SUPERCONDUCTIVITY THROUGH HUBBARD MODEL

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Teshome Kebede

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DEPARTMENT OF PHYSICS

The undersigned hereby certify that they have read and recommended to the Faculty of Science School of Graduate Studies for acceptance a thesis entitled "**Superconductivity through Hubbard model**" by **Teshome Kebede** in partial fulfillment of the requirements for the degree of **Master of Science in Physics**.

Name	Signature
Professor P. Singh, Advisor	______________
Dr. Tesgera Bedassa ,Examiner	_______________
Dr. Tewari H. S., Examiner	_______________

To My Families

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Addis Ababa, Ethiopia Teshome Kebede

Abstract

Superconductivity through Hubbard model has been studied following Hartree Fock Approximation. The theoretical study has been made on the origin of superconductivity in electron-electron interaction with coulomb repulsion which is not phononic. The former interaction is under some condition, qualitatively different as compared to the latter interaction . The study by considering a Hubbard model is focused and brought out by applying the canonical transformation method as well as by simple renormalization operation that excludes double occupancy in the effective Hubbard Hamiltonian of the system and goes over in to the t-J model Hamiltonian that serves as a reference point (fixed point). For small deviations from half filling holes move in the antiferromagnetic lattice and create disorder and establishes superconductivity. This Hamiltonian is used and theoretically examined in the second quantization notation by using Green's function formalism and suitable decoupling approximations the survival of superconductivity has been shown with the computation of supper conducting order parameter (Δ) and transition temperature (T_c) mathematically to make known its possibility. The phase diagram of the numerical estimates of the superconducting transition temperature versus values of electron (hole) boson coupling constant has been obtained and it is in agreement with the the experimental observation. We found that supper conductivity is obtained through Hubbard model.

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Introduction

Atomic clusters are aggregates containing from few to a few thousand atoms [1]. Due to their small nanometric or sub-nanometric size, many properties of the clusters are different from those of the corresponding macroscopic material. Those differences arise from the fact that a substantial fraction of atoms form the cluster surface, while this fraction becomes negligible in the case of a macroscopic piece of material. Many of the properties of clusters can also be understood as arising from the small volume of the potential well that confines the electrons. In this case the electrons fill discrete levels. An interesting question which still lacks a convincing answer is the following: how many atoms are required for a cluster to show the properties of the bulk material? But, even more important is the fact that the variation of a given property like the cluster geometry, or the values of the ionization potential, is often not smooth as the number of atoms in the cluster increases one by one. This possibility of tuning the value of a given magnitude by changing the number of atoms in the cluster opens up enormous possibilities for the technological applications of these interesting nanostructures. It becomes necessary to characterize the electronic, structural and chemical properties of clusters, and the optical, photo-electron and time-resolved spectroscopies help in this task, allowing the study of static and dynamic electron-electron correlations. The electronic levels are quantized in atomic clusters and nanostructures, reflecting the behavior of electrons in a potential well of finite size. The optical spectrum provides information on the electronic structure. It is sensitive to the size and the geometrical structure of the cluster. This is an important feature, since the knowledge of the geometrical structure is required for understanding many cluster properties. Understanding the spectroscopical properties of clusters means understanding their response to time-dependent external fields. One is often interested in the response to an external field that is not strong, and in such a case it is enough to consider the linear response to the external field. The current experimental trends, however, oblige us to devote special attention to the non-linear response to strong perturbations. In any case, we are confronted with many-electron systems, for which the straightforward solution of the Schrodinger equation is computationally unattainable. The methods based on the many-body wavefunction, such as the traditional quantum chemistry approaches, or Quantum-Montecarlo techniques, are possible alternatives, but their computing requirements grow rapidly with the size of the system. This problem is already severe when dealing with ground-state properties(total energy calculations), or when attempting to do lowest order perturbation theory, and it is aggravated in the non-perturbative regime of high-fields interaction.In the last decades, it has been shown how the problem of the ground and excited state properties of clusters can be conveniently attacked, for many purposes, with the help of density-functional theory (DFT) [27]. In particular, many excited state properties (e.g., the spectrum of optical excitations) can be calculated by the so called time-dependent density-functional theory (TDDFT) [811].

In this thesis we propose a different approach to the calculation of excitation energies which is based on a time dependent local density approximation. To extract excitation energies form TDLDA we exploit the fact that the frequency dependent linear response of a finite interacting system has discreet poles at the excitation energies $\omega_I = E_I - E_0$ of the unperturbed system. The idea is to calculate the shift of the Kohn-Sham orbital energy differences $\omega_{jk} = \epsilon_j - \epsilon_k$ (which are the poles of the Kohn-Sham response function) towards the true excitation energies ω_I in a systematic fashion.

To this end we first derive a formally exact representation of the linear density response $\rho(r, \omega)$ in terms of the Kohn-Sham response function and a frequency dependent exchange-correlation Kernel, which will used to calculate the shift of the poles. To determine the optical gap of hydrogenated nano-silicon we need to calculate the quasi-particle gap and exciton Coulomb energy from the knowledge of time-independent Kohn-Sham orbitals. Finally, to simplify the length scale of our problem we will employ the concept of pseudopotential.

Chapter 1

Theoretical Methods

In this chapter we revise the theoretical foundations of the methods and calculations that are employed in the thesis: density functional theory, both in its original formulation (DFT) and in its time-dependent version (TDDFT). We will only make a brief exposition of the basic principles, with no attempt to discuss mathematical subtleties. Since the theory itself is not the objective of the thesis, rather how the essence of its can be exploited for the nano-structure. Notwithstanding this, it is necessary to establish the origin and justification of the equations that are later on used in all the applications. The two first sections of this chapter revise respectively DFT and TDDFT: we enunciate the fundamental theorems that constitute the basis of the theories, and describe the various approximations to the exchange and correlation term that we have used, in the context of the numerous existing possibilities.

1.1 Density Functional Theory

Theoretically, the properties of solid can be obtained by solving the eigen-states of total Hamiltonian of the system. In the atomic unit system, non- relativistic

Hamiltonian of the system is given by

$$H = -\sum_i \nabla^2 + \frac{1}{2}\sum_{i\neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i V_{ion}(\mathbf{r}_i) + E_{ion}(\{\mathbf{R}_n\}), \tag{1.1}$$

where i- j- summations take over all electron positions, $\mathbf{R}_n$ is n^{th}-atom position. $V_{ion}(\mathbf{r}_i)$ is atom potential at $\mathbf{r}_i$, and $E_{ion}(\{\mathbf{R}_n\})$ is the ion-ion direct interaction.

Most of the properties of the system being in interest such as the total energy of the ground state, atom force, electron density and electrostatic potential, etc., can be obtained by solving *Schrödinger* equation:

$$H\Psi_0(\{\mathbf{r}_i\}) = E_0\Psi_0(\{\mathbf{r}_i\}). \tag{1.2}$$

One of attempts of non-empirical method to obtain the properties of solid is to solve the equation of the many-electron Hamiltonian Eq.(1.1) directly. In practice, the equation (1.2) is often rewritten through a Slater determinant which is composed of a lot of single-electron wavefunctions. This is the so-called Hartree-Fock approximation, where only the exchange effect is considered. In many problems, it is known that the exchange term only is not good. Further developments in order to include the correlation effect into account, many methods, such as the configuration interaction by expanding on many Slater determinants and the quantum Monte Carlo method, etc., have been devised.

Anyway, these approaches are all based upon the wavefunctions and express the electronic states of solid through the set of wave functions. In the configuration interaction method, the combination of wavefunctions is very complicated, resulting in severely the limitation of the size of problems.

Meanwhile, for the many-electron problems, another and very different approach called the density functional theory has been proposed. In this approach, the electron density is the quantity, from which the theory is developed. To solve one-electron equations which are derived from the density functional theory is much easier than solving Eq. (1.2). The correlation effect is taken into account, and the size of the system which can be handled is far larger. Since 1980, this method has established a position as one of the main methods of calculating the properties of solid and molecules from the first principles (called ab initio).

The work by Hohenberg and Kohn [1] is now known as a fundamental reference as the density functional theory. In this work, it is shown that the ground states energy of electrons is a unique functional of the electron density. Furthermore, given external potential, It is shown that the ground-state energy can be obtained by minimizing the energy functional, with respect to the electron density. When the density is the true ground-state electron density, this minimizes the energy functional. In a subsequent paper by Kohn and Sham [2], it is shown that the energy functional is recast by using orbitals as $E_{KS}(\{\Psi_i\})$ subjected to the orthogonalization condition of the set of one-electron wavefunctions $\Psi_i(r)$

$$\begin{aligned} E_{KS}(\{\Psi_i\}) &= -\sum_i n_i \int \Psi_i \nabla^2 \Psi_i d^3\mathbf{r} + \int \rho(\mathbf{r}) V_{ion}(\mathbf{r}) d^3\mathbf{r} \\ &+ \frac{e^2}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}\prime)}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r} d^3 d\mathbf{r}' + E_{xc}[\rho(\mathbf{r})] + E_{ion}(\{\mathbf{R}_n\}). \end{aligned} \tag{1.3}$$

where E_{KS} is Kohn-Sham functional energy, the i-summation takes over all one-electron orbits, n_i the number of occupations in i-state, E_{xc} the exchange energy, and $\rho(\mathbf{r})$ is the charge density and given by

$$\rho(\mathbf{r}) = \sum_i |\Psi_i(\mathbf{r})|^2. \tag{1.4}$$

The wave functions Ψ_i which minimize the Kohn-Sham functional energy in Eq.(1.1) satisfy the following eigenvalue equations

$$H_{HS}\Psi_i = \epsilon_i \Psi_i, \tag{1.5}$$

where H_{KS} is Kohn-Sham's Hamiltonian

$$H_{KS} = -\nabla^2 + V_{ion}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}). \tag{1.6}$$

Here, $V_H(r)$ is Hatree-Fock potential

$$V_H = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}', \tag{1.7}$$

V_{xc} is exchange correlation potential

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}, \tag{1.8}$$

and ϵ_i and Ψ_i denote the eigenvalues and eigenfunctions of the Kohn-Sham equation, respectively.

The wave functions calculated by Eq. (1.5) yield the charge density by Eq. (1.4), which is just $\rho(\mathbf{r})$ appearing in the Hartree-Fock and exchange potential. Hence, the Kohn-Sham equation must be solved self-consistently.

It seems that Eq. (1.6) plays a role of *Schröodinger* equation of one- electron wavefunction, but the thought underlying these equation is quite different. For the case of Hatree-Fock, the wavefunctions are treated as the most important quantity, and the charge density is second one, in other words, a dependent variable. On the other hand, in the density functional theory, the charge density comes first. Wavefunctions are something expedient, so that they are allowed to vary as far as the charge density is the same. In the case of nanostructure of spherical symmetry density at the interior of the dot is uniform and density at the surface is not uniform.

1.2 Local Density Approximation

A price of mathematical simplification of the density functional method, which replaces the many-electronic problem by one-electron problem is paid by introducing unknown functional of exchange and correlation E_{xc} of the charge density. Fortunately, there is an easy approximation for E_{xc}. The most widely used form of E_{xc} is the so-called local density approximation (LDA). That is, the exchange and correlation energy of uniform electron gas, which is well studied, is used. In this approximation, the exchange- correlation energy at each point of the real space, E_{xc}, is assumed to equal to that energy of a uniform electron gas with the same charge density.

$$E_{xc} = \int \epsilon_{xc}(\mathbf{r})\rho(\mathbf{r})d^3\mathbf{r}, \tag{1.9}$$

where $V_{xc}(\mathbf{r})$ is exchange potential and given by

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta\rho(\mathbf{r})} = \frac{\partial(\rho(\mathbf{r})\epsilon_{xc}(\mathbf{r}))}{\partial\rho(\mathbf{r})}, \tag{1.10}$$

where $\epsilon_{xc}(\mathbf{r})$ is

$$\epsilon_{xc}(\mathbf{r}) = \epsilon_{xc}^{hom}[\rho(\mathbf{r})], \tag{1.11}$$

where ϵ_{xc}^{hom} is the exchange-correlation energy in a uniform electron gas of that charge density. Actual form of the exchange and correlation energy as the function of the charge density is constructed, based on the most reliable studies about homogeneous electron gas, such as [7] or quantum Monte Carlo method [6]. Within the local density approximation, the exchange and correlation potentials become a local function of the charge density. Tremendous of calculations of for solids and molecules have shown effectiveness and accuracy of this approximation.

