hbar^2}{2M} \sum_\alpha \nabla_\alpha^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \\ & + \sum_{i\alpha} v(\mathbf{r}_i, \mathbf{R}_\alpha) + \frac{1}{2} \sum_{\alpha \neq \beta} v(\mathbf{R}_\alpha, \mathbf{R}_\beta) \end{aligned} \quad (\text{A.6})$$

where $v(\mathbf{r}_i, \mathbf{R}_\alpha)$ is the shielded Coulomb potential and $v(\mathbf{R}_\alpha, \mathbf{R}_\beta)$ is the short range potential between ions.

A.0.5.2 The adiabatic approximation

Recall from thermodynamics that a process that changes adiabatically is one in which the system remains in equilibrium instantaneously as some external thermodynamic variable changes. The quantum mechanical theory for such a process was developed by Born and Oppenheimer and is therefore called the Born-Oppenheimer approximation.

For the electron system in a solid, the total electronic configuration depends on the relative ions of vibrating ions in such a way that the electrons move so rapidly that they

adjust adiabatically to the much slower motion of the ions. On the hand, the ions view the electrons as a homogeneously smeared background. As a result, we can decouple the electronic and ionic degrees of freedom and study the two resulting ionic and electronic subsystems individually. The total wavefunction of the coupled system is therefore the product of the ionic and the electronic wavefunctions (in the adiabatic approximation). This wavefunction is actually an approximate solution to the total Hamiltonian with an error that depends on the ratio of the masses of the electron and the ion $-\left(\frac{m}{M}\right)^{\frac{1}{4}}$, which is very small.

The Hamiltonian for the interacting ion subsystem is then given by

$$\mathcal{H} = -\frac{\hbar^2}{2M} \sum_{\alpha} \nabla_{\alpha}^2 + \frac{1}{2} \sum_{\alpha \neq \beta} v(\mathbf{R}_{\alpha}, \mathbf{R}_{\beta}) + \sum_{\alpha} v_e(\mathbf{R}_{\alpha}) \quad (\text{A.7})$$

where $v_e(\mathbf{R}_{\alpha})$ is the background due to the electrons, which may be viewed as being homogeneous.

For the interacting electron system, the decoupled Hamiltonian is

$$\mathcal{H} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i v(\mathbf{r}_i) \quad (\text{A.8})$$

where $v(\mathbf{r}_i)$ is the potential provided by all ions to the i^{th} electron. For a periodic or homogeneous structure, we can assume that $v(\mathbf{r}_i)$ has the same form for all electrons inside the system.

Since we have decoupled the electron system from the ionic one, the ionic potential can be treated as an external potential for the electrons.

There are cases in which this decoupling breaks down, for instance, the Jahn-Teller effect. Another example is described in main body of this dissertation.

In general, the wavefunction of a many body system is a one-electron function of the coordinates of all the electrons, $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$, which is a well defined problem for the Schrodinger equation:

$$\left[-\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_i v(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N). \quad (\text{A.9})$$

Of course, equation (A.9) is easier to solve than the original equation with the Hamiltonian given in equation (A.4), but it is still in insurmountable problem unless we make more approximations. At this stage, it probably important to note that the complexity of the problem arises from the Coulomb interaction.

A.0.6 The Hartree Approximation

We can make one more approximation at this stage that will reduce the many electron equation (A9) to a single particle one (A3) in which the electrons move in an external potential $v_{eff}(r)$.

Let us start by neglecting the antisymmetric requirement of the many body wavefunction so that we write it (for N electrons) as the product of one electron wavefunctions as follows:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \prod_{i=1}^N \psi_i(\mathbf{r}_i). \quad (\text{A.10})$$

This is the equation for which Hartree suggested the variational calculation to minimize the energy:

$$E = \frac{\langle \Psi | \mathcal{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (\text{A.11})$$

If the Ψ were the exact ground state of the system, then E would be the exact ground state energy of the system. It is known from the variational principle that E is stationary with respect to variations of Ψ , and that it is an upper bound to the ground state energy.

Now, if we use equation (A10) we get a set of Hartree equations:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + v(\mathbf{r}) + \sum_j' e^2 \int \frac{\psi_j^*(\mathbf{r}') \psi_j(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \quad (\text{A.12})$$

where the prime rules out the case in which $j = i$, and ε_i are the variational parameters which look like the one-electron eigenvalues. It follows from equation (A12) that the effective potential can be defined to be

$$v_{eff} = v(\mathbf{r}) + \sum_j' e^2 \int \frac{\psi_j^*(\mathbf{r}') \psi_j(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}. \quad (\text{A.13})$$

This implies that equations (A.12) and (A.2) are equivalent, with the potential felt by each electron in equation (A.12) determined by the average distribution $\sum_j \psi_j^*(\mathbf{r}') \psi_j(\mathbf{r}')$ of all the other electrons.

