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# Survey of Techniques in Electronic Structure Theory

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## Introduction

The aim of this project was to learn the basic techniques of electronic structure theory and to gain some insight into the general theoretical framework of condensed matter physics. This was the studying phase of a prospective four phase project. So the focus was on building a strong theoretical foundation for future research work. Everything written in this report has been well established for some time. This report is roughly divided into two parts viz., the semi-empirical theory of band structure of solids and ab-initio methods of electronic structure theory. Although there is a significant overlap in the framework these two fields, here they have been presented with different perspectives.

In the first part, the emphasis is primarily on semi-empirical techniques of calculating band structures of solids. Various plane wave and tight binding methods are analyzed. In the second part, electronic structure theory is approached from an ab-initio perspective. The convenient formalism of second quantization is introduced first and subsequently used throughout the chapter. The Hartree-Fock theory and its application to free electron gas are examined. Finally the configuration interaction method of approximating electron-electron interactions has been touched upon.

# Contents

# Chapter 1

## Band Structures

The theory of electrons in matter has been among the greatest challenges in theoretical physics, because the number of atoms involved in condensed matter is great and the possibility of solving all the quantum mechanical equations in full detail is nonexistent. Use of approximations is inevitable. In this chapter, I will outline various methods of used to solve the problem of electronic structure in solids. The Born-Oppenheimer approximation of stationary nuclei and single particle approximation (simplistic but practically very decent and with good reason!) have been employed throughout.

### 1.1 Free electron gas [1]

In 1900, Drude proposed a theory of electronic and thermal conductivity of metals by applying the kinetic theory of gases to a gas of electrons. Although some predictions of this theory agreed with experiments (e.g. Hall's coefficient), some differed by orders of magnitude from observations (e.g. specific heat).

$$f_M(\mathbf{v}) = n \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T} \quad (1.1)$$

Sommerfeld applied quantum statistical mechanics to a free electron gas and managed resolve some anomalies of Drude's theory. He used the Fermi-Dirac statistics in place of the classical Maxwell-Boltzman statistics used by Drude. Mean square electronic speed according to Fermi statistics is about 100 times larger than predicted by Maxwell statistics.

$$\frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \quad (1.2)$$

$$f_F(\mathbf{v}) = \frac{m^3}{4\pi^3\hbar^3} \frac{1}{\exp[(\frac{mv^2}{2} - \mu)/k_B T] + 1} \quad (1.3)$$

Eigenstates of the hamiltonian are plane waves. At  $T = 0K$  (ground state) all states inside the Fermi sphere are occupied and average energy is non-zero. Properties at room temperature ( $\ll T_F$ ) are not drastically different from those at 0K. One of the successes of this theory was the correct prediction of linear variation of electronic contribution to specific heat with temperature.

$$n = \frac{k_F^3}{3\pi^2}, \quad \frac{E}{N} = \frac{3}{5}\hbar k_F, \quad c_v = \frac{\pi^2}{2} \left( \frac{k_B T}{E_F} \right) n k_B \quad (1.4)$$

Sommerfeld's model captures the features of some metals remarkably well, particularly the alkali metals. But it cannot be employed for any solid that happens to be an insulator. These discrepancies can be resolved to some extent by introduction of a periodic lattice potential.

## 1.2 Noninteracting electrons in a periodic potential

One of the mysteries surrounding motion of electrons in a metal was the observation of long mean free paths (much larger than atomic spacings). Bloch added back the interaction of electrons with the nuclei, treated as a static external potential. For general potentials the problem is still nearly intractable and Bloch made an additional simplification. He posed the problem of electrons moving about in a periodic potential. Bloch proposed that the electronic wavefunction in a such potentials is only a periodic modulation of a plane wave, thus explaining the long mean free paths. In this section, plane wave and tight binding methods used to solve the problem of noninteracting electrons in a periodic potential are discussed.

### 1.2.1 Plane wave methods

Plane wave methods provide general approaches for solving partial differential equations. Since plane waves are eigenstates of the Schrödinger equation with constant potential, they are a natural basis for explanation of band structure in weak potentials. These methods are generally applicable to metals and narrow band gap semiconductors, in which electrons are not strongly bound to the cores.

Let's first express the Schrödinger equation in a plane wave basis[1]. In position representation,

$$\frac{-\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (1.5)$$

Because the potential is periodic, it can be expressed as a Fourier series,

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} \quad (1.6)$$

where  $\mathbf{G}$  are reciprocal lattice vectors. Assuming periodic boundary conditions, wavefunction can also be written as a Fourier series,

$$|\psi\rangle = \sum_{\mathbf{q}} c_{\mathbf{q}} |\mathbf{q}\rangle \quad (1.7)$$

where  $c_{\mathbf{q}}$  are the components of  $|\psi\rangle$  in the orthonormal plane wave basis  $|\mathbf{q}\rangle$ . Substituting (1.5) and (1.6) into (1.5) and left multiplying by  $\langle\mathbf{q}'|$  we get,

$$\left(\frac{\hbar^2}{2m}\mathbf{q}'^2 - E\right) c_{\mathbf{q}'} + \sum_{\mathbf{G}} c_{\mathbf{q}'-\mathbf{G}} V_{\mathbf{G}} = 0 \quad (1.8)$$

Note that  $c_{\mathbf{q}'}$  only depends on the values of  $c_{\mathbf{q}-\mathbf{G}'}$ . Similar equations can be written by left multiplying (1.5) with  $\langle\mathbf{q}'-\mathbf{Q}|$ , where  $\mathbf{Q}$  is a reciprocal lattice vector. After rearranging and removing primes,

$$\left(\frac{\hbar^2}{2m}(\mathbf{q}-\mathbf{Q})^2 - E\right) c_{\mathbf{q}-\mathbf{Q}} + \sum_{\mathbf{G}} c_{\mathbf{q}-\mathbf{G}} V_{\mathbf{G}-\mathbf{Q}} = 0 \quad (1.9)$$