1.3 Time-dependent Density Functional Theory

DFT, reviewed in the previous section, is usually addressed as a ground-state theory. This is inexact: the excited states are also uniquely determined by the ground-state density, i.e. the excitation energies, for example, are also functionals of the ground state density. Unfortunately these functionals are unknown. Note that HK theorem is an existence statement and it does not provide with a constructive procedure for the functionals. However, our approach to the study of the electronic excited states is based on yet another extension: time-dependent local density approximation (TDLDA). Note that TDDFT is the extension of DFT to time-dependent phenomena. It allows for the calculation of excitations, but its scope is larger, since in fact, it is an exact reformulation of the time-dependent *Schrödinger* equation. In the following, We will shallowly review the foundations of the theory.

TDDFT is based on the Runge-Gross theorem [ ]: given a system of electrons prepared in a given initial state $\Phi(t_0)$, there is a biunivocal correspondence between the external time dependent potential v_{ext}, and the time dependent electron density, $\rho(\mathbf{r}, t)$. This is a generalization of time-dependent potentials and densities, of ordinary DFT one-to-one correspondence:

$$\rho(\mathbf{r}, t) \longleftrightarrow v(\mathbf{r}, t), \tag{1.12}$$

Note that in this case: (i) Two potentials are considered equivalent if they differ by any purely time-dependent function (because then they produce wave functions which are equal up to purely time-dependent phase, which is cancelled when any observable is calculated from them), and (ii) There is a dependence on the initial quantum state of the system [ ]. (iii) Contrary to intuition, the v-representability problem (the problem of the existence of a potential that produces a given density) is milder in the time-dependent case, and has been solved by van Leeuwen (see [ ]; this work is effectively an extension of the RG theorem) under very broad assumptions for the initial state of the system.

Armed with the Runge-Gross (RG) theorem, and in a similar way to the Kohn-Sham construction for the ground state density, we may build a time-dependent Kohn-Sham scheme. For that purpose, one has to introduce an auxiliary system of N noninteracting electrons, subject to a external potential v_{KS}. The time-dependent density of this independent electrons system coincides with the density $\rho(\mathbf{r}, t)$ of the original system. This density is obtained via the propagation a set of time-dependent *Schrödinger*-like equations (sometimes referred as time-dependent Kohn-Sham . TDKS . or Runge-Gross equations):

$$i\frac{d}{dt}|\Psi_j(t)\rangle = [\hat{t} + \hat{v}_{KS}[\rho]]|\Psi_j(t)\rangle, \tag{1.13}$$

$$|\Psi_j(t_0)\rangle = |\Psi_{j0}\rangle, \tag{1.14}$$

$$\rho(\mathbf{r}, t) = \sum_{j=1}^{N} \Psi_j^{\dagger}(\mathbf{r}, t)\Psi_j(\mathbf{r}, t). \tag{1.15}$$

The initial state $|\Phi(t_0)\rangle$ should be representable by an initial Slater determinant built with the set of one-electron orbitals $\{\Phi_{j0}\}_{j=1}^{N}$.

Regarding the time-dependent Kohn-Sham potential $v_{KS}[\rho]$, its formal definition is rather complex. The original formulation of Runge and Gross departed from the quantum mechanical action:

$$A[\Phi] = \int_{t_0}^{t_1} dt\langle\Phi(t)|i\frac{\partial}{\partial t} - \hat{H}(t)|\Phi(t)\rangle, \tag{1.16}$$

which is also a functional of the density by virtue of the RG theorem, $A = A[\rho]$.

Then, the exchange and correlation action, $A_{xc}[\rho]$, was defined as:

$$A_{xc}[\rho] = A_{KS}[\rho] - A[\rho] - \frac{1}{2}\int d\mathbf{r}d\mathbf{r\prime}\frac{\rho(\mathbf{r},t)\rho(\mathbf{r\prime},t)}{|\mathbf{r}-\mathbf{r\prime}|}, \tag{1.17}$$

where AKS is the action functional for the Kohn-Sham system. The exchange and correlation functional $v_{xc}[\rho](\mathbf{r},t)$ is its functional derivative:

$$v_{xc}[\rho](\mathbf{r},t) = \frac{\delta A_{xc}}{\delta\rho(\mathbf{r},t)}, \tag{1.18}$$

This completes the definition of the KS potential $v_{KS}[\rho]$:

$$v_{KS}[\rho](\mathbf{r},t) = v(\mathbf{r},t) + V_H[\rho](\mathbf{r},t) + v_{xc}[\rho](\mathbf{r},t), \tag{1.19}$$

where $V_H[\rho(\mathbf{r},t)]$ is once again the Hartree electrostatic potential energy functional, now dependent on time. In the same manner than in ground-state DFT, the exchange-correlation potential contains all the nontrivial many-body effects and has a complicated nonlocal dependence on ρ, both in time and in space.

This derivation contains two formal problems: breakdown of the principle of causality [ ] and one problem related to the boundary conditions in the variational principle that derives *Schrödinger* equation from the definition of the quantum mechanical action [ ]. These problems were solved by van Leeuwen [ ] with an alternative definition of $A[\rho]$ within the Keldysh formalism:

$$A[\rho] = -i\ln\langle\Phi(t_0)|\hat{U}(\tau_f,\tau_i)|\Phi(t_0)\rangle + \int_{\tau_0}^{\tau_1} d\tau\left(\frac{dt}{d\tau}\right)(\tau)\int d(\mathbf{r},\tau)v(\mathbf{r},\tau), \tag{1.20}$$

where $\hat{U}$ is the evolution operator, and τ is the Keldysh pseudo-time. The exchange and correlation action is then defined essentially as in Eq.(1.18), subtracting the action functional, and the electrostatic energy from the KS action functional. The exchange and correlation potential, which is the operative magnitude, is then defined once again by functional derivation:

$$v_{xc}[\rho](\mathbf{r},t)=\frac{\delta A_{xc}}{\delta\rho(\mathbf{r},\tau)}_{\rho=\rho(\mathbf{r})}, \tag{1.21}$$

In any case, the exact v_{xc} is unknown, and the quality of any calculation depends on the quality of the approximation of this term. We end this subsection by introducing the so-called time-dependent exchange-correlation kernel

$$f_{xc}(\mathbf{r},\mathbf{r}\prime,\omega)=\frac{\delta v_{xc}[\rho(\mathbf{r},\omega)]}{\delta(\mathbf{r}\prime,\omega)}|_{\delta v_{ext}=0} \tag{1.22}$$

whose usefulness will be demonstrated below.

1.3.1 Approximations to the (Time-Dependent) Exchange and Correlation Term

The simplest, and most commonly used, approximation to the xc functional in TDDFT is the adiabatic LDA (ALDA), in which the static LDA functional is used for the dynamical properties, evaluated at the time-dependent density:

$$v_{xc}^{ALDA}(\mathbf{r},t)=v_{xc}^{LDA}(\rho(\mathbf{r},t)). \tag{1.23}$$

In the ALDA, the f_{xc} kernel is a contact functional in time and space:

$$f_{xc}^{ALDA}(\mathbf{r},t;\mathbf{r}\prime,t)=\delta(t-t\prime)\delta(\mathbf{r}-\mathbf{r}\prime)\frac{dv_{xc}^{LDA}(\rho)}{d\rho}|_{\rho=\rho(\mathbf{r},t)} \tag{1.24}$$

1.4 Pseudopotential Approximation

The second approximation which follows the local density approximation is use of pseudopotential. The wavefunctions of solid is expanded here through the set of plane waves. Plane-wave expansion it is uneconomical to describe localized states, such as core states of atoms which exhibit strong oscillations in the core region. Fortunately, the physical and chemical characteristics of many materials are governed by the valence electrons which extend to more wide region, and the core states are insensitive to those properties. We then can make an approximation by using valence electrons solely in describing the chemical combining characters of materials. Therefore, needed potentials have relatively slowly varying characters and this is desired properties. The wave functions which simulate the valence electrons accords to that are called the pseudo-wave functions. The good reviews of pseudopotential method can be found in Ref. [8].

The pseudopotential are constructed so as they describe as much precisely as possible the electron scattering characters outside the core region. Good pseudo-wave function are called "transferable". In general, pseudopotentials of an atom have different scattering characters in each angular momentum and are non-local. Mathematically, pseudopotentials can be expressed as,

$$\hat{V}_{NL} = \sum_{\ell} |\ell m\rangle V_{\ell} \langle \ell m| \tag{1.25}$$

where $|\ell m\rangle$ is spherically harmonic functions, ℓ and m are the angular mo- mentum, and the projected angular momentum, respectively. The original bare potential is of course a local potential. Because the true wavefunction and the pseudo-wave function are matched outside the core region, non- locality of pseudopotential is limited in the core region. For light atoms, adding of higher than 2 components, $\ell > 2$, into a set of pseudopotentials is not necessary. Though many empirical potentials had been devised in the past to construct pseudopotentials [8], a great step had been achieved by introducing the concept "norm conservation" of wave function by Hamann [9]. As a result, it is not an exaggeration to say that pseudopotential method came to be used most generally today as a method to solve the problem of solid. In this procedure, a nodeless pseudo-wave function is initially taken so as to match to the true wavefunction outside core radius r_c. A norm-conserving condition, along with other conditions, the final form of potential is completed. The process is depicted in Fig. 1.1.

The pseudopotentials defined by expression (1.25) may be called semi-local one. The reason is that it is local for the radial element of the position, though it is non-local for the angle element. Kleinman and Bylander proposed the full-nonlocal type by which the radial element is treated non-local [11]. According to this, the potential is recast by

$$V_{ion} = V_L + \sum_{\ell m} \frac{|\Phi^0_{\ell m} \Delta V_\ell\rangle \langle \Delta V_\ell \Phi^0_{\ell m}|}{\langle \Phi^0_{\ell m} | \Delta V_\ell | \Phi^0_{\ell m} \rangle}, \tag{1.26}$$

where $\Phi^0_{\ell m}$ is the pseudo-wave function of the atom when the pseudopotential is constructed. ΔV_ℓ is obtained by

$$\Delta V_\ell = V_{\ell,NL} - V_L, \tag{1.27}$$

Giving nonlocal potential in this way, the calculation of non-local part of the potential is greatly accelerated. Further benefit is obtained in calculation of operating of non-local potential onto wavefunctions if the arbitrariness of V_L is utilized. In this section, the procedure for constructing an ab initio pseudopotential within density functional theory will be illustrated. Using the approach Kohn and Sham [15], one can write down a Hamiltonian corresponding to a one-electron *Schrödinger* equation. Here the major difficulty is the range of length scales involved. For example, in the case of a multi-electron atom, the most tightly bound, core electrons can be confined to within $\sim 0.01\mathring{A}$ whereas the outer valence electron may extend over $\sim 1 - 5\mathring{A}$. In addition, the nodal structure of the atomic wavefunctions are difficult to replicate with a simple

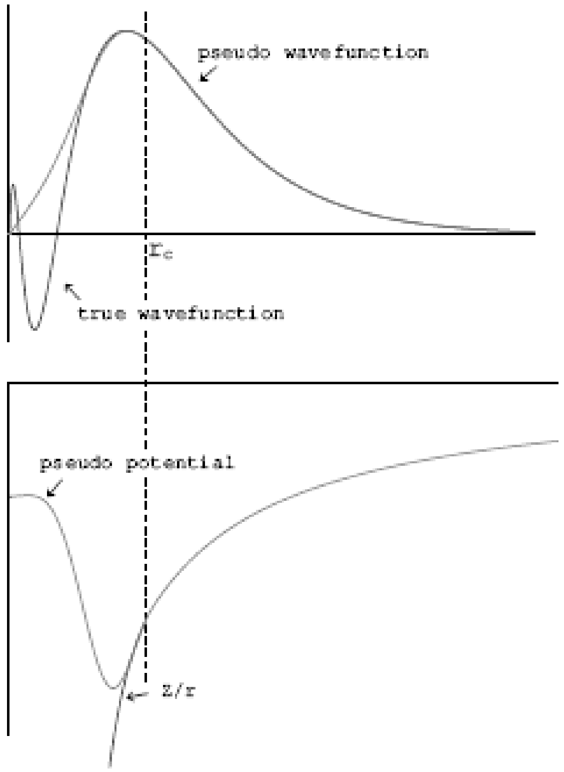

Figure 1.1: Outline of pseudopotential
A true wave function (solid curve) can be replaced with a pseudo-wave function (dashed curve). Wavefunction and potential of all electrons are the same each other in the chemically important area outside the core radius r_c

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basis, especially the wave function cusp at the origin where the Coulomb potential diverges. The pseudopotential approximation eliminates this problem and is quite efficacious when combined with density functional theory. However, it should be noted that the pseudopotential approximation is not dependent on the density functional theory. Pseudopotentials can be created without resort to density functional theory, e.g., pseudopotentials can be created within Hartree-Fock theory.