An important comment is that the ε_i are not truly the one-electron energies as clearly depicted in the equation below:

$$E = \frac{\langle \Psi | \mathcal{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \sum_i \varepsilon_i - \frac{1}{2} \sum_{i \neq j} e^2 \iint \frac{\psi_j^*(\mathbf{r}') \psi_j(\mathbf{r}') \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}. \quad (\text{A.14})$$

Equations (A.12), the Hartree equations can be solved self-consistently by iteration. Note that there is a sum of terms in (A.12), each of which depends on the coordinates of a single electron. The states ψ_i must be known in order to compute the interaction potential, while the interaction potential itself must be known in order to calculate the states. For this reason, a self-consistent calculation must be made. We can start by assuming a particular set of approximate eigenvalues that we use to calculate the effective potential and then use the calculated effective potential to determine a new set of eigenvalues. This process is repeated until a desired accuracy is achieved in successive eigenstates. This leads to a set of eigenstates that are consistent with the potential.

A.0.7 The Hartree-Fock Approximation

While the antisymmetry of the wavefunctions was ignored in the Hartree approximation, in the Hartree-Fock approximation it is included. It is reasonable to take a linear combination of product wavefunctions to satisfy this antisymmetric condition and then express it as a Slater determinant:

$$\Psi(\{\mathbf{r}_i\}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \dots & \psi_1(\mathbf{r}_N) \\ \dots & \dots & \dots \\ \psi_N(\mathbf{r}_1) & \dots & \psi_N(\mathbf{r}_N) \end{vmatrix}. \quad (\text{A.15})$$

This the Hartree-Fock approximation for a variational calculation leads to a set of Hartree-Fock equations:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + v(\mathbf{r}) + \sum_j' e^2 \int \frac{\psi_j^*(\mathbf{r}') \psi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right] \psi_i(\mathbf{r}) - \sum_j' \left[e^2 \int \frac{\psi_j^*(\mathbf{r}') \psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right] \psi_j(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}). \quad (\text{A.16})$$

From equation (A.16), the corresponding effective potential can easily be written down. The solution of these Hartree-Fock equations is also by the self-consistent algorithm.

The total energy will contain an additional term, that is different from the Hartree one, to $\sum_i \varepsilon_i$:

$$\frac{e^2}{2} \sum_{i \neq j} \iint \frac{\psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) \psi_j^*(\mathbf{r}') \psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (\text{A.17})$$

This extra term is known as the exchange energy, distinguished from the direct interaction in (A.14). The exchange interaction arises from every pair of parallel electrons.

When solving the Hartree-Fock equations for non-magnetic systems we can neglect spin, i.e. we assume that:

- i) every orbital is doubly occupied, and
- ii) the wavefunctions of the Slater determinants are spin singlets.

This is called the restricted Hartree-Fock method, otherwise it is the unrestricted Hartree-Fock method.

Appendix B

Pseudopotentials¹

We can categorize the electrons in an atom in its ground state as follows (<http://th.physik.uni-frankfurt.de/~engel/ncpp.html>):

- i) core electrons, and
- ii) valence electrons.

For most of the periodic table elements, the core electrons are tightly bound to the nucleus and hardly take part in chemical reactions, neither do they contribute to the electronic structure properties of a given substance. In other words, the wavefunctions of the core electrons are highly localized in space. As such, it is the (delocalized) valence electrons that are responsible for the chemical and physical phenomena that we see [83]. Examples of such phenomena include chemical reactivities, electrical conductivity, colour and magnetism, among others.

This is the fundamental observation fueling the concept of pseudopotentials (<http://th.physik.uni-frankfurt.de/~engel/ncpp.html>). If the core electrons are largely dormant, then we can reduce the degrees of freedom of the materials we describe quantum mechanically by considering only the behavior of the valence electrons and treating the core electrons as part of some effective ion potential that only affects the valence electrons in a predetermined way. This is a very worthwhile step also because inside the ions, within the spatial region of the core electrons, the all-electron effects are very complicated, yet we are only interested in what happens outside this region in the description of the aforementioned phenomena.