This is the Schrödinger equation with a periodic potential, written in momentum space. For each  $\mathbf{q}$  there is an eigenvalue equation, which is the same as that for  $\mathbf{q}-\mathbf{Q}$ . There are as many energy eigenvalues as there are reciprocal lattice vectors retained in the calculation (theoretically infinite). For each  $\mathbf{q}$  in the First Brillouin zone there are an infinite number of energy states labeled by the band index  $n$  and the solution can be expressed as,

$$|\psi_{\mathbf{qn}}\rangle = \sum_{\mathbf{G}} c_{\mathbf{G}n} |\mathbf{q}-\mathbf{G}\rangle \quad (1.10)$$

Bloch's theorem follows from this,

$$\psi_{\mathbf{qn}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{q}\cdot\mathbf{R}} \psi_{\mathbf{qn}}(\mathbf{r}) \quad (1.11)$$

where  $\mathbf{R}$  is a lattice vector.  $\mathbf{q}$  is called the crystal momentum of the state. In the limit of large volume  $\mathbf{q}$  values become continuous and the energy eigenvalues  $E_n(\mathbf{q})$  form bands. These Bloch states are filled with electrons according to the Fermi-Dirac statistics and thereby macroscopic properties can be predicted. It should be noted that this method of calculating the eigenstates, by directly solving the Schrödinger equation in momentum space, is of limited practical value because, the number of Fourier components of the lattice potential is fairly large.

### Nearly free electrons[4]

For a weak potential the problem of finding the eigenstates can be solved by perturbation theory. One has to be cautious of the degeneracies in the band structure. We saw above that the potential only mixes states that are separated by multiples of reciprocal lattice vectors. Thus unless  $E_{\mathbf{k}} = E_{\mathbf{k}+\mathbf{G}}$ , where  $\mathbf{G}$  is a reciprocal lattice vector, nondegenerate perturbation theory can be applied. This condition is satisfied at the Brillouin zone boundaries where degenerate perturbation theory should be used. Inside the zone boundaries,

$$E_{\mathbf{k}} = E_{\mathbf{k}}^0 + \langle \mathbf{k} | V(\mathbf{r}) | \mathbf{k} \rangle + \frac{2m}{\hbar^2} \sum_{\mathbf{G} \neq 0} \frac{|V_{\mathbf{G}}|^2}{\mathbf{k}^2 - (\mathbf{k} + \mathbf{G})^2} \quad (1.12)$$

where  $V(\mathbf{r})$  is assumed to be small. The first order term  $\langle \mathbf{k} | V | \mathbf{k} \rangle$  is just the average of the potential over a primitive lattice cell and is constant for all  $\mathbf{k}$ . Thus it can be ignored inside the BZ. The second order term is proportional to the square of the Fourier component of, which is assumed to be small. Therefore the band structure remains almost the same inside the BZ. At the zone boundaries the  $W$  matrix is given by,

$$\begin{pmatrix} \langle \mathbf{k} | V | \mathbf{k} \rangle & V_{\mathbf{G}} \\ V_{\mathbf{G}} & \langle \mathbf{k} | V | \mathbf{k} \rangle \end{pmatrix} \quad (1.13)$$

The eigenvalues give the following corrections at zone boundaries,

$$E^1 = \pm \sqrt{\frac{1}{a} [E_{\mathbf{k}}^0 - E_{\mathbf{k}+\mathbf{G}}^0]^2 + |V_{\mathbf{G}}|^2} \quad (1.14)$$

This significant first order correction gives rise to band gaps. This also provides the quantum mechanical justification of Bragg's law of diffraction.

### **k.p method**

This is another application of perturbation theory. Substituting a wavefunction of Bloch form ( $e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}n}(\mathbf{r})$ ) in Schrödinger equation, we get the following



equation for  $u_{\mathbf{k}n}(\mathbf{r})$ ,

$$\left[ \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) + \frac{\hbar}{m} \mathbf{k} \cdot \mathbf{p} + \frac{\hbar^2 \mathbf{k}^2}{2m} \right] u_{\mathbf{k}n}(\mathbf{r}) = E_{\mathbf{k}n} u_{\mathbf{k}n}(\mathbf{r}) \quad (1.15)$$

The hamiltonian can be split as,

$$\mathcal{H}_0 = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}), \quad \mathcal{H}_{\mathbf{k}} = \frac{\hbar}{m} \mathbf{k} \cdot \mathbf{p} + \frac{\hbar^2 \mathbf{k}^2}{2m} \quad (1.16)$$

Using the eigenstates at the  $\Gamma$  point (highly symmetric), perturbations can be calculated for  $\mathbf{k}$  values nearby.

$$\begin{aligned} \langle u_{0n} | \mathcal{H}_{\mathbf{k}} | u_{0n} \rangle &= \hbar \mathbf{k} \cdot \nabla_{\mathbf{k}} E_n(\mathbf{k})|_{\mathbf{k}=0} + \frac{\hbar^2 \mathbf{k}^2}{2m} \\ &= \frac{\hbar^2 \mathbf{k}^2}{2m} \end{aligned} \quad (1.17)$$

Because the dispersion relation has an extremum at the  $\Gamma$  point. Including the second order terms the energy is given by,

$$E_n(\mathbf{k}) = E_n(0) + \frac{\hbar^2 \mathbf{k}^2}{2m} + \frac{\hbar^2}{m^2} \sum_{n \neq m} \frac{\langle u_{0n} | \mathbf{k} \cdot \mathbf{p} | u_{0m} \rangle \langle u_{0m} | \mathbf{k} \cdot \mathbf{p} | u_{0n} \rangle}{E_n(0) - E_m(0)} \quad (1.18)$$

Effective mass matrix is given as,

$$M_{ij}^{-1} = \frac{1}{\hbar^2} \frac{\partial^2 E_n}{\partial k_i \partial k_j} = \frac{1}{m} \delta_{ij} + \frac{2}{m^2} \sum_{n \neq m} \frac{\langle u_{0n} | \mathbf{k} \cdot \mathbf{p} | u_{0m} \rangle \langle u_{0m} | \mathbf{k} \cdot \mathbf{p} | u_{0n} \rangle}{E_n(0) - E_m(0)} \quad (1.19)$$

This method can be used to calculate spin-orbit coupling effects in cubic semiconductors.