In 1980, Kerker [ ] proposed a straightforward method for constructing local density pseudo potentials that retained the norm conserving criterion. He suggested that the pseudo-wave function have the following form,

$$\phi_p(r) = r^{\ell} exp(p(r)) \qquad for \quad r < r_c, \tag{1.28}$$

where $p(r)$ is a simple polynomial: $p(r) = -a_0 r^4 - a_1 r^3 - a_2 r^2 - a_3$ and

$$\phi_p(r) = \psi_{AE}(r) \qquad for \quad r > r_c. \tag{1.29}$$

This form of the pseudo-wave function for ϕ_p assures that the function will be nodeless and have the correct behavior at large r. Kerker proposed a criteria for fixing the parameters $(a_0, a_1, a_2$ and $a_3)$. One criteria is that the wave function be norm conserving. Other criteria include: (a) The all electron and pseudo-wave functions have the same valence eigenvalue. (b) The pseudo-wave function be nodeless and be identical to the all-electron wave function for $r > r_c$. (c) The pseudo-wave function must be continuous as well as the first and second derivatives of the wave function at r_c.

Once the pseudo-wave defined as in Eqs. (1.28) and (1.29) one can invert the Kohn-Sham equation and solve for the ion core pseudopotential, $V_{ion,p}$:

$$V^n_{ion,p}(\vec{r}) = E_n - V_H(\vec{r}) - V_{xc}[\vec{r}, \rho(\vec{r})] + \frac{\hbar^2 \nabla^2 \phi_{p,n}}{2m\phi_{p,n}}, \tag{1.30}$$

This potential, when self-consistently screened by the pseudo-charge density:

$$\rho(\vec{r}) = -e \sum_{n,occup} |\phi_{p,n}(\vec{r})|^2, \tag{1.31}$$

will yield the eigenvalue of E_n and a pseudo-wavefunction $\phi_{p,n}$. The pseudo wave function by construction will agree with the all electron wave function away from the core.

The important issue to consider for nanosilicon is about the details of this construction. First, the potential is state dependent as written in Eq. (1.30), i.e., the pseudopotential is dependent on the quantum state n. This issue can be handled by recognizing the nonlocality of the pseudopotential. The potential is different for an $s-, p-$, or $d-$ electron. The nonlocality appears in the angular dependence of the potential, but not in the radial coordinate. Since the core potential is highly bound, the ion core potential is highly localized and is not sensitive to the ground state configuration used to compute the pseudopotential. This pseudopotential should converge to the all electron potential outside of the core. A significant source of error here is the local density approximation. The LDA yields a potential that scales exponentially at large distances and not as one would expect for an image charge, i.e., intuitively, the true potential should incorporate an image potential such that $V_{xc}(r \to \infty) \to -\frac{e^2}{r}$.

Nonlocality in the pseudopotential is often treated in Fourier space, but it may also be expressed in real space. The interactions between valence electrons and pseudo-ionic cores may be separated into a local potential and Kleinman and Bylander [ ] form a nonlocal pseudopotential in real space [ ],

$$V^{p}_{ion}(\vec{r})\phi_n(\vec{r}) = \sum_a V_{loc}(|\vec{r}_a|)\phi_n(\vec{r}) + \sum_{a,n,\ell m} G^a_{n,\ell m} u_{\ell m}(\vec{r}_a)\Delta V_\ell(r_a), \tag{1.32}$$

$$K^a_{n,\ell m} = \frac{1}{\langle \Delta V^a_{\ell m}\rangle} \int u_{\ell m}(\vec{r}_a)\Delta V_\ell(r_a)\psi_n(\vec{r})d^3r, \tag{1.33}$$

and $\langle \Delta V^a_{\ell m}\rangle$ is the normalization factor,

$$\langle \Delta V^a_{\ell m}\rangle = \int u_{\ell m}(\vec{r}_a)\Delta V_\ell(r_a)u_{\ell m}(r_a)d^3r, \tag{1.34}$$

where $\vec{r}_a = \vec{r} - \vec{R}_a$, and the $u_{\ell m}$ are the atomic pseudopotential wavefunctions of angular momentum quantum numbers (ℓ, m), from which the ℓ dependent ionic pseudopotential, $V_\ell(r)$, is generated. $\Delta V_\ell(r) = V_\ell(r) - V_{loc}(r)$ is the difference between the ℓ component of the ionic pseudopotential and the local ionic potential.

Chapter 2

Time Dependent Based Linear Response Theory

In this chapter we start with the time dependent Kohn-Sham equation. Also, we present the general equations of TDDFT-based linear response theory, necessary for photo-absorption calculations.

The Self-consistent single particle time-dependent Kohn-Sham equation is given by

$$\left(-\frac{1}{2}\nabla^2 + v_{eff}[\rho(\mathbf{r},t)]\right)\psi(\mathbf{r},t) = i\frac{\partial}{\partial t}\psi(\mathbf{r},t). \tag{2.1}$$

Here the single particle wavefunctions, $\psi_i(\mathbf{r},t)$, and the effective potential,$v_{eff}[\rho(\mathbf{r},t)]$, explicitly depend on time. The mathematical expression for the effective potential is

$$v_{eff} = \sum_a v_{ion}(\mathbf{r}-\mathbf{r}_a) + V_H[\rho(\mathbf{r},t)] + v_{xc}[\rho(\mathbf{r},t)]. \tag{2.2}$$

In the adiabatic approximation, which is local in time, the exchange-correlation potential and its first derivative can be expressed in terms of the time-independent exchange-correlation energy, $E_{xc}[\rho]$,

$$v_{xc}[\rho(\mathbf{r},t)] \cong \frac{\delta E[\rho]}{\delta\rho(\mathbf{r})}, \tag{2.3}$$

$$\frac{v_{xc}[\rho(\mathbf{r},t)]}{\delta\rho(\mathbf{r'},t')} \cong \delta(t-t')\frac{\delta^2 E_{xc}[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r'})}, \tag{2.4}$$

The LDA makes a separate local approximation, i.e, with in the LDA, the exchange-correlation energy density is local in space.

The local density approximation in time dependent density functional theory interestingly agree with experimental investigations. Most implementations of the time dependent density functional theory are based on the local density approximation or the generalized gradient approximation []. However, these approximations are known to have the wrong asymptotic behavior, e.g. the potential does not scale as $\frac{1}{r}$ for large distances. It is widely believed that more accurate TDLDA methods will necessitate other forms of the density functional. Examples of such an approach are the asymptotically corrected local density approximations introduced by Caside and Slahub [], and by Leeuwen and Baerends []. The potentials have recently investigated using the current formalism [].

2.1 Time Dependent Response Theory

The linear response formalism with in TDDFT provides a theoretical basis for the TDLDA excitation energies and oscillator strengths are derived from the single-electron Kohn-Sham eigenvalues and eigenfunctions. The response of the Kohn-Sham density matrix within TDDFT is obtained by introducing a time-dependent perturbation $\delta v_{appl}(\mathbf{r},t)$. Due to the self consistent nature of the Kohn-Sham Hamiltonian, the effective perturbation includes the response of the self-consistent field. Consider a basis set of time-independent orthonormal spin-orbits $\psi_{i\sigma}$, where i and σ refer to space and spin indices respectively. These orbitals are the molecular orbitals of the unperturbed system. The corresponding annihilation operators are $\hat{a}_{i\sigma}$.

The linear response of the applied field is

$$\delta\hat{v}(t) = \sum_{ij\sigma} \delta v_{ij\sigma}^{appl}(t)\hat{a}_{i\sigma}\hat{a}_{j\sigma}. \tag{2.5}$$

The density matrix is given by $P_{ij\sigma}(t) = \langle\Psi_0(t)|\hat{a}_{i\sigma}\hat{a}_{j\sigma}|\Psi_0(t)\rangle$ and hence its linear response is

$$\delta P_{ij\sigma}(t) = \langle\delta\Psi_0(t)|\hat{a}_{i\sigma}\hat{a}_{j\sigma}|\Psi_0(t)\rangle + \langle\Psi_0(t)|\hat{a}_{i\sigma}\hat{a}_{j\sigma}|\delta\Psi_0(t)\rangle, \tag{2.6}$$

which is conventionally expressed in terms of the generalized susceptibility as

$$\delta P_{ij\sigma}(t) = \sum_{k\ell\tau} \int_{-\infty}^{\infty} \chi_{ij\sigma,k\ell\tau}(t-t')\delta v_{k\ell\tau}^{appl}(t')dt'. \tag{2.7}$$

Introducing the Fourier transform convention

$$f(\omega) = \int_{-\infty}^{\infty} e^{i\omega t} f(t)dt, \qquad f(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\omega t} f(\omega)d\omega, \tag{2.8}$$

and making use of the convolution theorem

$$h(t) = \int_{-\infty}^{\infty} g(t-t')f(t')dt' \Longleftrightarrow h(\omega) = g(\omega)f(\omega), \tag{2.9}$$

allows Eq.(2.7) to be written as

$$\delta P_{ij\sigma}(\omega) = \sum_{k\ell\tau} \chi_{ij\sigma,k\ell\tau}(\omega)\delta v_{k\ell\tau}^{appl}(\omega) \tag{2.10}$$

2.1.1 Derivation of Generalized Susceptibility

Consider a perturbation

$$\delta\hat{w}(t) = e^{-\eta(t_1-t)}\delta\hat{v}_{appl}, \tag{2.11}$$

where η is a positive infinitesimal such that $\delta w(t_1) = \delta v(t_1)$. From time-dependent perturbation theory we know that

$$|\delta\Psi_0(t_1)\rangle = -i\sum_{I\neq 0}|\Psi_I(t_1)\rangle\int_{-\infty}^{t_1}\langle\Psi_I(t)|\delta\hat{w}(t)|\Psi_0(t)\rangle dt, \tag{2.12}$$

where $\Psi_I(t) = e^{-E_I(t)}\Psi_I$

$$\begin{aligned}|\delta\Psi_0(t_1)\rangle &= -i\sum_{I\neq 0}|\Psi_I(t_1)\rangle\int_{-\infty}^{t_1}\langle e^{iE_It}\Psi_I|\delta\hat{w}(t)|e^{-iE_0t}\Psi_0\rangle dt\\ &= -i\sum_{I\neq 0}\int_{-\infty}^{t_1}|\Psi_I(t_1)\rangle\langle\Psi_I|\delta\hat{v}_{appl}|\Psi_0\rangle e^{-iE_1(t_1-t)-iE_0t-\eta(t_1-t)}dt,\end{aligned} \tag{2.13}$$

Taking its complex conjugate we have

$$\langle\delta\Psi_0(t_1)| = i\sum_{I\neq 0}\int_{-\infty}^{t_1}\langle\Psi_I|\langle\Psi_I|\delta\hat{v}_{appl}|\Psi_0\rangle e^{iE_I(t_1-t)+iE_0t-\eta(t_1-t)}dt, \tag{2.14}$$

The linear response of the density matrix at time t_1 is

$$\begin{aligned}\delta P_{ij\sigma}(t_1) &= \langle\delta\Psi_0(t_1)|\hat{a}^\dagger_{i\sigma}\hat{a}_{j\sigma}|\Psi_0(t_1)\rangle + \langle\Psi_0(t_1)|\hat{a}^\dagger_{i\sigma}\hat{a}_{j\sigma}|\delta\Psi_0(t_1)\rangle\\ &= i\sum_{I\neq 0}\int_{-\infty}^{t_1}[\langle\Psi_I|\hat{a}^\dagger_{i\sigma}\hat{a}_{j\sigma}|\Psi_0 e^{-iE_0t_1}\rangle\langle\Psi_0|\sum_{k\ell\tau}\delta v^{appl}_{k\ell\tau}\hat{a}^\dagger_{k\tau}\hat{a}_{\ell\tau}|\Psi_I\rangle e^{iE_I(t_1-t)+iE_0t-\eta(t_1-t)}\\ &- i\langle\Psi_0 e^{iE_0t_1}|\hat{a}^\dagger_{i\sigma}\hat{a}_{\ell\tau}|\Psi_I\rangle\langle\Psi_I|\sum_{k\ell\tau}\delta v^{appl}_{k\ell\tau}\hat{a}^\dagger_{i\sigma}\hat{a}_{j\sigma}|\Psi_0\rangle e^{-iE_I(t_1-t)-iE_0t-\eta(t_1-t)}],\end{aligned} \tag{2.15}$$

$$\begin{aligned}\delta P_{ij\sigma} &= \sum_{k\ell\tau}\int_{-\infty}^{\infty}[-i\Theta(t_1-t)\sum_{I\neq 0}[\langle\Psi_0|\hat{a}^\dagger_{i\sigma}\hat{a}_{j\sigma}|\Psi_I\rangle\langle\Psi_I|\hat{a}^\dagger_{k\tau}\hat{a}_{\ell\tau}|\Psi_0\rangle e^{-i(E_I-E_0-i\eta)(t_1-t)}\\ &- \langle\Psi_0|\hat{a}^\dagger_{k\tau}\hat{a}_{\ell\tau}|\Psi_I\rangle\langle\Psi_I|\hat{a}^\dagger_{i\sigma}\hat{a}_{j\sigma}|\Psi_0\rangle e^{-i(E_0-E_I-i\eta)(t_1-t)}]],\end{aligned} \tag{2.16}$$

where

$$\Theta(t_1 - t) = \begin{cases} 1 & t_1 > t \\ 0 & t_1 < t \end{cases},$$

is the heavy side function. Now, comparing Eq.(2.10)and Eq.(2.16)we have,

$$\begin{aligned} \chi_{ij\sigma,k\ell\tau} &= -i\Theta(t_1 - t) \sum_{I \neq 0} [\langle \Psi_0 | \hat{a}^\dagger_{i\sigma} \hat{a}_{j\sigma} | \Psi_I \rangle \langle \Psi_I | \hat{a}^\dagger_{k\tau} \hat{a}_{\ell\tau} | \Psi_0 \rangle e^{-i(E_I - E_0 - i\eta)(t_1 - t)} \\ &- \langle \Psi_0 | \hat{a}^\dagger_{k\tau} \hat{a}_{\ell\tau} | \Psi_I \rangle \langle \Psi_I | \hat{a}^\dagger_{i\sigma} \hat{a}_{j\sigma} | \Psi_0 \rangle e^{-i(E_0 - E_I - i\eta)(t_1 - t)}], \end{aligned} \quad (2.17)$$