Exceptions in this description are the transition metals and the rare-earth elements, in which the inner d and f electrons interfere with the valency electrons. Another exception is the case in which charge centers are present such that the core electrons are

¹Mainly based on chapter 11 of Richard Martin's book [83].

no longer sufficiently attracted by their own nuclei, loosening the essential condition that the core electrons are strongly attracted by their own nuclei (<http://th.physik.uni-frankfurt.de/~engel/ncpp.html>). In such cases, the pseudopotential description gives problems because if the spatial or energetic separation between the core and valence shells breaks down in a material/atom the pseudopotential description breaks down as well. In such cases, it becomes imperative to consider the complete shell (rather than just the valency orbitals) to which the d and f electrons belong as valence space. In this description, the more strongly bound, but relevant states are called semi-core states. (<http://th.physik.uni-frankfurt.de/~engel/ncpp.html>)

In the pseudopotential description, the molecular and crystalline pseudopotential is simply a superposition of the atomic pseudopotentials [83].

B.0.8 Origins of pseudopotentials

The concept of pseudopotentials is not alien in physics. In scattering theory for example, the effective potential from which particles scatter is a pseudopotential. Here, pseudopotential theory is used to find useful pseudopotentials that faithfully represent the scattering phenomena over a desired energy range [83, 40, 38]. The modern day mathematical formulation of pseudopotentials in electronic structure theory has its roots firmly grounded in the Orthogonalized Plane Waves (OPW) method of calculating electronic structure properties [83, 58, 59].

In the OPW method, the valence electrons have states

$$\chi_q^{OPW}(\mathbf{r}) = \frac{1}{\Omega} \left\{ e^{i\mathbf{q}\cdot\mathbf{r}} - \sum_i \langle u_i | \mathbf{q} \rangle u_i(\mathbf{r}) \right\} \quad (\text{B.1})$$

where

$$\langle u_i | \mathbf{q} \rangle \equiv - \int d\mathbf{r} u_i(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} \quad (\text{B.2})$$

and $\mathbf{q}$ is momentum [58, 83]. The electron states $\chi_q^{OPW}(\mathbf{r})$ are orthogonal to the functions $u_i(\mathbf{r})$ (which are left unspecified for the time being, but are required to be localized around each nucleus).

An intelligent choice of $u_i(\mathbf{r})$ divides the valence states into a smooth part plus a localized part.

In crystalline materials, the smooth part can be represented conveniently by plane waves as follows:

$$\frac{1}{2}\nabla^2 u_i + (E_i - V_i) u_i \quad (\text{B.3})$$

where i labels the i^{th} atom with $V_i = V_i(\mathbf{r})$ and u_i chosen to be optimal for the problem.

This is the statement that deems the OPW method the prescience of modern pseudopotential theory and Projector Augmented Wave (PAW) methods [83].

The orthogonalized form of the valence states with angular momentum l, m takes the form

$$\Psi_{lm}^v(\mathbf{r}) = \psi_{lm}^v(\mathbf{r}) + \sum_i B_{lmi} u_{lmi}(\mathbf{r}) \quad (\text{B.4})$$

where

$\Psi_{lm}^v(\mathbf{r}) = \int d\mathbf{q} c_{lm}(\mathbf{q}) \chi_q^{OPW}(\mathbf{r})$ is the valence function,

$\psi_{lm}^v(\mathbf{r}) = \int d\mathbf{q} c_{lm}(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}}$ is the smooth part, and

$B_{lmj} u_{lmi}(\mathbf{r}) = \int d\mathbf{q} c_{lm}(\mathbf{q}) \langle u_i | \mathbf{q} \rangle$ is the localized part.²

A simple choice of the local states u_{lmi} is to equate them to the core orbitals Ψ_{lmi}^c which are also highly localized. This assumes that the potential in equation (B.3) is the actual potential of the atom, taken to be spherically symmetric near the nucleus so that the core states Ψ_{lmi}^c become the lowest eigenstates of the Hamiltonian:

$$H\Psi_{lmi}^c = \varepsilon_{li}^c \Psi_{lmi}^c. \quad (\text{B.5})$$

Since the valence state Ψ_{lm}^v is orthogonal to the core states Ψ_{lmi}^c , the radial part of the valence state $\Psi_l^v(\mathbf{r})$ must have as many nodes as there are core orbitals with that angular momentum. For the s wave, these are zero.