### 1.2.2 Orthogonalized plane wave (OPW) method

OPWs were introduced by Herring in 1940. They were the basis for the first quantitative band structure calculations. The plane waves are not well suited to approximate the rapidly oscillating wavefunction near cores of nuclei. This was combated by using plane waves orthogonalized to core levels. These are used to approximate the valence electron wave functions. The OPW  $\phi_{\mathbf{k}}$  is given by,

$$\phi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} + \sum_c b_c \psi_{\mathbf{k}}^c(\mathbf{r}) \quad (1.20)$$

where the sum is over all core levels with Bloch wave vector  $\mathbf{k}$ . The coefficients  $c_{\mathbf{k}}$  are chosen such that,

$$\langle \phi_{\mathbf{k}} | \psi_{\mathbf{k}}^c \rangle = 0 \implies b_c = - \int d\mathbf{r} \psi_{\mathbf{k}}^{c*} e^{i\mathbf{k} \cdot \mathbf{r}} \quad (1.21)$$

With a smart choice of the core wavefunctions OPWs can mimic the behavior of electronic wavefunctions efficiently in both core and interstitial regions. As both  $e^{i\mathbf{k} \cdot \mathbf{r}}$  and  $\psi_{\mathbf{k}(\mathbf{r})}^c$  are Bloch functions so is  $\phi_{\mathbf{k}}(\mathbf{r})$ . Thus they can be used to expand the energy eigenstates.

$$\psi_{\mathbf{k}} = \sum_{\mathbf{K}} c_{\mathbf{K}} \phi_{\mathbf{k}+\mathbf{K}} \quad (1.22)$$

The coefficients  $c_{\mathbf{K}}$  can be found by variation.

### 1.2.3 Pseudopotentials

This was proposed as an extension of the method of OPWs. The effect of core electrons on the valence states is expressed through an effective pseudopotential.

$$\psi_{\mathbf{k}}^v(\mathbf{r}) = \phi_{\mathbf{k}}^v(\mathbf{r}) + \sum_c b_c \psi_{\mathbf{k}}^c(\mathbf{r}) \quad (1.23)$$

where,

$$\phi_{\mathbf{k}}^v(\mathbf{r}) = \sum_{\mathbf{K}} c_{\mathbf{K}} e^{i(\mathbf{k}+\mathbf{K}) \cdot \mathbf{r}} \quad (1.24)$$

Demanding orthogonality of plane wave and core parts gives,

$$b_c = \int \psi_{\mathbf{k}}^{c*}(\mathbf{r}) \phi_{\mathbf{k}}^v(\mathbf{r}) d^3\mathbf{r} \quad (1.25)$$

Substituting this form in the Schrödinger equation we get,

$$(\mathcal{H} + V^R) \phi_{\mathbf{k}}^v = E_{\mathbf{k}}^v \phi_{\mathbf{k}}^v \quad (1.26)$$

where,

$$V^R \psi(\mathbf{r}) = \sum_c (E_{\mathbf{k}}^v - E_{\mathbf{k}}^c) \left( \int \psi_{\mathbf{k}}^{c*}(\mathbf{r}') \psi(\mathbf{r}') d^3\mathbf{r}' \right) \psi_{\mathbf{k}}^c(\mathbf{r}) \quad (1.27)$$

The pseudopotential defined as,

$$V^{PS} = V + V^R \quad (1.28)$$

$V^R$  is positive definite because  $E_{\mathbf{k}}^v - E_{\mathbf{k}}^c$  is positive. Thus the added potential has a screening effect on the valence electrons. This is the reason that the

free electron method gives surprisingly good results despite the simplistic assumptions it makes. Pseudopotential method gives these results a logically sound base. This potential is periodic and can be solved by the plane waves method much more efficiently than the original equation because, the number of plane waves that need to be retained in the calculation are much less. In the semi-empirical method, pseudopotentials are fitted to experimentally observed data.

### 1.2.4 Tight binding model

Plane wave methods are suitable for calculation of electronic structure in metals where, the electrons are delocalized. In insulators and broad gap semiconductors electrons are relatively strongly bound to the cores and are localized. The basis of plane waves is inefficient in such solids. Thus in the tight binding method, as the name suggests, a basis of localized wavefunctions is used. First step is to create a Bloch state from a linear combination of hydrogen-like atomic states localized on lattice points. Consider,

$$\phi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} a_n^{at}(\mathbf{r} - \mathbf{R}) \quad (1.29)$$

where  $a_n^{at}(\mathbf{r} - \mathbf{R})$  is the atomic wavefunction centered at  $\mathbf{R}$ . It's easy to check that this is a Bloch state. This is known as the LCAO (linear combination of atomic orbitals) approximation. Linear combination of such states is used as the trial wavefunction,

$$\sum_{n'} C_{nn'} \langle \phi_{n''\mathbf{k}} | \mathcal{H} - \mathcal{E} | \phi_{n'\mathbf{k}} \rangle = 0 \quad (1.30)$$

Which leads to the matrix equation,

$$\sum_{n'} C_{nn'} \mathcal{H}_{n''n'} - \mathcal{E}_n \mathcal{S}_{n''n'} | \phi_{n'\mathbf{k}} \rangle = 0 \quad (1.31)$$

where,

$$\mathcal{H} = \frac{\hbar^2}{2m} \nabla^2 + \sum_{\mathbf{R}} U^{at}(\mathbf{r} - \mathbf{R}) \quad (1.32)$$