Thus,the Fourier transform of the generalized susceptibility is

$$\chi_{ij\sigma,k\ell\tau} = \sum_{I \neq 0} [\frac{\langle \Psi_0 | \hat{a}^\dagger_{i\sigma} \hat{a}_{j\sigma} | \Psi_I \rangle \langle \Psi_I | \hat{a}^\dagger_{k\tau} \hat{a}_{\ell\tau} | \Psi_0 \rangle}{\omega - (E_I - E_0) + i\eta} - \frac{\langle \Psi_0 | \hat{a}^\dagger_{k\tau} \hat{a}_{\ell\tau} | \Psi_I \rangle \langle \Psi_I | \hat{a}^\dagger_{i\sigma} \hat{a}_{j\sigma} | \Psi_0 \rangle}{\omega + (E_I - E_0) + i\eta}], \quad (2.18)$$

If a single particle system is initially in orbital $\psi_{m\mu}$ and the unperturbed stationary states are taken as the orthonormal basis set underlying the second quantized notation, then Eq.(2.18) can be written as

$$\begin{aligned} \chi_{ij\sigma,k\ell\tau} &= \sum_{I \neq 0} [\frac{\langle \Psi_{m\mu} | \hat{a}^\dagger_{i\sigma} \hat{a}_{j\sigma} | \Psi_I \rangle \langle \Psi_I | \hat{a}^\dagger_{k\tau} \hat{a}_{\ell\tau} | \Psi_{m\mu} \rangle}{\omega - (E_I - E_0) + i\eta} - \frac{\langle \Psi_{m\mu} | \hat{a}^\dagger_{k\tau} \hat{a}_{\ell\tau} | \Psi_I \rangle \langle \Psi_I | \hat{a}^\dagger_{i\sigma} \hat{a}_{j\sigma} | \Psi_{m\mu} \rangle}{\omega + (E_I - E_0) + i\eta}] \\ &= \delta_{\sigma,\tau} \delta_{\sigma,\mu} \delta_{j,\ell} \frac{\delta_{j,m} - \delta_{i,m}}{\omega - (\epsilon_{i\sigma} - \epsilon_{j\sigma})}. \end{aligned} \quad (2.19)$$

Since the response of the density matrix of systems of N independent particles with (possibly fractional) occupation numbers $n_{i\sigma}$ is the occupation number weighted sum of the response of the density matrices for the individual orbitals, assuming that no change in occupation number is induced by the perturbation, the generalized susceptibility can be rewritten as

$$\begin{aligned} \chi_{ij\sigma,k\ell\tau}(\omega) &= \sum_{m\mu} n_{m\mu} \delta_{\sigma,\tau} \delta_{\sigma,\mu} \delta_{j,\ell} \frac{\delta_{j,m} - \delta_{i,m}}{\omega - (\epsilon_{i\sigma} - \epsilon_{j\sigma})} \\ &= \delta_{\sigma,\tau} \delta_{\sigma,\mu} \delta_{j,\ell} \frac{n_{j,\sigma} - n_{i,\sigma}}{\omega - (\epsilon_{i\sigma} - \epsilon_{j\sigma})} \end{aligned} \quad (2.20)$$

This is ageneric expression for nano-clusters of arbitrary number of atoms with no overall symmetry.

2.2 Linear Response of the Density Matrix

The perturbation induced into the Kohn-Sham hamiltonian by turning on an applied field $\delta v^{\sigma}_{eff}(\mathbf{r},t)$ is, to linear order,

$$\delta v^{\sigma}_{eff}(\mathbf{r},t) = \delta v_{appl}(\mathbf{r},t) + \delta v^{\sigma}_{SCF}(\mathbf{r},t), \tag{2.21}$$

where $v^{\sigma}_{SCF}(\mathbf{r},t)$ is the linear response of the self-consistent field arising from the change in the charge density. Thus the quasi-independent particle nature of the Kohn-Sham equation means that the independent particle nature of the generalized susceptibility Eq.(2.20), can be used together with the perturbation $\delta v^{\sigma}_{eff}(\mathbf{r},t)$ to write down the linear response of the Kohn-Sham density matrix to the applied field. In the basis of the unperturded molecular orbitals,

$$\delta P_{ij\sigma}(\omega) = \sum_{k\ell\tau} \chi_{ij\sigma,k\ell\tau}(\omega)\delta v^{eff}_{k\ell\tau} = \frac{n_{j\sigma} - n_{i\sigma}}{\omega - (\epsilon_{i\sigma} - \epsilon_{j\sigma})}\delta v^{eff}_{ij\sigma}(\omega). \tag{2.22}$$

The previous equation is however, complicated by the fact that $\delta v^{SCF}_{ij\sigma}(\omega)$ depends on the response of the density matrix,

$$\begin{aligned} \delta v^{SCF}_{ij\sigma}(\omega) &= \sum_{k\ell\tau} \frac{\partial v^{SCF}_{ij\sigma}}{\partial P_{k\ell\tau}} \delta P_{k\ell\tau} \\ &= \sum_{k\ell\tau} K_{ij\sigma}, k\ell\tau \delta P_{k\ell\tau}, \end{aligned} \tag{2.23}$$

where the coupling matrix $K_{ij\sigma,k\ell\tau}(t) = \frac{\partial v^{SCF}_{ij\sigma}(t)}{\partial P_{k\ell\tau}(t)}$ describes the response the self-consistent field to changes in the charge density. Taking the Fourier transform of the coupling matrix we get,

$$\begin{aligned}
K_{ij\sigma,k\ell\tau}(\omega) &= \int_{-\infty}^{\infty} e^{+i\omega(t-t')}\frac{\partial v^{SCF}_{ij\sigma}(t)}{\partial P_{k\ell\tau}(t')}d(t-t'), \\
&= \int_{-\infty}^{\infty} e^{i\omega(t-t')}\left[\sum_{\mu}\int\int \frac{\delta v^{SCF}_{ij\sigma}(t)}{\delta\rho_{mu}(\mathbf{r},t'')}\frac{\partial\rho_{\mu}(\mathbf{r},t'')}{\partial P_{k\ell\tau}(t')}drdt''\right]d(t-t'), \\
&= \int\int \Psi^*_{i\sigma}(\mathbf{r})\Psi_{j\sigma}(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}\Psi_{k\tau}(\mathbf{r}')\Psi^*_{\ell\tau}(\mathbf{r}') \\
&+ \int_{-\infty}^{\infty} e^{+i\omega(t-t')}\left[\int\int \Psi^*_{i\sigma}(\mathbf{r})\Psi_{j\sigma}(\mathbf{r})\frac{\delta^2 E_{xc}[\rho]}{\delta\rho_\sigma(\mathbf{r},t)\delta\rho_\tau(\mathbf{r}',t)}\Psi_{k\tau}(\mathbf{r}')\Psi^*_{\ell\tau}(\mathbf{r}')d\mathbf{r}d\mathbf{r}'\right]d(t-t'), \\
&= \int\int \Psi^*_{i\sigma}(\mathbf{r})\Psi_{j\sigma}(\mathbf{r})\left[\frac{1}{|\mathbf{r}-\mathbf{r}'|}+\frac{\delta^2 E_{xc}[\rho]}{\delta\rho_\sigma(\mathbf{r})\delta\rho_\tau(\mathbf{r}')}\right]\Psi_{k\tau}(\mathbf{r}')\Psi^*_{\ell\tau}(\mathbf{r}')d\mathbf{r}d\mathbf{r}', \qquad (2.24)
\end{aligned}$$

where the functional derivative is evaluated using the unperturbed spin-up and spin-down charge densities. Using Eqs.(2.21),(2.23)and(2.24), Eq.(2.22) can be written as

$$\delta P_{ij\sigma}(\omega) = \frac{n_{j\sigma}-n_{i\sigma}}{\omega-(\epsilon_{i\sigma}-\epsilon_{j\sigma})}\left[\delta v^{appl}_{ij\sigma}(\omega)+\sum_{k\ell\tau}K_{ij\sigma,k\ell\tau}(\omega)\delta P_{k\ell\tau}(\omega)\right], \qquad (2.25)$$

rearranging the above equation we get

$$\sum_{k\ell\tau}^{n_{k\tau}-n_{\ell\tau}\neq 0}\left[\delta_{\sigma,\tau}\delta_{i,k}\delta_{j,\ell}\frac{\omega-(\epsilon_{k\sigma}-\epsilon_{\ell\sigma})}{n_{k\tau}-n_{\ell\tau}}-K_{ij\sigma,k\ell\tau}(\omega)\right]\delta P_{k\ell\tau}(\omega)=\delta v^{appl}_{ij\sigma}(\omega), \qquad (2.26)$$

where $n_{k\tau} \neq n_{\ell\tau}$. Solving the above equation for $\delta P(\omega)$ then allows response properties to be calculated. From Eq.(2.24)we see that the coupling matrix satisfies the following relation:

1. $$K_{ij\sigma,k\ell\tau}(\omega) = [K_{k\ell\tau,ij\sigma}(\omega)]^*. \qquad (2.27)$$

2. When the molecular orbitals are real, as in the usual case in quantum mechanical calculations,

$$K_{ij\sigma,k\ell\tau}(\omega) = K_{ij\sigma,\ell k\tau}(\omega) = K_{ji\sigma,\ell k\tau}(\omega) = K_{ji\sigma,k\ell\tau}(\omega). \qquad (2.28)$$

3. In the adiabatic approximation, the replacement $\frac{A_{xc}}{\delta\rho_{\mathbf{r},t}\delta\rho_{\mathbf{r'},t'}} \rightarrow \delta(t-t')\frac{\delta E_{xc}}{\delta\rho_\sigma(\mathbf{r})\delta\rho_\tau(\mathbf{r'})}$ results in a coupling matrix which is no longer a function of ω, and which is real when the MOs are real. And hence K is hermitian,

$$K_{ij\sigma,k\ell\tau} = K^*_{ji\sigma,\ell k\tau} \tag{2.29}$$

Furthermore K is real when MOs are real, but even in this case

$$K_{ij\sigma,k\ell\tau} \neq K_{ij\sigma,\ell k\tau} \tag{2.30}$$

Since only the particle-hole (ph) $n_{i\sigma} > n_{j\sigma}$ elements $\delta P_{ij\sigma}$ of the response of the density matrix are nonzero and divide $\delta P_{ij\sigma}$ into particle-hole (ph) and hole-particle (hp) parts.