The choice $u_{li} = \Psi_{li}^c$ indeed leads to a smooth function ψ_l^v that has zero radial nodes. It is smoother than $\Psi_l^v(\mathbf{r})$.

These core states can then be assumed to be the same in a molecule or solid as in the atoms that make up that molecule or solid.³

Now, in the OPW method, the set of OPWs is not orthonormal and each wave has a norm that is less than unity:

²Here, we have used Fourier transforms in expressing these terms.

³This is the basis for the actual calculations in the OPW method [57].

$$\langle \chi_{\mathbf{q}}^{OPW} | \chi_{\mathbf{q}}^{OPW} \rangle = 1 - \sum_i |\langle u_i | \mathbf{q} \rangle|^2. \quad (\text{B.6})$$

This implies that the equations of the OPWs have the form of a generalized eigenvalue problem with an overlap matrix [83].

B.0.9 The pseudopotential transformation

Hellmann, who was probably the first person to use pseudopotentials in 1935 [55, 56], developed an effective potential theory to describe scattering of the valence electrons from ion cores in metals. Unfortunately, his potential was too strong to give good results [26].

Phillips and Kleinman [94], and Antoncik [11, 12] (PKA) later (in the 1950s) described a weaker effective potential by showing that the OPW method of Herring [58, 59] could be recast in the form of equations (for the valence electrons) that only involves a weaker potential as briefly outlined below [83].

If $V(\mathbf{r})$ is the effective potential (pseudopotential) which the valence electrons “feel,” then valence electrons obey the following Schrodinger-like equation:

$$H\Psi_i^v(\mathbf{r}) \equiv \left[-\frac{1}{2}\nabla^2 + V(\mathbf{r}) \right] \Psi_i^v(\mathbf{r}) = \varepsilon_i^v \Psi_i^v(\mathbf{r}). \quad (\text{B.7})$$

Inserting equation (B.4) into equation (B.7) yields the following equation for the smooth valence functions:

$$H^{PKA}\psi_i^v(\mathbf{r}) \equiv \left[-\frac{1}{2}\nabla^2 + V^{PKA} \right] \psi_i^v(\mathbf{r}) = \varepsilon_i^v \psi_i^v(\mathbf{r}) \quad (\text{B.8})$$

where

$$V^{PKA} = V + V^R \quad (\text{B.9})$$

is the effective potential due to Phillips and Kleinman, and Antoncik (PKA). Here, V^R is a non-local potential operator that has the following effect on the smooth valence functions:

$$V^R\psi_i^v(\mathbf{r}) = \sum_j (\varepsilon_i^v - \varepsilon_j^c) \langle \Psi_j^c | \psi_i^v(\mathbf{r}) \rangle \Psi_j^c(\mathbf{r}). \quad (\text{B.10})$$

Equation (B.10) suggests that $V^R > 0$, i.e. V^R is always repulsive⁴ since $\varepsilon_i^v - \varepsilon_j^c > 0$

⁴Repulsive potentials can be thought of as positive while attractive potentials are negative.

i.e. always positive. As pointed out by Phillips and Kleinman, and Antoncik, if the nuclear potential is stronger, i.e. more attractive, we get deeper core states so that the potential V^R becomes more repulsive. Adding this repulsive term to the attractive nuclear potential leads to the so called “cancellation theorem” that was derived in a more general form by Cohen and Heine in 1961 [83, 32].

The resulting potential V^{PKA} is therefore much weaker than the original one $V(\mathbf{r})$, though somewhat more complicated by its non-local component V^R [83].

The smooth pseudofunctions $\psi_i^v(\mathbf{r})$ are not orthonormal since the complete function $\Psi_i^v(\mathbf{r})$ contains the sum over core orbitals, equation (B.4).

Likewise, the solution to the pseudopotential problem is a generalized eigenvalue problem.

Further, the presence of core states in equation (B.10) means that we do not have a smooth pseudopotential [83].

In scattering theory, the effective potential (pseudopotential) is not unique, i.e. the same scattering properties can be produced by different potentials. Combining this with the formal properties of V^{PKA} , we see that we can choose pseudopotentials that are both smooth and weak, which we can expand in a small number of Fourier components. This has great conceptual and computational advantages [83].

B.0.10 Model ion potentials

There are two basic ways of building ionic pseudopotentials. One is to consider **all** the valence electrons as moving in an effective pseudopotential generated by the atomic nucleus and the tightly bound core electrons. The other is to consider **each** valence electron to be moving in potential generated by nucleus, the core electrons and all the other valence electrons. While the latter approach has been shown to give an accurate description of electron bands [83, 54, 31], we concentrate here on the former approach that is obviously easier to transfer from a given atom(s) to any material or molecule built up from these atoms [83]. The former approach also gives the same scattering properties as the pseudopotentials of equations (B.9) and (B.10) and more general forms.