$\mathcal{S}$  is called the overlap matrix. Let us assume that  $n$  assumes only one value say  $s$ . If the atomic orbitals are chosen so that,

$$\int a^{at}(\mathbf{r} + \mathbf{R}') a^{at}(\mathbf{r} + \mathbf{R}) d^3\mathbf{r} \quad (1.33)$$

is nonzero only for nearest neighbors (separated by  $d$ ), then the matrices  $\mathcal{S}$  and  $\mathcal{H}$  can be written as,

$$\mathcal{S}_{ss} = 1 + \sum_{\mathbf{d}} e^{i \mathbf{k} \cdot \mathbf{d}} \alpha \quad (1.34)$$

$$\mathcal{H}_{ss} = \mathcal{E}^{at} (1 + \sum_{\mathbf{d}} e^{i \mathbf{k} \cdot \mathbf{d}} \alpha) + \mathcal{U} + t \sum_{\mathbf{d}} e^{i \mathbf{k} \cdot \mathbf{d}} \quad (1.35)$$

where,

$$\alpha = \int a^{at}(\mathbf{r}) a^{at}(\mathbf{r} + \mathbf{d}) d^3 \mathbf{r} \quad (1.36)$$

$$\mathcal{U} = \int a^{at}(\mathbf{r}) [U(\mathbf{r} - U^{at}(\mathbf{r}))] a^{at}(\mathbf{r}) d^3 \mathbf{r} \quad (1.37)$$

$$t = \int a^{at}(\mathbf{r}) [U(\mathbf{r} - U^{at}(\mathbf{r} + \mathbf{d}))] a^{at}(\mathbf{r} + \mathbf{d}) d^3 \mathbf{r} \quad (1.38)$$

Substituting in (1.131) we get,

$$\mathcal{E}_{\mathbf{k}} \approx \mathcal{E}^{at} + \mathcal{U} + t \sum_{\boldsymbol{\delta}} e^{i \mathbf{k} \cdot \boldsymbol{\delta}} \quad (1.39)$$

The last term is called the hopping term, as it describes the interaction of electrons with neighboring nuclei.

### Wannier functions and Effective mass approximation

In tight binding the neighboring atomic wavefunctions in general have a nonzero overlap. Wannier functions are also localized on lattice sites but are designed to have zero overlap between neighbors. They can be defined for a given band, in terms of Bloch eigenfunctions as follows,

$$w_n(\mathbf{r} - \mathbf{R}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i \mathbf{k} \cdot \mathbf{R}} \psi_{n\mathbf{k}}(\mathbf{r}) \quad (1.40)$$

where,  $\psi_{n\mathbf{k}}$  are Bloch states. Consider the inner product of Wannier functions located at two distinct sites,

$$\begin{aligned} \langle w_n(\mathbf{r} - \mathbf{R}) | w_m(\mathbf{r} - \mathbf{R}') \rangle &= \int \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \frac{1}{N} e^{i \mathbf{k}' \cdot \mathbf{R}' - i \mathbf{k} \cdot \mathbf{R}} \psi_{n\mathbf{k}}^*(\mathbf{r}) \psi_{m\mathbf{k}'}(\mathbf{r}) \\ &= \delta_{\mathbf{R}, \mathbf{R}'} \delta_{m,n} \end{aligned} \quad (1.41)$$

Thus any two Wannier functions localized at distinct sites are orthogonal to each other. Inversely the Bloch functions can be expanded in terms of Wannier functions,

$$\phi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} w_n(\mathbf{r} - \mathbf{R}) \quad (1.42)$$

The Wannier functions can be used to solve the Schrödinger equation in a slowly varying perturbing potential.

$$[\mathcal{H}_0(\mathbf{r}) + \mathcal{H}_1(\mathbf{r})] \psi(\mathbf{r}) = \mathcal{E}_n \psi(\mathbf{r}) \quad (1.43)$$

where,  $\mathcal{H}$  is the original hamiltonian  $\mathcal{H}_1$  is the perturbation. Expanding  $\psi(\mathbf{r})$  in terms of the Wannier functions we get<sup>1</sup>,

$$[\mathcal{H}_0(\mathbf{r}) + \mathcal{H}_1(\mathbf{r})] \sum_{\mathbf{R}} \Phi_n(\mathbf{R}) w_n(\mathbf{r} - \mathbf{R}) = \mathcal{E}_n \sum_{\mathbf{R}} \Phi_n(\mathbf{R}) w_n(\mathbf{r} - \mathbf{R}) \quad (1.44)$$

Left multiplying with  $\langle w_n(\mathbf{r} - \mathbf{R}') |$ ,

$$\sum_{\mathbf{R}} \langle w_n(\mathbf{r} - \mathbf{R}') | \mathcal{H}_0(\mathbf{r}) | w_n(\mathbf{r} - \mathbf{R}) \rangle \Phi_n(\mathbf{R}) + \mathcal{H}_1(\mathbf{R}') \Phi_n(\mathbf{R}') = \mathcal{E}_n \Phi_n(\mathbf{R}') \quad (1.45)$$

where  $\mathcal{H}_1$  is assumed to be slowly varying. First term can be calculated by expanding Wannier functions in terms of Bloch functions. This leads to,

$$(\mathcal{E}_0(-i\nabla) + \mathcal{H}_1(\mathbf{R}')) \Phi_n(\mathbf{R}') = \mathcal{E}_n \Phi_n(\mathbf{R}') \quad (1.46)$$

Approximating the dispersion relation by a parabola near  $k = 0$ , we get,

$$\left( -\frac{\hbar^2}{2m^*} \nabla^2 + \mathcal{H}_1(\mathbf{R}) \right) \Phi_n(R) = \mathcal{E} \Phi_n(\mathbf{R}) \quad (1.47)$$

where  $m^*$  is the effective mass.