We start by ordering the orbital basis $\Psi_{i\sigma}$ such that $i < j \leftrightarrow n_{i\sigma} \geq n_{j\sigma}$. Now consider $n_{i\sigma} > n_{j\sigma}$. Then the $\delta P_{ij\sigma}$are the ph matrix elements and $\delta P_{ji\sigma}$ are the hp matrix elements, and can be written as two separate equations, the first giving the ph part of δv^{appl},

$$\begin{aligned}\sum_{k\ell\tau}^{n_{k\tau}-n_{\ell\tau}>0}\left[\delta_{\sigma,\tau}\delta_{i,k}\delta_{j,\ell}\frac{\omega-(\epsilon_{k\sigma}-\epsilon_{\ell\sigma})}{n_{k\tau}-n_{\ell\tau}} - K_{ij\sigma,k\ell\tau}(\omega)\right]\delta P_{k\ell\tau}(\omega)\\ -\sum_{k\ell\tau}^{n_{k\tau}-n_{\ell\tau}>0} K_{ij\sigma,k\ell\tau}(\omega)\delta P_{\ell k\tau}(\omega) = \delta v^{appl}_{ij\sigma}(\omega),\end{aligned} \tag{2.31}$$

and the second giving the hp part of δv^{appl},

$$\begin{aligned}\sum_{k\ell\tau}^{n_{k\tau}-n_{\ell\tau}>0}[\delta_{\sigma,\tau}\delta_{i,k}\delta_{j,\ell}\frac{\omega-(\epsilon_{\ell\sigma}-\epsilon_{k\sigma})}{n_{\ell\tau}-n_{k\tau}} - K_{ji\sigma,k\ell\tau}(\omega)]\delta P_{k\ell\tau}(\omega)\\ -\sum_{k\ell\tau}^{n_{k\tau}-n_{\ell\tau}>0} K_{ji\sigma,k\ell\tau}(\omega)\delta P_{k\ell\tau}(\omega) = \delta v^{appl}_{ji\sigma}(\omega),\end{aligned} \tag{2.32}$$

If the molecular orbitals are real, using the symmetry property in Eq.(2.30), we can combine Eqs.(2.31) and (2.32) into a single matrix equation as,

$$\left[\begin{pmatrix} \mathbf{A}(\omega) & \mathbf{B}(\omega) \\ \mathbf{B}(\omega) & \mathbf{A}(\omega) \end{pmatrix} - \omega \begin{pmatrix} \mathbf{C} & 0 \\ 0 & -\mathbf{C} \end{pmatrix}\right] \begin{pmatrix} \delta P(\omega) \\ \delta \mathbf{P}^*(\omega) \end{pmatrix} = \begin{pmatrix} v_{appl}(\omega) \\ \delta v^*_{appl}(\omega) \end{pmatrix} \tag{2.33}$$

where:

$$\begin{aligned} \mathbf{A}_{ij\sigma,k\ell\tau}(\omega) &= \delta_{\sigma,\tau}\delta_{i,k}\delta_{j,\ell}\frac{\epsilon_{k\tau}-\epsilon_{\ell\tau}}{n_{k\tau}-n_{\ell\tau}} - K_{ij\sigma,k\ell\tau}, \\ \mathbf{B}_{ij\sigma,k\ell\tau}(\omega) &= -K_{ji\sigma,k\ell\tau}(\omega), \\ \mathbf{C} &= \frac{\delta_{\sigma\tau}\delta_{i,k}\delta_{j,\ell}}{n_{k\tau}-n_{\ell\tau}}. \end{aligned}$$

Here, $\delta P(\omega)$ denotes the Fourier transform of $\delta P(t)$ (so $\delta P_{\ell k\tau}(\omega) = \delta P^*_{k\ell\tau}(\omega)$) and similarly for $\delta v^*_{appl}(\omega)$. Note that in each block, the rows are labelled by $ij\sigma$ with $n_{i\sigma} > n_{j\sigma}$ and the columns are labelled by $k\ell\tau$ with $n_{k\tau} > n_{\ell\tau}$.

A suitable unitary transformation of Eq.(2.33) gives

$$\left[\begin{pmatrix} \mathbf{A}(\omega)+\mathbf{B}(\omega) & 0 \\ 0 & \mathbf{B}(\omega)+\mathbf{A}(\omega) \end{pmatrix} - \omega \begin{pmatrix} -\mathbf{C} & 0 \\ 0 & -\mathbf{C} \end{pmatrix}\right] \begin{pmatrix} \Re\delta P(\omega) \\ -i\Im\delta \mathbf{P}^*(\omega) \end{pmatrix} = \begin{pmatrix} \Re\delta v_{appl}(\omega) \\ -i\Im\delta v^*_{appl}(\omega) \end{pmatrix} \tag{2.34}$$

Which can be used to obtain the real and imaginary parts of δP,

$$\left[[\mathbf{A}(\omega)-\mathbf{B}(\omega)] - \omega^2\mathbf{C}[\mathbf{A}(\omega)-\mathbf{B}(\omega)]^{-1}\mathbf{C}\right](\Im\delta P)(\omega) = \Im\delta v_{appl}(\omega) \tag{2.35}$$

and for the real part

$$-i\omega\mathbf{C}[\mathbf{A}(\omega)+\mathbf{B}(\omega)]^{-1}(\Re\delta P_{k\ell\tau})(\omega) = \Re\delta v_{appl}(\omega) \tag{2.36}$$

For real perturbations, the real part of the response of the density matrix is given by

$$\begin{aligned} &\sum_{k\ell\tau}^{n_{k\tau}-n_{\ell\tau}>0} [\delta_{k\ell}\delta_{i,k}\delta_{j,\ell}\frac{\epsilon_{k\sigma}-\epsilon_{\ell\tau}}{n_{k\tau}-n_{\ell\tau}} - 2K_{ij\sigma,k\ell\tau}(\omega) \\ -\omega^2&\frac{\delta_{\sigma,\tau}\delta_{i,k}\delta_{j,\ell}}{(n_{k\ell}-n_{\ell,\tau})(\epsilon_{k\tau}-\epsilon_{\ell\tau})}](\Re\delta P_{k\ell\tau})(\omega) = \delta v^{appl}_{ij\sigma}(\omega) \end{aligned} \tag{2.37}$$

2.3 Solving The Eigenvalue Problem

Once the pseudopotential has been determined, the resulting eigenvalue problem needs to be solved for the system of interest is,

$$\ell \left[-\frac{\hbar^2 \nabla^2}{2m} + V^p_{ion}(\vec{r}) + V_H(\vec{r}) + V_{xc}[\vec{r}, \rho(\vec{r})] \right] \phi_n(\vec{r}) = 0 \tag{2.38}$$

where V^p_{ion} is the ionic potential for the system. Since the ion can be treated as the chemically inert and highly localized, it is a simple matter to write:

$$V^p_{ion}(\vec{r}) = \sum_{\vec{R}_a} V^p_{ion,a}(\vec{r} - \vec{R}_a) \tag{2.39}$$

where $V^p_{ion,a}$ is the ion core pseudopotential associated with the atom, a, at a position R_a.

Chapter 3

Results for Excitation Energies and Optical Gap

3.1 Calculation of Excitation Energies and Oscillator Strength

The interaction of an atom or a molecule with light can be modelled as the the interaction with an electric field varying sinusoidally in time. Excitation energies and oscillator strengths can then be obtained from the poles and residues of the dynamic polarizability.

The dynamic polarizability can be obtained by introducing a perturbation

$$\delta v_{appl}(t) = \hat{\gamma}\varepsilon_{\gamma}(t), \tag{3.1}$$

and expanding the $\hat{\gamma}$ component of the dipole moment to first order in the function $\varepsilon_{\gamma}(t)$,

$$\mu_{\beta}(t) = \mu_{\beta} + \int_{-\infty}^{\infty} \alpha_{\gamma\beta}(t-t')\varepsilon_{\gamma}(t')dt' + ..., \tag{3.2}$$

where the first term on the right hand side refers to the permanent dipole moment.

Then, from the convolution theorem

$$\alpha_{\beta\gamma}(\omega) = \frac{\delta\mu_\beta(\omega)}{\varepsilon_\gamma(\omega)}, \tag{3.3}$$

where $\delta\mu_\beta(\omega)$ is the linear response of the dipole moment.

Since

$$\delta\mu_\beta(\omega) = -\sum_{ij\sigma} \beta_{ji\sigma}\delta P_{ij\sigma} = -\sum_{ij\sigma,k\ell\tau} \beta_{ji\sigma}\chi_{ij\sigma,k\ell\tau}(\omega)\gamma_{k\ell\tau}\varepsilon_\gamma(\omega), \tag{3.4}$$

It follows that

$$\alpha_{\gamma\beta}(\omega) = -\sum_{ij\sigma,k\ell\tau} \beta_{ji\sigma}\chi_{ij\sigma,k\ell\tau}(\omega)\gamma_{k\ell\tau}. \tag{3.5}$$

Using Eq.(2.18), Eq.(3.5) can be written as,

$$\begin{aligned}
\alpha_{\beta\gamma}(\omega) &= -\sum_{ij\sigma,k\ell\tau} \beta_{ji\sigma}[\sum_I \frac{\langle\Psi_0|\hat{a}^\dagger_{j\sigma}\hat{a}_{i\sigma}|\Psi_I\rangle\langle\Psi_I|\hat{a}^\dagger_{\ell\tau}\hat{a}_{k\tau}|\Psi_0\rangle}{\omega-(E_I-E_0)} \\
&- \frac{\langle\Psi_I|\hat{a}^\dagger_{\ell\tau}\hat{a}k\tau|\Psi_0\rangle\langle\Psi_0|\hat{a}^\dagger_{j\sigma}\hat{i\sigma}|\Psi_I\rangle}{\omega+(E_I-E_0)}]\gamma_{k\ell\tau} \\
&= -\sum_I \left[\frac{\langle\Psi_I|\hat{\beta}|\Psi_0\rangle\langle\Psi_0|\hat{\gamma}|\Psi_I\rangle}{\omega-(E_I-E_0)} - \frac{\langle\Psi_I|\hat{\gamma}|\Psi_0\rangle\langle\Psi_0|\hat{\beta}|\Psi_I\rangle}{\omega+(E_I-E_0)}\right]
\end{aligned} \tag{3.6}$$

Using the fact that $\langle\Psi_I|\hat{\beta}|\Psi_0\rangle\langle\Psi_0|\hat{\gamma}|\Psi_I\rangle = \langle\Psi_I|\hat{\gamma}|\Psi_0\rangle\langle\Psi_0|\hat{\beta}|\Psi_I\rangle$ the above equation will reduce to

$$\alpha_{\beta\gamma}(\omega) = \sum_I \frac{2\langle\Psi_I|\hat{\beta}|\Psi_0\rangle\langle\Psi_0|\hat{\gamma}|\Psi_I\rangle}{(E_I-E_0)^2-\omega^2} \tag{3.7}$$

This expression is interesting due to the fact that it shows the spectroscopic oscillator strengths,

$$f_I = \frac{2}{3}\sum_I (E_I-E_0)\left[|\langle\Psi_0|\hat{\gamma}|\Psi_I\rangle|^2 + |\langle\Psi_0|\hat{\beta}|\Psi_I\rangle|^2\right] \tag{3.8}$$

and the excitation energies $\omega_I = E_I - E_0$ are poles and residues of the mean polarizability,

$$\bar{\alpha}(\omega) = \frac{1}{3}tr\left(\alpha(\omega)\right) = \sum_I \frac{f_I}{\omega_I^2-\omega^2}. \tag{3.9}$$

For real perturbation, the polarizability will only involve the real part of δP, using Eq.(3.5), the real part of the dynamic polarizability tensor is given by

$$\alpha_{\beta\gamma}(\omega) = -2 \sum_{ij\gamma}^{n_{i\sigma}-n_{j\sigma}>0} \frac{\beta_{ij\sigma}\Re\delta P_{ij\sigma}}{\varepsilon_\gamma}. \tag{3.10}$$

Considering Eq.(2.35), let

$$\mathbf{S}(\omega) = -\mathbf{C}(\mathbf{A}-\mathbf{B})^{-1}\mathbf{C}, \tag{3.11}$$

and

$$\Omega(\omega) = -\mathbf{S}^{-\frac{1}{2}}(\mathbf{A}+\mathbf{B})^{-1}\mathbf{S}^{-\frac{1}{2}}, \tag{3.12}$$

with the above expressions the real part of the linear response of the density matrix is given by

$$(\Re\delta P(\omega)) = \mathbf{S}^{-\frac{1}{2}}\left[\omega^2\mathbf{1} - \mathbf{\Omega}(\omega)\right]^{-1}\mathbf{S}^{-\frac{1}{2}}(\Re\delta v_{appl}(\omega)). \tag{3.13}$$

The simplified matrix forms of $\mathbf{S}$ and $\mathbf{\Omega}$ are given by

$$\mathbf{S}(\omega) = -\frac{\delta_{\sigma,\tau}\delta_{i,k}\delta_{j,\ell}}{(n_{k\tau}-n_{\ell\tau})(\epsilon_{k\tau}-\epsilon_{\ell\tau})}. \tag{3.14}$$

and

$$\mathbf{\Omega}(\omega) = \delta_{\sigma,\tau}\delta_{i,k}\delta_{j,\ell}(\epsilon_{\ell\tau}-\epsilon_{k\tau})^2 + 2\sqrt{(n_{i\sigma}-n_{j\sigma})(\epsilon_{j\sigma}-\epsilon_{i\sigma})}K_{i,j,\sigma,k\ell\tau}\sqrt{(n_{k\tau}-n_{\ell\tau})(\epsilon_{\ell\tau}-\epsilon_{k\tau})}. \tag{3.15}$$

Using Eq.(3.13), Eq.(3.10) can be written as

$$\alpha_{\beta\gamma} = 2\beta^\dagger\mathbf{S}^{-\frac{1}{2}}\left[\mathbf{\Omega}(\omega)-\omega^2\mathbf{1}\right]\mathbf{S}^{-\frac{1}{2}}\gamma \tag{3.16}$$

The excitation energies and the oscillator strengths may be obtained by comparing the above equation with the SOS formula for the polarizability. Since $\alpha(\omega)$ has poles at the excitation energies, ω_I, it follows that the excitation energies are the solutions of the psuedoeigen value problem,

$$\mathbf{\Omega}(\omega)\mathbf{F}_I = \omega_I^2\mathbf{F}_I \tag{3.17}$$

It is also clear from the SOS formula that $\alpha(\omega)$ is even function of ω, thus $\Omega(\omega)$ and $K(\omega)$ must also be even functions of ω, and hence Eq.(2.27) are hermitian matrices.