Since the model potential replaces the potential of the nucleus and its corresponding core electrons, it must be spherically symmetric. Each angular momentum l, m can also be treated separately, leading to non-local l -dependent model pseudopotentials [83].

Outside the core region, the model pseudopotential is $\frac{Z_{ion}}{r}$. Inside the core region, the potential must be repulsive to a degree that depends on l [83, 32].

We can therefore write the pseudopotential as a non-local operator in this way:

$$V_{SL} = \sum_{lm} |Y_{lm}\rangle V_l(r) \langle Y_{lm}| \quad (\text{B.11})$$

where

$$Y_{lm}(\theta, \phi) = P_l(\cos \theta) e^{im\theta}. \quad (\text{B.12})$$

Semi-local (SL) here means that V_{SL} is local in r but non-local in θ and ϕ .

When operating on an arbitrary function $f(r, \theta', \phi')$, V_{SL} yields

$$[V_{SL}f]_{r,\theta,\phi} = \sum_{lm} Y_{lm}(\theta, \phi) V_l(r) \int d(\cos \theta') d\phi' Y_{lm}(\theta', \phi') f(r, \theta', \phi'). \quad (\text{B.13})$$

All the information is encoded into the radial functions $V_l(r)$ or their Fourier transforms.

An electronic structure calculation involves the calculation of the matrix elements of V_{SL} between Ψ_i and Ψ_j :

$$\langle \Psi_i | V_{SL} | \Psi_j \rangle = \int dr \Psi_i(r, \theta, \phi) [V_{SL} \Psi_j]_{r,\theta,\phi}. \quad (\text{B.14})$$

Now, potentials are usually defined as being either empirical or *ab-initio* [83].

Empirical potentials are fitted to atomic or solid state data. Examples are the “empty core” [13] and “square well” [2, 8, 9] potentials.

On the other hand, *ab-initio* potentials are constructed to fit the valence properties calculated for the atom. They are not fitted to atomic or solid state data. A very good and widely used example are the norm-conserving potentials [83].

B.0.11 Norm-conserving pseudopotentials

Let us start by replacing the PKA pseudofunctions $\Psi_i^v(\mathbf{r})$ (that are generally not orthonormal) in equations (B.8) and (B.10) by a special class of pseudofunctions that obey the following orthonormality condition:⁵

$$\langle \Psi_i^{PS} | \Psi_j^{PS} \rangle = \delta_{ij} \quad (\text{B.15})$$

The valence electrons now move in a norm-conserving pseudopotential which is chosen to reproduce the valence electron properties from some all-electron calculation.

⁵We are ignoring the spin labels for simplicity.

In the Kohn-Sham scheme, the Kohn-Sham equations become (ignoring spin again)

$$(H_{KS}^{PS} - \varepsilon_i) \Psi_i^{PS}(\mathbf{r}) = 0 \quad (\text{B.16})$$

where the external potential is now the norm-conserving potential.

The norm-conserving condition Hamann, Schluter and Chiang (HSC) [34] defined a list of properties that must be exhibited by good pseudopotentials as the following [83]:

- i) all-electron and pseudo valence eigenvalues must agree for the chosen atomic reference configuration.
- ii) all-electron and pseudo valence wavefunctions must agree beyond a chosen core radius R_c .
- iii) the logarithmic derivatives of the all-electron and pseudo wavefunctions must agree on the boundary of the core radius R_c .
- iv) the integrated charge inside R_c for each wavefunction must agree (norm-conservation).
- v) the first energy derivative of the logarithmic derivatives of the all-electron and pseudo wavefunctions must agree at R_c .

The first two points imply that the norm-conserving pseudopotential should equal the atomic potential outside the core region of radius R_c . This is because the potential is uniquely determined (except for a constant that is fixed if the potential is zero at infinity) by the wavefunction and the energy ε that need not be an eigenenergy.

The third point follows since the wavefunction $\Psi_l(r)$ and its radial derivative $\Psi'_l(r)$ are continuous at R_c for any smooth potential.