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<sup>1</sup> Assuming that  $\mathcal{H}_1$  is weak enough to not cause inter-band transitions

## Chapter 2

# Ab initio Electronic Structure Theory

Most of the physical systems are many-body systems. Quantum mechanical treatment of such systems entails solving the Schrödinger equation for,

$$\mathcal{H} = - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 - \sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 + \frac{1}{4\pi\epsilon_0} \sum_{i < j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \frac{1}{4\pi\epsilon_0} \sum_{I,i} \frac{e^2 Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} + \frac{1}{4\pi\epsilon_0} \sum_{I < J} \frac{e^2 Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \quad (2.1)$$

where  $r_i$  are the electronic degrees of freedom while  $R_I$  are the nuclear degrees of freedom. In this discussion, I will only deal with the electronic hamiltonian working under the Born-Oppenheimer approximation. In this chapter, I will review some first principle methods of electronic structure theory. The formulation of second quantization is illustrated. Then the Hartree-Fock theory is discussed along with its application to degenerate electron gas. Finally the configuration interaction theory is briefly presented.

## 2.1 Second quantization of fermionic systems [6]

Second quantization provides an elegant framework for formulating quantum mechanics of many-body systems. It has its origins in relativistic quantum field theory, but it has been used extensively in studying non-relativistic quantum many-body systems. It should be noted that second quantization does not introduce any new physical concepts and it exactly reformulates the Schrödinger equation albeit in a convenient form suited for many-body systems. The second-quantized operators incorporate quantum statistics at

each step, which contrasts with the more cumbersome approach of using symmetrized or antisymmetrized products of single-particle wave functions.

### 2.1.1 Occupation number representation

Consider a system of  $n$  identical fermions. Let  $|\phi_r\rangle_\alpha$  be the complete orthonormal set of vectors spanning the one particle Hilbert space  $\mathcal{F}_1$ . The  $n$ -particle Hilbert space is the tensor product of  $n$  such single particle spaces. A basis set for this space denoted by  $\mathcal{F}_n$  is the set of Slater determinant basis given by,

$$|n [n_1 n_2 \dots]\rangle_n = \frac{1}{n!} \begin{vmatrix} |\phi_r\rangle_1 & |\phi_r\rangle_2 & \cdots & |\phi_r\rangle_n \\ |\phi_s\rangle_1 & |\phi_s\rangle_2 & \cdots & |\phi_s\rangle_n \\ \vdots & \vdots & \ddots & \vdots \\ |\phi_t\rangle_1 & |\phi_t\rangle_2 & \cdots & |\phi_t\rangle_n \end{vmatrix} \quad (2.2)$$

where,  $r < s < \dots < t$ . This state is inherently antisymmetric, and thus obeys the Pauli exclusion principle, because of the properties of determinants.  $n_r$  denotes the number of particles in state  $|\phi_r\rangle$ .

$$n_r = 0 \text{ or } 1 \quad \sum_{r=1}^{\infty} n_r = n \quad (2.3)$$

These states are orthonormal (because the one particle basis is orthonormal).

$$\sum_{n_1 n_2 \dots}^f |n [n_1 n_2 \dots]\rangle_n \langle n [n_1 n_2 \dots]| = 1 \quad (2.4)$$

where,

$$\sum_{n_1 n_2 \dots}^f = \sum_{n_1=0}^1 \sum_{n_2=0}^1 \dots \delta_{nn'} \quad (2.5)$$

$$n' = \sum_{j=1}^{\infty} n_j \quad (2.6)$$

A general  $n$ -fermion state can be represented as,

$$|\psi\rangle_n = \sum_{n_1 n_2 \dots}^f |n [n_1 n_2 \dots]\rangle_n \langle n [n_1 n_2 \dots]| \psi \rangle_n \quad (2.7)$$

### 2.1.2 Fock space

In the last section the occupation number representation of fermionic states was introduced. Fermionic Hilbert spaces of all number of particles can be combined into one space called the Fock space.

$$\mathcal{F} = \mathcal{F}_0 \oplus \mathcal{F}_1 \oplus \dots \oplus \mathcal{F}_n \oplus \dots \quad (2.8)$$

$\psi = (\psi_0, \psi_1, \dots, \psi_n, \dots)$  is a vector in the Fock space where,  $\psi_k \in \mathcal{F}_k$ . Addition and scalar multiplication are done componentwise. The inner product on the Fock space is induced from that on the one particle space,

$$\langle \psi | \chi \rangle = \sum_{n=0}^{\infty} \langle \psi_n | \chi_n \rangle \quad (2.9)$$

In the nonrelativistic theory any state in the Fock space can have only one nonzero component (e.g.  $\psi = (0, 0, \dots, \psi_n, \dots)$ ). A basis can be defined on  $\mathcal{F}$  as follows,

$$|n [n_1 n_2 \dots]\rangle = (0, 0, \dots, |n [n_1 n_2 \dots]\rangle_n, \dots) \quad (2.10)$$

These states define an orthonormal basis,

$$\sum_{nn_1 n_2 \dots}^f |n [n_1 n_2 \dots]\rangle \langle n [n_1 n_2 \dots]| = 1 \quad (2.11)$$

where,

$$\sum_{nn_1 n_2 \dots}^f = \sum_{n=0}^{\infty} \sum_{n_1 n_2}^f \quad (2.12)$$

and,

$$\langle n [n_1 n_2 \dots] | n' [n'_1 n'_2 \dots] \rangle = \delta_{nn'} \delta_{n_1 n'_1} \delta_{n_2 n'_2} \dots \quad (2.13)$$

Zero state is added by hand and is called the vacuum state, denoted by  $|0\rangle$ .