Taking the spectral expansion of the SOS formula, we have

$$\left[\mathbf{\Omega}(\omega) - \omega^2\mathbf{1}\right]^{-1} = \sum_I \frac{R_I}{\omega_I^2 - \omega^2}\mathbf{F}_I\mathbf{F}_I^\dagger \tag{3.18}$$

Note that $R_I \neq 1$ if the pseudoeigen vectors $\mathbf{F}_I^\dagger$ are normalized to 1.(unless Ω is independent of ω). Instead, it is convenient to normalize the $\tilde{\mathbf{F}}_\mathbf{I}^\dagger$ such that $R_I = 1$.

The value of R_I is most easily determined for non-degenerate states, in which case

$$\left[\mathbf{\Omega}(\omega) - \omega^2\mathbf{1}\right]^{-1} \cong \frac{R_I}{\omega_I^2 - \omega^2}\tilde{\mathbf{F}}_I\mathbf{F}_I^\dagger \tag{3.19}$$

near $\omega = \omega_I$. Then

$$R_I^{-1} \cong \mathbf{F}_I^\dagger \frac{\mathbf{\Omega}(\omega) - \omega^2\mathbf{1}}{\omega^2 - \omega_I^2}\mathbf{F}_I \longrightarrow \mathbf{F}_I^\dagger \left[1 - \left[\frac{\partial\Omega(\omega)}{\partial\omega^2}\right]_{\omega=\omega_I}\right]\mathbf{F}_I, \tag{3.20}$$

as $\omega \longrightarrow \omega_I$. Renormalizing the pseudoeigen vectors such that

$$\mathbf{F}_I^\dagger \left[1 - \left[\frac{\partial\Omega(\omega)}{\partial\omega^2}\right]_{\omega=\omega_I}\right]\mathbf{F}_I = 1, \tag{3.21}$$

then yields $R_I = 1$. Hence $\mathbf{F}_I$ will always refer to these normalized peudoeigen vectors. Rewriting the expression for the dynamic polarizability using the spectral expansion in terms of the renormalized $\mathbf{F}_I$, and comparing with the SOS formula Eq.(3.7) we get

$$\beta^\dagger\mathbf{S}^{-\frac{1}{2}}\mathbf{F}_I = \omega_I^{\frac{1}{2}}\langle\Psi_0|\hat{\gamma}|\Psi_I\rangle \tag{3.22}$$

so that the oscillator strength is given by

$$f_I = \frac{2}{3}\left[|x^{\dagger}\mathbf{S}^{-\frac{1}{2}}\mathbf{F}_I|^2 + |y^{\dagger}\mathbf{S}^{-\frac{1}{2}}\mathbf{F}_I|^2 |z^{\dagger}\mathbf{S}^{-\frac{1}{2}}\mathbf{F}_I|^2\right] \tag{3.23}$$

According to the Thomas-Reiche-Kuhn (TRK) sum rule [], the sum of the oscillator strengths should be equal to the number of electrons. This can be used to gauge the quality of the basis set, when working with frequency-independent approximations for K. When Ω is independent of ω, the renormalized $\mathbf{F}_I$ from a complete orthonormal set,

$$\mathbf{F}_I\mathbf{F}_I^{\dagger} = 1. \tag{3.24}$$

It then follows that

$$f_I = \frac{2}{3}\left[|x^{\dagger}\mathbf{S}^{-\frac{1}{2}}\mathbf{F}_I|^2 + |y^{\dagger}\mathbf{S}^{-\frac{1}{2}}\mathbf{F}_I|^2 |z^{\dagger}\mathbf{S}^{-\frac{1}{2}}\mathbf{F}_I|^2\right]. \tag{3.25}$$

3.2 Approximation of the Exchange-Correlation Kernel

For simplicity one can split the exchange-correlation kernel given in Eq. (2.24) in to two parts: $K = K^{(I)} + K^{(II)}$. The first term represents a double integral over $\frac{1}{|\mathbf{r}-\mathbf{r}\prime|}$. Instead of performing the costly double integration by direct summation, we calculate this term by solving the Poisson equation with in the boundary domain. The conjugate-gradient method is employed to solve this equation.

$$\nabla^2\Phi_{ij\sigma} = -4\pi\psi_{i\sigma}(\mathbf{r})\psi_{j\sigma}(\mathbf{r}). \tag{3.26}$$

The first term in Eq.(2.24) is calculated as

$$K^{(I)}_{ij\sigma,k\ell\tau} = \int \Phi_{ij\sigma}(\mathbf{r})\psi_{k\tau}(\mathbf{r})\psi_{\ell\tau}(\mathbf{r})d\mathbf{r}. \tag{3.27}$$

The second term in Eq. (2.24) represents a double integral over the functional derivative of the exchange-correlation energy, $\delta^2 E_{xc}[\rho]/\delta\rho_\sigma(\mathbf{r})\delta\rho_\tau(\mathbf{r\prime})$. Within the local approximation of the exchange-correlation potential this term is reduced to a single integral,

$$K^{(II)}_{ij\sigma,k\ell\tau} = \int \psi_{i\sigma(\mathbf{r})}\psi_{j\sigma(\mathbf{r})}\frac{\delta^2 E_{xc}[\rho]}{\delta\rho_\sigma(\mathbf{r})\delta\rho_\tau(\mathbf{r})}\psi_{k\tau(\mathbf{r})}\psi_{\ell\tau(\mathbf{r})}d\mathbf{r}, \tag{3.28}$$

The above equation requires the evaluation of the second derivatives for the spin-up and spin-down charge densities. The LDA exchange energy per particle is normally approximated by that of the homogeneous electron gas, []

$$\epsilon_x[\rho_\sigma(\mathbf{r})] = -\frac{3}{4\pi}\left(6\pi^2\rho_\sigma(\mathbf{r})\right)^{\frac{1}{3}} \qquad \sigma = \{\uparrow,\downarrow\}. \tag{3.29}$$

The first derivative of the total exchange energy determines the LDA exchange potential,

$$\frac{\delta E_x[\rho]}{\delta\rho_\sigma} = v_x[\rho_\sigma] = -\frac{1}{\pi}\left(6\pi^2\rho_\sigma(\mathbf{r})\right)^{\frac{1}{3}} \qquad \sigma = \{\uparrow,\downarrow\}. \tag{3.30}$$

The second derivatives are:

$$\frac{\delta^2 E_x[\rho]}{\delta\rho_\uparrow\delta\rho_\uparrow} = -\left(\frac{2}{9\pi}\right)^{\frac{1}{3}}\rho_\downarrow^{-\frac{2}{3}}, \qquad \frac{\delta^2 E_x[\rho]}{\delta\rho_\uparrow\delta\rho_\downarrow} = 0. \tag{3.31}$$

A parameterized form of Ceperley-Alder functional [] can be used for the LDA correlation energy. This functional is based on two different analytical expressions for $r_s < 1$ and $r_s \geq 1$, where $r_s = (3/4\pi\rho)^{1/3}$ is the local Seitz radius and $\rho = \rho_\uparrow + \rho_\downarrow$. One can adjust the parametr for $r_s < 1$ to guarantee a continuous second derivative of the correlation energy. The adjusted interpolation formula for the correlation energy per particle is given by []

$$\epsilon_c^{U,P} = \begin{cases} A\ln r_s + B + Cr_s + Dr_s + Xr_s^2\ln r_s & r_s \geq 1 \\ \gamma/(1+\beta_1\sqrt{r_s}+\beta_2 r_s) & r_s < 1 \end{cases} \tag{3.32}$$

where two separate sets of coefficients are used for the polarized spin (P) and unpolarized spin (U) cases. The numerical values of all fitting parameters appearing in Eq. (3.32) can be found in Ref. []. The adjusted interpolation formula for the correlation energy is continuous up to its second derivative, while the original Perdew-Zunger parametrization is not [].

Equations (3.29) .. (3.32) describe only the cases of the completely polarized and unpolarized spin. For intermediate spin polarizations, the correlation energy can be obtained with a simple interpolation formula,

$$\epsilon_c = \epsilon_c^U + \xi(\rho)[\epsilon_c^P - \epsilon_c^U], \tag{3.33}$$

where

$$\xi(\rho) = \frac{1}{1-2^{-1/3}}\left(x_\uparrow^{4/3} + x_\downarrow^{4/3} - 2^{-1/3}\right); \qquad \textit{with} \qquad x_\uparrow = \frac{\rho_\uparrow}{\rho}, \quad x_\downarrow = \frac{\rho_\downarrow}{\rho}. \tag{3.34}$$

The expression for the second derivative of the correlation energy in case of an arbitrary spin polarization can be written as

$$\frac{\delta^2 E_c[\rho]}{\delta\rho_\sigma\delta\rho_\tau} = \frac{\delta^2 E_c^U}{\rho^2} + \xi(\rho)\left(\frac{\delta^2 E_c^P}{\delta\rho^2} - \frac{\delta^2 E_c^U}{\delta\rho^2}\right) \tag{3.35}$$

$$\left(\frac{\partial\xi(\rho)}{\partial\rho_\sigma} + \frac{\partial\xi(\rho)}{\partial\rho_\tau}\right)\left(\frac{\delta E_c^P}{\delta\rho} - \frac{\delta E_c^U}{\delta\rho}\right) + \frac{\partial^2\xi(\rho)}{\partial\rho_\sigma\partial\rho_\tau}\rho\left(\epsilon_c^P - \epsilon_c^U\right), \quad \sigma,\tau = \{\uparrow,\downarrow\}, \tag{3.36}$$

where the spin polarization function, $\xi(\rho)$, and its derivatives are given by

$$\frac{\partial\xi(\rho)}{\partial\rho_\uparrow} = \frac{4}{3\rho\left(1-2^{-1/3}\right)}\left(x_\uparrow^{1/3} - x_\uparrow^{4/3} - x_\downarrow^{1/3}\right), \tag{3.37}$$

$$\frac{\partial^2\xi(\rho)}{\partial\rho_\uparrow\partial\rho_\uparrow} = \frac{4}{9\rho^2\left(1-2^{-1/3}\right)}\left(x_\uparrow^{-2/3} - 8x_\uparrow^{1/3} + 7(x_\uparrow^{1/3} + x_\downarrow^{4/3})\right), \tag{3.38}$$

$$\frac{\partial^2\xi(\rho)}{\partial\rho_\uparrow\partial\rho_\downarrow} = \frac{4}{9\rho^2\left(1-2^{-1/3}\right)}\left(7(x_\uparrow^{4/3} + x_\downarrow^{4/3}) - 4(x_\uparrow^{4/3} + x_\downarrow^{1/3})\right). \tag{3.39}$$

The TDLDA formalism presented in previous sections can be further simplified for systems with the unpolarized spin. In this case, the spin-up and spin-down charge densities are equal, $\rho_\uparrow = \rho_\downarrow$, and Eqs. (3.34), (3.36)-(3.38) yield

$$\xi(\rho) = 0, \qquad \frac{\partial^2 \xi(\rho)}{\partial \rho_\uparrow \partial \rho_\uparrow} = \frac{4}{9\rho^2\left(2^{1/3} - 1\right)} \tag{3.40}$$

$$\frac{\partial \xi(\rho)}{\partial \rho_\uparrow} = 0, \qquad \frac{\partial^2 \xi(\rho)}{\partial \rho_\uparrow \partial \rho_\downarrow} = -\frac{4}{9\rho^2\left(2^{1/3} - 1\right)} \tag{3.41}$$