The dimensionless derivative is defined by

$$D_l(\varepsilon, r) \equiv \frac{r\Psi'_l(\varepsilon, r)}{\Psi_l(\varepsilon, r)} = r \frac{d}{dr} \ln \Psi_l(\varepsilon, r). \quad (\text{B.17})$$

The fourth point ensures:

- a) that the total charge inside the core region is correct, and
- b) that the normalized pseudo-orbital is equal to the true orbital outside of the core region R_c .

Mathematically stated, this (4th) point says that the integrated charge

$$Q_l = \int_0^{R_c} dr r^2 |\Psi_l(r)|^2 = \int_0^{R_c} dr \Phi_l(r)^2 \quad (\text{B.18})$$

This is a good point because the potential outside a spherically symmetric charge distribution only depends on the total charge enclosed in the sphere.

The last (5th) point follows from the forth. This is what HSC and others showed. It ensures transferability of the pseudopotential to other environments.

B.0.12 Construction of norm-conserving pseudopotentials

The generation of pseudopotentials starts off with an all-electron calculation. Given the results of the all-electron calculation, one then endeavors to identify the valence states and generate the pseudopotentials $V_l(r)$ and the pseudo-orbitals $\Psi_l^{PS}(r) = r\Phi_l^{PS}(r)$.

This procedure is done in two major steps:

- i) one finds a total “screened” pseudopotential acting on the valence electrons in the atom, and
- ii) “unscreen” the total pseudopotential by subtracting the sum of the Hartree and exchange-correlation potentials $V_{Hxc}^{PS}(r) = V_{Hartree}^{PS}(r) + V_{xc}^{PS}(r)$ to get

$$V_l(r) \equiv V_{l,total}(r) - V_{Hxc}^{PS}(r) \quad (\text{B.19})$$

where $V_{Hxc}^{PS}(r)$ is defined for the valence electrons in their pseudo-orbitals [83].

Step (i) yields a one-to-one relationship between the valence pseudofunction and total pseudopotential, rendering the pseudopotential nontransferable. To make the pseudopotential transferable, it is necessary to unscreen the total pseudopotential to get the bare-ion pseudopotential. The process of unscreening is not straightforward and it is actually complicated by the form of the exchange-correlation potential which is not a linear functional of the density.

It is a good idea to split the ionic potential into a local and non-local part as follows:

$$V_l(r) = V_{local}(r) + \delta V(r). \quad (\text{B.20})$$

Since the eigenvalues are required to be the same for the pseudo and all-electron case outside the core region ($r > R_c$), each potential $V_l(r)$ equals the local (l -dependent) all-electron potential and $V_l(r) \rightarrow -\frac{Z_{ion}}{r}$ as $r \rightarrow \infty$. Thus $\delta V_l(r) = 0$ for $r > R_c$ and

all the long range effects of the Coulomb potential are included in the local potential $V_{local}(r)$.

The semi-local operator can be written as

$$V_{SL} = V_{local}(r) + \sum_{lm} |Y_{lm}\rangle \delta V_l(r) \langle Y_{lm}|. \quad (\text{B.21})$$

Even if norm-conservation is imposed, the potential remains non-unique and therefore transferable, i.e. there is still no single best pseudopotential for any given element. There may be many best choices depending on the intended use of the pseudopotential.

On a general level, there are two competing factors [83]:

- i) accuracy and transferability which lead to small cut-off core radii R_c , and hard⁶ potentials since one would want an accurate description of the wavefunction in the region near the atom, and
- ii) smoothness of the resulting pseudopotential, which leads to larger cut-off radii R_c and soft potentials since one would desire to describe the wavefunction with the smallest number of basis functions possible (which may be plane waves).

One way of constructing the pseudopotentials is to start from an assumed form of the potential and then vary parameters until the wavefunction has the desired properties. This approach has been used by Bachelet, Hamann and Schlüter (BHS) [42] as well as Vanderbilt [111].

Christiansen et al [85], and Kerker [69] use a simpler procedure. They define a Pseudofunction $\Phi_l^{PS}(r)$ with the desired properties for each angular momentum l and numerically invert the Schrodinger equation to find the potential $V_l(r)$ for which $\Phi_l^{PS}(r)$ is a solution with energy ε . Outside the core radius, the pseudo wavefunction equals the true wavefunction and at the boundary ($r = R_c$) the wavefunction is matched to a parametrized analytic function [83].