### 2.1.3 Operators in second quantization

Analogous to the ladder operators of the harmonic oscillator following creation and annihilation operators are defined on  $\mathcal{F}$ . Consider the operator,

$$\mathbf{A} = |n [n_1 n_1 \dots n_p = 0 \dots]\rangle \langle n [n_1 n_2 \dots n_p = 1 \dots]| \quad (2.14)$$

It acts only on a wavefunction that has the  $p$ th one-particle state occupied, and gives a wavefunction with the  $p$ th state empty. If we want an operator



that acts on any wavefunction for which  $n$ , we should sum over all other possibilities of  $n_i$ .

$$F_r^\dagger = \sum_{nn_1n_2\ldots}^f (-1)^{m_r} (1 - n_r) |n + 1 [n_1n_2\ldots n_r + 1\ldots]\rangle \langle n [n_1n_2\ldots n_r\ldots]| \quad (2.15)$$

where  $m_r = \sum_{s=1}^{r-1} n_s$  is added to get the correct sign in the determinant (ordering inside the Slater determinant). This is the  $r$  state creation operator. Similarly the  $r$  state annihilation operator is defined as,

$$F_r = \sum_{nn_1n_2\ldots}^f (-1)^{m_r} n_r |n [n_1n_2\ldots n_r - 1\ldots]\rangle \langle n + 1 [n_1n_2\ldots n_r\ldots]| \quad (2.16)$$

again  $m_r = \sum_{s=1}^{r-1} n_s$  Thus,

$$F_r^\dagger |n [n_1n_2\ldots 0\ldots]\rangle = (-1)^{m_r} |n + 1 [n_1n_2\ldots 1\ldots]\rangle \quad (2.17)$$

$$F_r |n + 1 [n_1n_2\ldots 1\ldots]\rangle = (-1)^{m_r} |n [n_1n_2\ldots 0\ldots]\rangle \quad (2.18)$$

and,

$$F_r^\dagger |n [n_1n_2\ldots 1\ldots]\rangle = 0 \quad (2.19)$$

$$F_r |n [n_1n_2\ldots 0\ldots]\rangle = 0 \quad (2.20)$$

$$F_r^2 = F_r^{\dagger 2} = 0 \quad (2.21)$$

$$|n [n_1n_2\ldots]\rangle = F_r^\dagger F_s^\dagger F_t^\dagger |0\rangle \quad (2.22)$$

Number operator is defined as,

$$N_r = F_r^\dagger F_r, \quad N = \sum_{r=1}^{\infty} N_r \quad (2.23)$$

$N_r$  is hermitian and idempotent. It is easy to see that it has eigenvalue zero when it operates on a state for which  $n_r$  is zero, and has eigenvalue unity when it operates on a state that has  $n_r = 1$ . Also,

$$F_r F_r^\dagger |n [n_1n_2\ldots n_r = 1\ldots]\rangle = 0 \quad (2.24)$$

Thus,

$$F_r^\dagger F_r + F_r F_r^\dagger = 1 \quad \text{i.e.} \quad \{F_r^\dagger, F_r\} = 1 \quad (2.25)$$

Other relations can be established using similar arguments (or by using the definitions of  $F_r^\dagger$  and  $F_r$ ),

$$\{F_r^\dagger, F_s^\dagger\} = \{F_r, F_s\} = 0 \quad (2.26)$$

$$\{F_r, F_s^\dagger\} = \delta_{rs} \quad (2.27)$$

One particle operators are of the form,

$$A(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n) = \sum_{i=1}^n A(\mathbf{x}_i) \quad (2.28)$$

Kinetic energy, for example, is a one particle operator. Their action on states in the Fock space is derived from that in the single particle space,

$$A(0, 0, \dots, |n[n_1 n_2 \dots]\rangle_n, 0, \dots) = (0, 0, \dots, A|n[n_1 n_2 \dots]\rangle_n, 0, \dots)_n \quad (2.29)$$

They cannot induce transitions between subspaces with different particle numbers. The matrix element of a one particle operator in the Fock space basis is,

$$\langle n[n_1 n_2 \dots] | A | n'[n'_1 n'_2 \dots] \rangle = \delta_{nn'} \langle n[n_1 n_2 \dots] | A | n[n'_1 n'_2 \dots] \rangle_n \quad (2.30)$$

nonzero only when, there is a difference of no more than one state (two occupation numbers) between the states. Therefore,

$$A = \sum_{r,s} \langle \phi_r | A | \phi_s \rangle F_r^\dagger F_s \quad (2.31)$$

Let's work out the total kinetic energy (T) operator in the momentum basis.

$$\begin{aligned} T_{\mathbf{k}\mathbf{k}'} &= \Omega^{-1} \int e^{-i\mathbf{k}\cdot\mathbf{r}} \left( \frac{-\hbar^2}{2m} \nabla^2 \right) e^{i\mathbf{k}'\cdot\mathbf{r}} d^3\mathbf{r} \\ &= \frac{\hbar^2 \mathbf{k}^2}{2m} \delta_{\mathbf{k}\mathbf{k}'} \end{aligned} \quad (2.32)$$

Therefore,

$$T = \sum_{\mathbf{k}} \frac{\hbar^2 \mathbf{k}^2}{2m} F_{\mathbf{k}}^\dagger F_{\mathbf{k}} \quad (2.33)$$

Second quantization is most useful when there are inter-particle interactions in the problem. A two particle operator is defined as,

$$A(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n) = \frac{1}{2} \sum_{i,j} A(\mathbf{x}_i, \mathbf{x}_j) \quad (2.34)$$

In his case the matrix element is nonzero between states differing by no more than two particles. Its expansion in terms of the annihilation and creation operators is given by,

$$A = \sum_{r,s,t,u} \langle \phi_r \phi_s | A | \phi_u \phi_t \rangle F_r^\dagger F_s^\dagger F_t F_u \quad (2.35)$$

As an example, the potential energy of two-body interaction of fermions in plane wave basis is,

$$\begin{aligned} V_{\mathbf{k},\mathbf{k}',\mathbf{k}'',\mathbf{k}'''} &= \Omega^{-2} \int e^{i(\mathbf{k}'''-\mathbf{k})\cdot\mathbf{r}_1} e^{i(\mathbf{k}''-\mathbf{k}')\cdot\mathbf{r}_2} V(\mathbf{r}_1 - \mathbf{r}_2) d^3\mathbf{r}_1 d^3\mathbf{r}_2 \\ &= \Omega^{-2} \int e^{i(\mathbf{k}'''-\mathbf{k}+\mathbf{k}''-\mathbf{k}')\cdot\mathbf{R}} d^3\mathbf{R} \int e^{\frac{i}{2}(\mathbf{k}'''-\mathbf{k}-\mathbf{k}''+\mathbf{k}')\cdot\mathbf{r}} d^3\mathbf{r} \\ &= \delta_{\mathbf{k}+\mathbf{k}',\mathbf{k}'''+\mathbf{k}''} V_{\mathbf{k}-\mathbf{k}''} \end{aligned} \quad (2.36)$$

where  $V_{\mathbf{k}-\mathbf{k}''}$  is the Fourier transform component of  $V$ . The transformation  $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$  and  $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$  is used in the second step. Therefore,

$$V = \frac{1}{2} \sum_{\mathbf{k},\mathbf{k}',\mathbf{k}''} V_{\mathbf{k}'-\mathbf{k}''} F_{\mathbf{k}}^\dagger F_{\mathbf{k}'}^\dagger F_{\mathbf{k}''} F_{\mathbf{k}+\mathbf{k}'+\mathbf{k}''} \quad (2.37)$$