Since the coordinate parts of spin-up and spin-down Kohn-Sham wave functions for systems with the unpolarized spin are identical, $\psi_{i\uparrow} = \psi_{i\downarrow}$,it follows that $\Omega_{ij\uparrow,k\ell\uparrow} = \Omega_{ij\downarrow,k\ell\downarrow}$ and $Q_{ij\uparrow,k\ell\downarrow} = \Omega_{ij\downarrow,k\ell\uparrow}$. This allows us to separate "singlet" and "triplet" transitions by representing Eq. (3.17) in the basis set of $\{\mathbf{F}_+, \mathbf{F}_-\}$, chosen as

$$\mathbf{F}_{ij}^{\{+,-\}} = \frac{1}{\sqrt{2}}(\mathbf{F}_{ij\uparrow} \pm \mathbf{F}_{ij\downarrow}). \tag{3.42}$$

In this basis, the matrix $\mathbf{\Omega}$ becomes

$$\mathbf{\Omega}_{ij,k\ell}^{\{+,-\}} = \delta_{i,k}\delta_{j,\ell}\omega_{k\ell}^2 + 2\sqrt{\lambda_{ij}\omega_{ij}}\mathbf{K}_{ij,k\ell}^{\{+,-\}}\sqrt{\lambda_{k\ell}\omega_{k\ell}}, \tag{3.43}$$

where $\mathbf{K}_{ij,k\ell}^{\{+,-\}} = \mathbf{K}_{ij\uparrow,k\ell\downarrow}$. The components of $\mathbf{K}^{\{+,-\}}$ in their explicit form are given by

$$\begin{aligned} \mathbf{K}_{ij,k\ell}^{+} &= 2\int\int \frac{\psi_i(\mathbf{r})\psi_j(\mathbf{r\prime})\psi_\ell(\mathbf{r\prime})}{|\mathbf{r} - \mathbf{r\prime}|} d\mathbf{r} d\mathbf{r\prime} \\ &+ 2\int \psi_i(\mathbf{r})\psi_j(\mathbf{r}) \left(\frac{\delta^2 E_c^U}{\delta\rho^2} - \frac{1}{(9\pi)^{1/3}\rho^{2/3}}\right)\psi_k(\mathbf{r})\psi_\ell(\mathbf{r}) d\mathbf{r}, \end{aligned} \tag{3.44}$$

$$\mathbf{K}_{ij,k\ell}^{-} = 2\int \psi_i(\mathbf{r})\psi_j(\mathbf{r}) \left(\frac{4(\epsilon_c^P - \epsilon_c^U)}{9(2^{1/3} - 1)} - \frac{1}{(9\pi)^{1/3}\rho^{2/3}}\right)\psi_k(\mathbf{r})\psi_\ell(\mathbf{r}) d\mathbf{r}. \tag{3.45}$$

For most practical applications, only "singlet" transitions represented by the $\mathbf{F}_+$ basis vectors are of interest. Triplet transitions described by the $\mathbf{F}_-$ vectors have zero dipole oscillator strength and do not contribute to optical absorption.

3.3 Calculation of Optical Gap

The first step in the calculation of optical gap involves the calculation of the quasi-particle gap, which is the energy needed to create a non-interacting electron-hole pair. The second component is due to the direct Coulomb (E_{Coul}) and exchange (E_{ex}) electron-hole interactions comprising the exciton binding energy.

For an n-electron system, the quasi-particle gap ε_g^{qp} can be expressed in terms of the ground state total energies E of the (n+1)-, (n-1)-, and n-electron system as

$$\varepsilon_g^{qp} = (E_{n+1} - E_n) - (E_n - E_{n-1}) = E_{n+1} + E_{n-1} - 2E_n = \varepsilon_g^{HL} + \Sigma, \qquad (3.46)$$

where Σ is the self-energy correction to the HOMO-LUMO gap ε_g^{HL} obtained with in LDA. This definition is quite convenient for the calculation of the quasi-particle gap, as it is possible to excite individual electrons or holes from the ground state to electronic configuration of a confined system. Eq. (3.26) yields the correct quasi-particle gap ε_g^{qp} if the exchange-correlation functional is used.

Q.dot	ε_g^{HL}	ε_g^{qp}	GW
SiH_4	7.9	12.3	12.7
Si_2H_6	6.7	10.7	10.6
Si_5H_{12}	6.0	9.7	9.8
$\mathrm{Si}_{14}H_{20}$	4.4	7.6	8.0

Table 3.1: HOMO-LUMO and quasi-particle gaps (Eq.3.26) calculated for hydrogen terminated Si clusters compared to the quasiparticle gaps calculated with in the GW approximation [ ]. All energies are in eV.

For a dot having comparable size to the exciton binding energy the quasi-particle gap can not be used directly to measure the optical gap. Quantum confinement in nano-structures enhances the bare exciton Coulomb interaction, and reduces the electronic screening so that the exciton Coulomb energy becomes comparable to the quasi-particle gap,

$$\varepsilon_g^{opt} = \varepsilon_g^{qp} - E_{Coul}, \tag{3.47}$$

Since the exciton exchange-correlation energies are much smaller than E_{Coul} for the quantum dots it will be neglected. E_{Coul} is better calculated using ab initio pseudo wave functions. The exciton Coulomb energy can be written as

$$\begin{aligned} E_{Coul} &= \int d\mathbf{r}_1 |\psi_e(\mathbf{r}_1)|^2 V_{scr}^h(\mathbf{r}_1), \\ &= \int d\mathbf{r}_1 |\psi_e|^2 \int d\mathbf{r} \epsilon^{-1}(\mathbf{r}_1, r) V_{unscr}^h(\mathbf{r}), \\ &= \int\int\int \epsilon^{-1}(\mathbf{r}_1, r) \frac{|\psi_e(\mathbf{r}_1)|^2 |\psi_h(\mathbf{r}_2)|^2}{|\mathbf{r} - \mathbf{r}_2|} d\mathbf{r} d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned} \tag{3.48}$$

In the above expression V_{scr}^h and V_{unscr}^h are the screened and unscreened potentials due to holes, ψ_e and ψ_h are the electron and hole wave functions, and ϵ^{-1} is the inverse of the microscopic dielectric matrix. One can define ϵ^{-1} as

$$\int \frac{\epsilon^{-1}}{|\mathbf{r} - \mathbf{r}_1|} dr \equiv \frac{\tilde{\epsilon}^{-1}}{|\mathbf{r}_1 - \mathbf{r}_2|}. \tag{3.49}$$

Then the exciton Coulomb energy can be written as

$$E_{Coul} = \int\int \tilde{\epsilon}^{-1} \frac{|\psi_e(\mathbf{r}_1)|^2 |\psi_h(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2, \tag{3.50}$$

if $\tilde{\epsilon}^{-1}$ is taken to be unity the unscreened Coulomb energy can be determined.

In order to calculate Eq.(3.30), $\epsilon(\mathbf{r}, \mathbf{r}')$ needs to be calculated. With in density functional linear response theory, $\epsilon(\mathbf{r}, \mathbf{r}')$ can be shown to have

$$\epsilon = \delta(\mathbf{r} - \mathbf{r}') - \int d\mathbf{r}_1 \left[\frac{1}{|\mathbf{r} - \mathbf{r}_1|} + \frac{\delta^2 E_{xc}}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}_1)} \right] \chi_0(\mathbf{r}_1, \mathbf{r}'), \tag{3.51}$$

where E_{xc} is the exchange correlation functional and $\chi_0(\mathbf{r}, \mathbf{r}')$ is the independent particle polarizability:

$$\chi_0(r, r\prime) = \sum_{i,j} (n_i - n_j) \frac{\psi_i^*(r)\psi_j(r)\psi_j^*(r\prime)\psi_i(r\prime)}{\epsilon_i - \epsilon_j}, \tag{3.52}$$

as expressed in terms of the Kohn-Sham wave functions and eigenvalues, $\psi_i(\mathbf{r})$ and ε_i having occupation number n_i.

With real wave functions and integer occupation numbers, the excitation for ϵ can be simplified by taking spin degeneracy into account as,

$$\epsilon(\mathbf{r}, \mathbf{r}\prime) = \delta(\mathbf{r} - \mathbf{r}') + 4 \sum_{v,c} [J_{vc}(\mathbf{r}) + K_{vc}(\mathbf{r})] \frac{\psi_v(\mathbf{r'})\psi_c(\mathbf{r'})}{\varepsilon_c - \varepsilon_v}, \tag{3.53}$$

where the summations v, care over the valence and conduction orbitals, and the integrals $J_{vc}(\mathbf{r})$ and $K_{vc}(\mathbf{r})$ are define as

$$J_{vc}(r) = \int d\mathbf{r}_1 \frac{\psi_v \psi_c}{|\mathbf{r} - \mathbf{r}_1|} \tag{3.54}$$

and

$$K_{vc}(\mathbf{r}) = \int d\mathbf{r}_1 \frac{\delta^2 E_{xc}}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}_1)} \psi_v \psi_c = \frac{\delta^2 E_{xc}}{\delta\rho^2(\mathbf{r})} \psi_v \psi_c, \tag{3.55}$$

For calculating exciton Coulomb energies and many other physical quantities, the inverse of the $\epsilon(r, r\prime)$ matrix is needed. Both the computational cost and storage requirement of ϵ^{-1} become critical problems for $N \sim 10^4$. The form of the dielectric response function in Eq. (3.33) allows us to reduce this computational cost and storage requirement significantly by observing that ϵ^{-1} is separable in r and $r\prime$. This makes it possible to express the matrix ϵ in terms of identity matrix I and rank $N_{vc} = N_v \times N_c$ matrices U and V, where N_v and N_c are the number of valence and conduction orbitals, respectively. The matrices U and V are defined as $U = 2(J_{vc} + K_{vc})$ and $V = \frac{2\psi_v\psi_c}{\epsilon_c - \epsilon_v}$ for which the rows are labelled (from 1 to N) by grid points, and the columns are labelled (from 1 to N_{vc}) by valence and conduction orbital pairs. This leads to the following matrix expression for the response function:

$$\epsilon = I + UV^T, \tag{3.56}$$

where V^T is the transpose of matrix V. Expressing the ϵ matrix in this fashion allows us to calculate its inverse in terms of the inverse of the matrix $X = I + V^T U$ as follows:

$$\epsilon^{-1} = (I + UV^\dagger)^{-1} = I - U\chi^{-1}V^T, \tag{3.57}$$

On a Cartesian grid of uniform spacing h, the elements of the inverse dielectric matrix can finally be written as

$$\epsilon_{ij} = \frac{1}{h^3}\left(\delta_{ij} - \sum_{k\ell=i}^{N_{vc}} U_{i,k} X^{-1}_{k\ell} V^T_{\ell,j}\right). \tag{3.58}$$

We note that X is a $N_{vc} \times N_{vc}$ matrix.

3.4 Computational Methods

A key aspect of our work is the availability of higher order expansions for the kinetic-energy operator, that is, expansion of the Laplacian. We impose a simple, uniform orthogonal three dimensional gird on our system where the points are described in a finite domain by (x_i, y_j, z_k). We approximate $\frac{\partial^2\psi}{\partial x^2}$ at $(x_i, y_j, z_k)$by

$$\frac{\partial^2\psi}{\partial x^2} = \sum_{n=-N}^{n=N} C_n \psi(x_i + nh, y_i, z_k) + O(h^{2N+2}), \tag{3.59}$$

where h is the grid spacing and N is a positive integer. This approximation is accurate to $O(h^{2N+2})$ upon the assumption that ψ can be approximated accurately by a power series in h. Algorithms are available to compute the coefficients C_n for arbitrary order in h. Expansion coefficients fir a uniform grid are shown in Table 3.2.