For a nodeless function $\Phi_l^{PS}(r)$, the inverted wavefunction for each angular momentum l reads

$$V_{l,total}(r) = \varepsilon - \frac{\hbar^2}{2m_e} \left[\frac{l(l+1)}{2r^2} - \frac{\frac{d^2}{dr^2} \Phi_l^{PS}(r)}{\Phi_l^{PS}(r)} \right] \quad (\text{B.22})$$

⁶Hardness can be defined as a measure of the variation in real space which is quantified by the extent of the potential in Fourier space, in which case hard potentials describe the properties of the localized, rigid ion cores and are more transferable from one material to another. Alternatively, it can be defined as a measure of the ability of the valence pseudo-electrons to describe the response of the system to a change in the environment properly.

where m_e is the mass of the electron.

Kerker's choice of the analytic form is $\Phi_l^{PS}(r) = e^{p(r)}$ for $r < R_c$, where $p(r)$ is a polynomial to fourth power, whose coefficients are fixed by requiring continuous first and second derivatives at R_c as well as norm-conservation.

Troullier and Martins [108] have extended the Kerker [69] method to make it smoother by using a higher order polynomial and matching more derivatives of the wavefunction. This allows the use of fewer basis functions in the description of the wavefunctions, which reduces the size of the calculations [83].⁷

B.0.13 Relativistic effects

Relativistic effects can be incorporated into pseudopotentials since they originate deep inside the atom, near the nucleus. They include shifts due to scalar relativistic effects and spin-orbit (SO) interactions.

To cater for these effects, we start generating a pseudopotential from a relativistic all-electron calculation on an atom for $j = l \pm \frac{1}{2}$. We then define [95, 42]

$$V_l = \frac{l}{2l+1} \left[(l+1) V_{l+\frac{1}{2}} + l V_{l-\frac{1}{2}} \right] \quad (\text{B.23})$$

and

$$\delta V_l^{SO} = \frac{2}{2l+1} \left[V_{l+\frac{1}{2}} + V_{l-\frac{1}{2}} \right]. \quad (\text{B.24})$$

Scalar relativistic effects are included in equation (B.23) and the spin-orbit effects are included in equation (B.24) in a short range non-local term [61, 106]

$$\delta V_l^{SO} = \sum_{lm} |Y_{lm}\rangle \delta V_l^{SO}(r) \mathbf{L} \cdot \mathbf{S} |Y_{lm}\rangle. \quad (\text{B.25})$$

The consequences for the valence electrons can easily be carried into molecular or solid state calculations.

Relativistic effects are particularly essential for heavy atoms.

⁷A further step in reducing the size of the calculations is to minimize the kinetic energy of the pseudofunctions explicitly for the chosen core radius.

B.0.14 Ultrasoft pseudopotentials

Norm-conserving pseudopotentials sacrifice smoothness for accuracy, which translates to longer computational time. Ultrasoft pseudopotentials are ultrasoft and therefore very fast. [83]

With ultrasoft pseudopotentials, the problem is expressed in terms of a smooth function and an auxiliary function around each ion core that represents the rapidly varying part of the density [83]. The resulting equations are formally related to OPW and PKA equations, but the ultrasoft pseudopotentials are a practical approach for solving equations beyond the applicability of these formulations.

Blöchl [18] and Vanderbilt [112] proposed re-writing the non-local potential in a form that involves a smooth function $\varphi = r\psi^8$ which is not norm-conserving. The difference in the norm-equation (B.18) from this norm-conserving function $\Phi = r\Psi$ (be it an all-electron or a pseudofunction) is given by

$$\Delta Q_{s,s'} = \int_0^{R_c} dr \Delta Q_{s,s'}(r) \quad (\text{B.26})$$

where

$$\Delta Q_{s,s'}(r) = \Phi_s^*(r) \Phi_{s'}(r) - \varphi_s^*(r) \varphi_{s'}(r). \quad (\text{B.27})$$

A new non-local operator that operates on $\psi_{s'}$ can now be defined to be

$$\delta V_{NL}^{US} = \sum_{s,s'} D_{s,s'} |\beta_s\rangle \langle \beta_{s'}| \quad (\text{B.28})$$

where

$$D_{s,s'} = B_{s,s'} + \varepsilon_{s'} \Delta Q_{s,s'} \quad (\text{B.29})$$

and

$$\beta_s = \sum_{s'} B_{s,s'}^{-1} \chi_{s'} \quad (\text{B.30})$$

with χ_s defined when constructing generalized pseudofunctions Ψ_s from all-electron calculations at different energies ε_s :

$$\chi_{lm}^{PS}(\mathbf{r}) \equiv \left\{ \varepsilon_l - \left[-\frac{1}{2} \nabla^2 + V_{local}(r) \right] \right\} \Psi_{lm}^{PS}(\mathbf{r}). \quad (\text{B.31})$$

⁸Here, we are omitting the labels PS, l , m and spin for simplicity.

s and s' label atomic states.