### Field operators

The basis used in the one particle Hilbert space has been used throughout these derivations without making any direct reference to it. Of particular importance is the position basis  $\{|\mathbf{x}m_s\rangle\}$ , which also includes the spin degrees of freedom. In this case the creation and annihilation operators are called field operators. As we have been considering a denumerable basis so far, it is not very rigorous to extend the same formalism to continuous basis states. The following are stated as a generalization of the discrete case,

$$F_{m_s}(\mathbf{x})^\dagger |0\rangle = (0, |\mathbf{x}m_x\rangle, 0, \dots) \quad (2.38)$$

$F_{m_s}(\mathbf{x})^\dagger$  are traditionally called  $\hat{\psi}^\dagger(\mathbf{x})$ . Relation between  $F_r$ (basis  $|\phi\rangle$ ) and  $\hat{\psi}^\dagger(\mathbf{x})$  is given by,

$$\hat{\psi}^\dagger(\mathbf{x}) = \sum_r \phi_r^*(\mathbf{x}) F_r^\dagger \quad (2.39)$$

Similar relations exist for the annihilation operators. Some treatments use field operators derived from the wavefunction as the starting point of second quantization. Hence the name second quantization.

## 2.2 Hartree-Fock Theory

Hamiltonian in  $\mathcal{F}$  can be written as,

$$\mathcal{H} = \sum_r \mathcal{E}_r F_r^\dagger F_r + \frac{1}{2} \sum_{r,s,t,u} \langle \phi_r \phi_s | V | \phi_u \phi_t \rangle F_r^\dagger F_s^\dagger F_t F_u - \sum_{r,s} \langle \phi_r | \mathcal{V} | \phi_s \rangle F_r^\dagger F_s \quad (2.40)$$

where,

$$[T(\xi_\alpha) + U(\xi_\alpha) + \mathcal{V}(\xi_\alpha)] |\phi_r\rangle = \mathcal{E}_r |\phi_r\rangle \quad (2.41)$$

$$\mathcal{H}_0 = \sum_\alpha [T(\xi_\alpha) + U(\xi_\alpha) + \mathcal{V}(\xi_\alpha)] \quad (2.42)$$

$\mathcal{V}$  is the central part of the fermion two body interaction  $V$ . It is chosen such that  $\mathcal{H}_0$  is a good approximation to  $\mathcal{H}$ .  $\mathcal{H}_0$  describes the independent particle model. The ground state of this model is given by,

$$|F\rangle = F_1^\dagger \dots F_n^\dagger |0\rangle \quad (2.43)$$

with  $\mathcal{E}_1 \leq \mathcal{E}_2 \leq \dots$ . The choice of  $\mathcal{V}$  is critical for this approximation to be good. The choice that gives the best approximation is given by the Hartree-Fock potential,

$$\langle \phi_r | \mathcal{V} | \phi_s \rangle = \sum_t \langle \phi_r \phi_t | V | \phi_s \phi_t \rangle - \langle \phi_r \phi_t | V | \phi_t \phi_s \rangle \quad (2.44)$$

Practically, this is one of the most important techniques in computing electronic structure. These can be cast into a discrete matrix form called the Roothaan's equations by using a finite basis.

### 2.2.1 Degenerate electron gas[2]

Consider a system of interacting electron gas placed in a uniformly distributed positive background chosen to ensure that the total system is neutral (jellium). Volume of the system is  $\Omega$ . Periodic conditions are applied at the boundaries. Hamiltonian for the system can be written using the calculations done in previous sections,

$$\mathcal{H} = T + V^{el-b} + V^{el} + V^b \quad (2.45)$$

where,  $V^+$  is the interaction between the background and the electrons,  $W^+$  is the self interaction of the background. Let's write each of these terms in second quantized form.

$$T = \sum_{\mathbf{k}\sigma} \frac{\hbar^2 \mathbf{k}^2}{2m} F_{\mathbf{k},\sigma}^\dagger F_{\mathbf{k},\sigma} \quad (2.46)$$

$$V^{el-b} = \sum_{\mathbf{k}\mathbf{q}\sigma} V_{\mathbf{q}}^{el-b} F_{\mathbf{k}-\mathbf{q},\sigma}^{\dagger} F_{\mathbf{k},\sigma} = -NV_0^{el-b} \quad (2.47)$$

$$V^{el} = \frac{1}{2} \sum_{\mathbf{k}\mathbf{k}'\sigma_1\sigma_2} V_0^{el} F_{\mathbf{k},\sigma_1}^{\dagger} F_{\mathbf{k}',\sigma_2}^{\dagger} F_{\mathbf{k}',\sigma_2} F_{\mathbf{k},\sigma_1} + \frac{1}{2} \sum_{\mathbf{k}\mathbf{k}'\mathbf{q}\neq 0\sigma_1\sigma_2} V_{\mathbf{q}}^{el} F_{\mathbf{k}-\mathbf{q},\sigma_1}^{\dagger} F_{\mathbf{k}'+\mathbf{q},\sigma_2}^{\dagger} F_{\mathbf{k}',\sigma_2} F_{\mathbf{k},\sigma_1} \quad (2.48)$$

$$V^b = \sum_{\mathbf{k}\mathbf{q}\sigma} V_{\mathbf{q}}^b F_{\mathbf{k}-\mathbf{q},\sigma}^{\dagger} F_{\mathbf{k},\sigma} = NV_0^{el-b}/2 \quad (2.49)$$

$$\frac{1}{2} \sum_{\mathbf{k}\mathbf{k}'\sigma_1\sigma_2} V_0^{el} F_{\mathbf{k},\sigma_1}^{\dagger} F_{\mathbf{k}',\sigma_2}^{\dagger} F_{\mathbf{k}',\sigma_2} F_{\mathbf{k},\sigma_1} = \frac{1}{2} N(N-1)V_0 \quad (2.50)$$