Within the kinetic energy operator expanded as in Eq.(3.59), one can set up a one electron *Schrödinger* equation over the grid. We will employ the local-density

-	C$_i$	C$_{i+1}$	C$_{i+2}$	C$_{i+3}$	C$_{i+4}$	C$_{i+5}$	C$_{i+6}$
N=1	-2	0	0	0	0	0	0
N=2	$-\frac{5}{2}$	0	0	0	0	0	0
N=3	$-\frac{49}{18}$	$\frac{3}{2}$	$-\frac{1}{12}$	$\frac{1}{90}$	0	0	0
N=4	$-\frac{205}{72}$	$\frac{16}{5}$	$-\frac{1}{515}$	-$\frac{1}{560}$	0	0	0
N=5	$-\frac{5269}{1800}$	-$\frac{5}{21}$	$-\frac{5}{126}$	-$\frac{5}{1008}$	$-\frac{1}{540}$	$\frac{2}{3150}$	0
N=6	$-\frac{5369}{1800}$	$\frac{12}{7}$	$-\frac{15}{56}$	-$\frac{10}{119}$	$-\frac{1}{112}$	$\frac{2}{1925}$	$-\frac{1}{16632}$

Table 3.2: Expansion coefficients $C_n n = 0, ... \pm N$, for higher-order finite-difference expressions of the second derivative.

approximation in setting up the *chrödinger*. We solve for $\psi(x_i, y_j, z_k)$ on the grid by the secular equation:

$$\begin{aligned}
- & \frac{\hbar^2}{2m}[\sum_{n_1=-N}^{n=N} C_{n_1}\psi(x_i + n_1 h, y_j, z_k) + \sum_{n_1=-N}^{N} C_{n_2}\psi(x_i, y_j + n_2 h, z_k) \\
+ & \sum_{n_3=-N}^{N} C_{n_3}\psi(x_i, y_j, z_k + n_3 h)] + [V_{ion}(x_i, y_j, z_k) + V_H(x_i, y_j, z_k) + V_{xc}(x_i, y_j, z_k)]\psi(x_i, y_j, z_k) \\
= & E(x_i, y_j, z_k)\psi(x_i, y_j, z_k) \qquad (3.60)
\end{aligned}$$

If there are M grid points, the size of the full matrix resulting the above eigenvalue problem is $M \times M$. V_{ion} is the nonlocal ionic pseudopotential, V_H is the Hartree potential, and V_{xc} is the local-density expression for the exchange correlation potential. The two parameters used in setting up the matrix are the grid spacing h, and the order N.

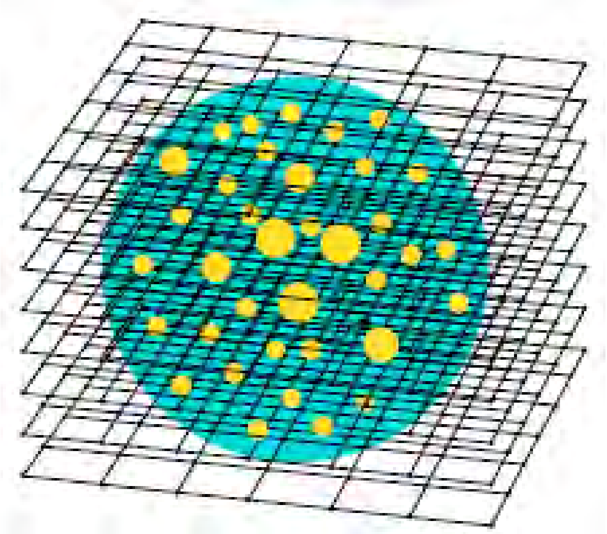

Figure 3.1: Uniform grid illustrating a typical configuration for examining the electronic structure of a localized system. The gray sphere represents the domain where the wavefunctions are allowed to be non-zero. The light spheres within the domain are atoms.

Chapter 4

Result and Discussion

In this chapter we will summarize and relate our theoretical calculations with experimental data.

4.1 Absorption Spectra of Hydrogenated Nanosilicon

Absorption Spectra of Si_nH_m clusters were calculated in two steps. First, the minimum energy cluster structure were obtained using real space pseudopotentil method and LDA exchange correlation potential. The optimized geometries of Si_nH_m clusters are shown in Fig.(4.1). After that, the linear response TDLDA formalism is applied to compute the the spectra of Si_nH_m clusters. Since all theoretical spectra were computed for the same cluster structures, the differences in the calculated spectra could be directly linked to the properties of the exchange-correlation functionals.

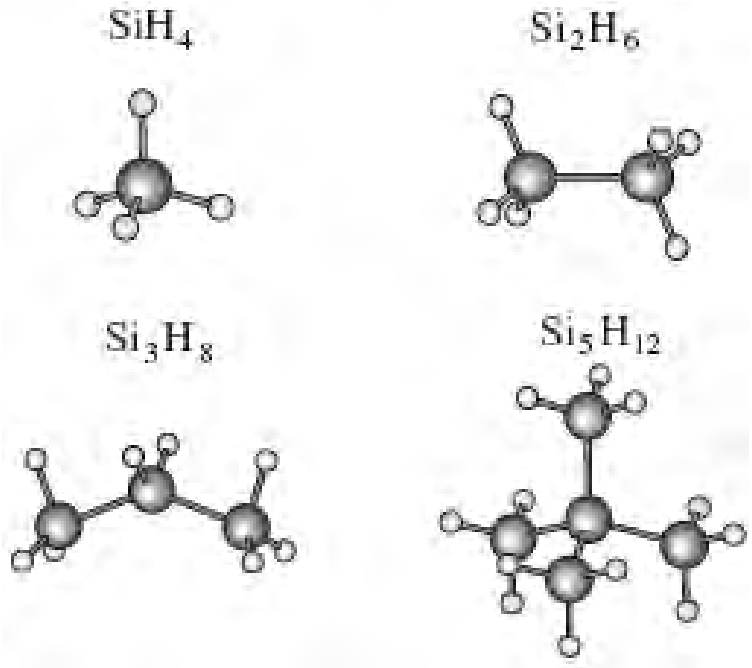

Figure 4.1: Structures of Si_nH_m clusters.[]

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4.2 Optical Gap Of Hydrogenated Nanosilicon

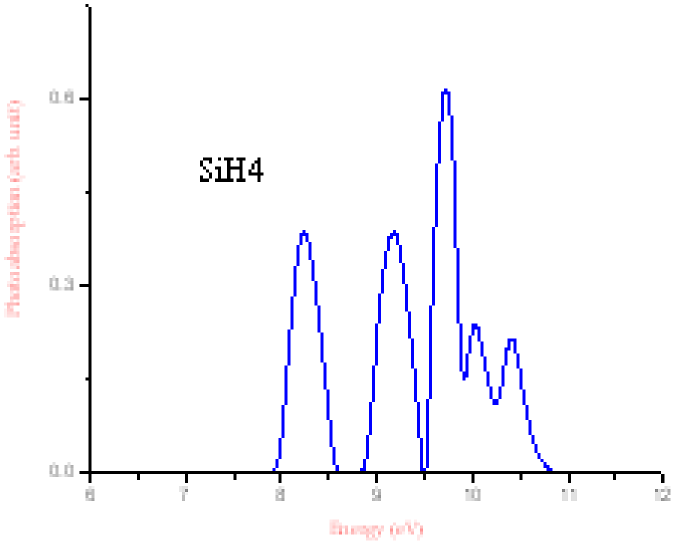

Figure 4.2: Photoabsorption verses Photon energy for SiH_4

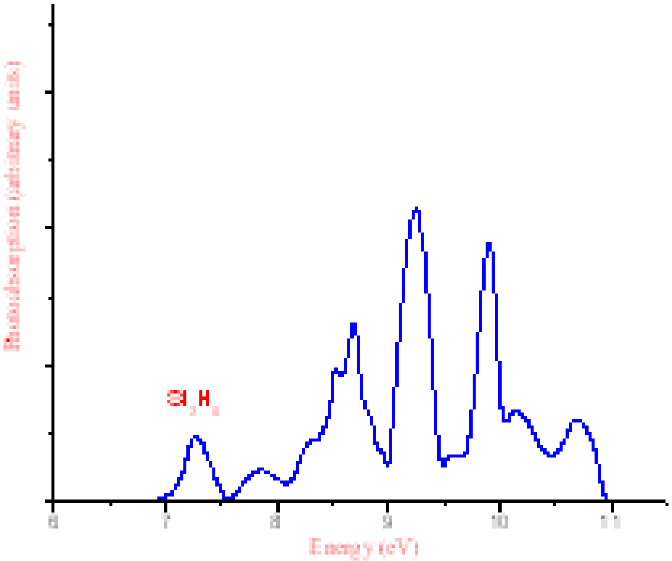

Figure 4.3: Photoabsorption verses Photon energy for Si_2H_6

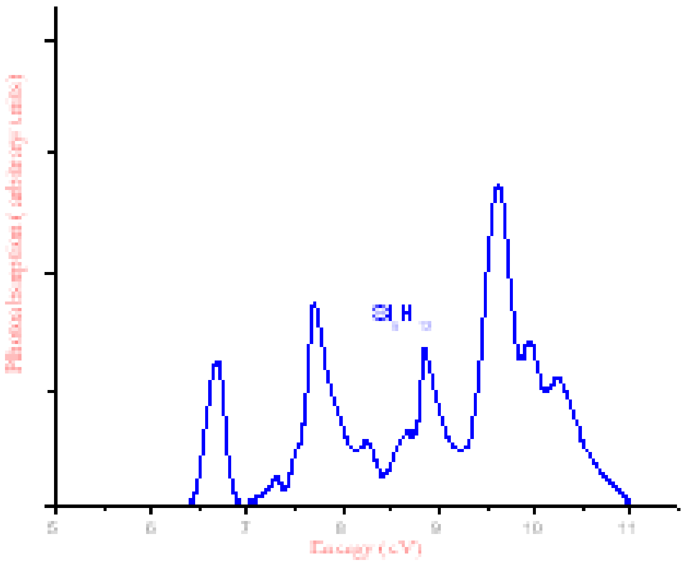

Figure 4.4: Photoabsorption verses Photon energy for Si_5H_{12}

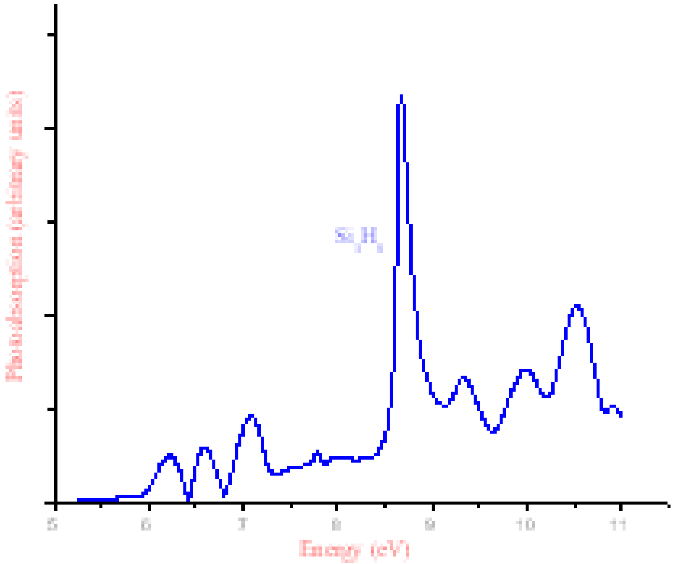

Figure 4.5: Photoabsorption verses Photon energy for Si_3H_8

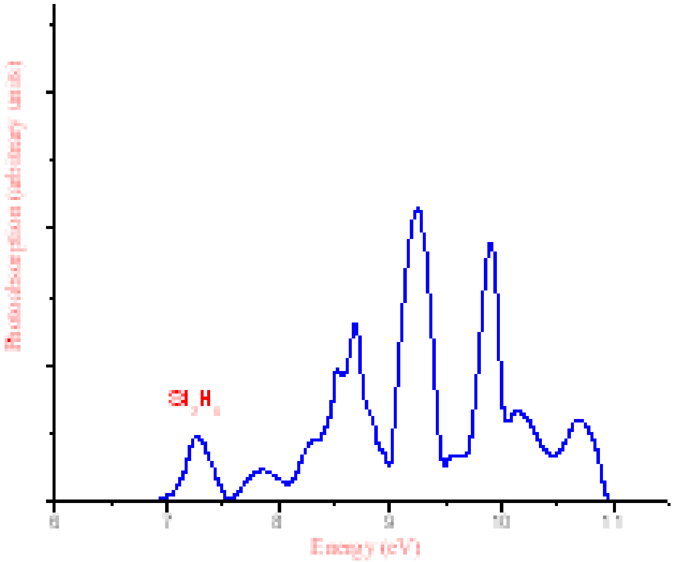

Figure 4.6: Photoabsorption verses Photon energy for Si_2H_6

	Excitation Energies		Ionization Energy
Cluster	Experiment	TDLDA	$-\varepsilon_{HOMO}^{LDA}$
SiH_4	8.8	8.2	8.6
	9.7	9.2	
	10.7	9.7	
Si_2H_6	7.6	7.2	7.5
	8.4	8.6	
Si_3H_8	6.6	6.2	6.9
	7.5	7.0	
	9.3	8.8	
Si_5H_{12}	6.5	6.6	7.3

Table 4.1: Excitation and excitation energies of Si_nH_m clusters. Experimental excitation energies are adapted from Refs. [3, 4]. All values are in eV.

Chapter 5

Summary And Conclusion

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