It can be shown that the smooth functions ψ_s are the solutions of the generalized eigenvalue problem for each reference atomic state s :

$$[H - \varepsilon_s S] \psi_s = 0 \quad (\text{B.32})$$

where

$$H = -\frac{1}{2}\nabla^2 + V_{local} + \delta V_{NL}^{US} \quad (\text{B.33})$$

and

$$S = \mathbf{1} + \sum_{s,s'} \Delta Q_{s,s'} |\beta_s\rangle \langle \beta_{s'}| \quad (\text{B.34})$$

is an overlap operator which is not unity inside the core radius.

The eigenvalues ε_s agree with the all-electron calculation at as many energies s as desired [83].

The full density can be constructed from the functions $\Delta Q_{s,s'}(r)$ which can be replaced by a smooth version of the all-electron density [83].

The norm-conservation condition $\Delta Q_{s,s'} = 0$ is relaxed with the advantage that each smooth pseudofunction ψ_s can be formed independently with only the constraint that $\psi_s(R_c) = \Psi_s(R_c)$ (at the boundary of the core radius). It therefore becomes possible to choose a much larger core radius R_c than for norm-conserving pseudopotentials.

The desired accuracy is maintained by adding the auxiliary functions $\Delta Q_{s,s'}(r)$ as well as the overlap operator S .

In a calculation that uses an ultrasoft pseudopotential, the solutions for the smooth functions $\psi_i(\mathbf{r})$ are orthonormalized according to

$$\langle \psi_i | S | \psi_{i'} \rangle = \delta_{i,i'} \quad (\text{B.35})$$

and the valence density is defined to be

$$n_v(\mathbf{r}) = \sum_i^{occ} \psi_i^*(\mathbf{r}) \psi_{i'}(\mathbf{r}) + \sum_{s,s'} \rho_{s,s'} \Delta Q_{s,s'}(\mathbf{r}) \quad (\text{B.36})$$

where

$$\rho_{s,s'} = \sum_i^{occ} \langle \psi_i | \beta_{s'} \rangle \langle \beta_s | \psi_i \rangle. \quad (\text{B.37})$$

Minimizing the total energy gives the solution

$$\begin{aligned}
 E_{total} = & \sum_i^{occ} \langle \psi_i | -\frac{1}{2} \nabla^2 + V_{local}^{ion} + \sum_{s,s'} D_{s,s'}^{ion} |\beta_s\rangle \langle \beta_{s'}| | \psi_i \rangle \\
 & + E_{Hartree} [n_v] + E_{II} + E_{xc} [n_v].
 \end{aligned} \tag{B.38}$$

Defining the unscreened bare ion pseudopotential by $V_{local}^{ion} \equiv V_{local} - V_{Hxc}$ and $D_{s,s'}^{ion} \equiv D_{s,s'} - D_{s,s'}^{Hxc}$ with

$$D_{s,s'}^{Hxc} = \int d\mathbf{r} V_{Hxc}(\mathbf{r}) \triangle Q_{s,s'}(r) \tag{B.39}$$

leads to the generalized eigenvalue problem

$$\left[-\frac{1}{2} \nabla^2 + V_{local} + \delta V_{NL}^{US} - \varepsilon_i S \right] \psi_i = 0 \tag{B.40}$$

where δV_{NL}^{US} is given by the sum over all ions of equation (B.28).

Equation (B.40) can easily be solved numerically.

Appendix C

The Electromagnetic Spectrum

Figure C.1 shows the visible part of the electromagnetic spectrum adapted from Table 8.1 of ref. [46].

Table C.1: The visible part of the electromagnetic spectrum.

Colour	Wavelength (m)	Frequency (Hz)
Near ultraviolet	3.0×10^{-7}	10×10^{14}
Shortest visible blue	4.0×10^{-7}	7.5×10^{14}
Blue	4.6×10^{-7}	6.5×10^{14}
Green	5.4×10^{-7}	5.6×10^{14}
Yellow	5.9×10^{-7}	5.1×10^{14}
Orange	6.1×10^{-7}	4.9×10^{14}
Longest visible red	7.6×10^{-7}	3.9×10^{14}
Near infrared	10.0×10^{-7}	3.0×10^{14}

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