In the thermodynamic limit all three potential terms diverge separately, but when added they cancel out, leaving

$$\mathcal{H} = \sum_{\mathbf{k}\sigma} \frac{\hbar^2 \mathbf{k}^2}{2m} F_{\mathbf{k},\sigma}^{\dagger} F_{\mathbf{k},\sigma} + \frac{1}{2} \sum_{\mathbf{k}\mathbf{k}'\mathbf{q}\neq 0\sigma_1\sigma_2} \frac{2\pi e^2}{\Omega \mathbf{q}^2} F_{\mathbf{k}-\mathbf{q},\sigma_1}^{\dagger} F_{\mathbf{k}'+\mathbf{q},\sigma_2}^{\dagger} F_{\mathbf{k}',\sigma_2} F_{\mathbf{k},\sigma_1} \quad (2.51)$$

This cannot be solved exactly. The kinetic energy part has plane waves as eigenstates. The interaction potential can be treated as a perturbation in the high density limit. The unperturbed energies and states are the same as in Sommerfeld's theory. First order perturbation to energy is given by,

$$|\Phi\rangle = \left( \prod_{\mathbf{k}_i\sigma_i} F_{\mathbf{k}_i,\sigma_i}^{\dagger} \right) |0\rangle \quad (2.52)$$

$$\mathcal{E} = \langle \Phi | \mathcal{H}_0 + V | \Phi \rangle \quad (2.53)$$

$$\mathcal{E}^{(1)} = \frac{1}{2} \sum_{\mathbf{k}\mathbf{k}'\mathbf{q}\neq 0\sigma_1\sigma_2} \frac{2\pi e^2}{\Omega \mathbf{q}^2} \langle \Phi | F_{\mathbf{k}-\mathbf{q},\sigma_1}^{\dagger} F_{\mathbf{k}'+\mathbf{q},\sigma_2}^{\dagger} F_{\mathbf{k}',\sigma_2} F_{\mathbf{k},\sigma_1} | \Phi \rangle \quad (2.54)$$

Substituting the Sommerfeld solution,

$$\mathcal{E}^{(1)} = -e^2 \frac{4\pi\Omega}{(2\pi)^6} \int d^3q q^{-2} \int d^3P \theta(\mathbf{k}_F - |\mathbf{P} + 1/2\mathbf{q}|) \theta(\mathbf{k}_F - |\mathbf{P} - 1/2\mathbf{q}|) \quad (2.55)$$

where  $\mathbf{k}_F$  is the Fermi vector. This integral involves calculating the volume shared between two intersecting spheres. The final result is<sup>1</sup>,

$$\mathcal{E}^{(1)} = -\frac{3e^2 N}{4\pi a_0 r_s} \left( \frac{9\pi}{4} \right)^{1/3} \quad (2.56)$$

---

<sup>1</sup>Hartree-Fock calculation give the same result for the ground state energy as the first perturbation. This is due to the fact that the Hartree-Fock solutions for the jellium model turn out to be plane waves.

$$\frac{\mathcal{E}}{N} \approx \frac{e^2}{2a_0} \left[ \frac{2.21}{r_s^2} - \frac{0.916}{r_s} \right] \quad (2.57)$$

The first term is the kinetic energy of the Fermi gas of electrons, it becomes the dominant term as in the limit of very high densities. The second term is known as the exchange energy and is negative.

## 2.3 Configuration Interaction[8]

Hartree-Fock approximation gives erroneous results for energies of excited states and molecular dissociations. The part of the e-e interaction left out of the HF approximation is called the correlation energy. The basic idea behind CI is, to use the linear combination of multiple Slater determinants as a solution ansatz. In principle, CI provides an exact solution of the many-electron problem, as Slater determinants form a complete basis. In practice, only some determinants can be retained in the calculation. Consequently CI provides only upper bounds to the exact energies.

Solving Roothaan's equations in a finite basis set gives a set of  $2K$  spin orbitals. The determinant formed from the  $N$  lowest energy spin orbitals is the ground state  $|\Psi_0\rangle$ . Many other Slater determinants can be formed from the  $2k$  orbitals. These other determinants can be described by stating how they differ from the ground state. These are used as the basis of expansion. The full CI expansion is,

$$|\Phi_0\rangle = c_0|\psi_0\rangle + \sum_{ar} c_a^r |\Psi_a^r\rangle + \sum_{a<b, r<s} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \dots \quad (2.58)$$

Thus the total number of  $n$ -tuply excited determinants is  $\binom{N}{n} \binom{2K-N}{n}$ . The number of  $n$ -tuply excited determinants is extremely large. The difference between the lowest eigenvalue and the Hartree-Fock energy obtained within the same one-electron basis is called the basis set correlation energy. As the one-electron basis set approaches completeness, this basis set correlation energy approaches the exact correlation energy.

Let's substitute the full CI ansatz into the Schrödinger equation.

$$\langle \Psi_0 | \mathcal{H} - \mathcal{E}_0 | \Phi \rangle = \sum_{c<d, t<u} c_{cd}^{tu} \langle \Psi_0 | \mathcal{H} | \Psi_{cd}^{tu} \rangle \quad (2.59)$$

As  $\mathcal{H}$  only has upto two electron operators, any higher terms do not mix with  $|\Psi_0\rangle$ . The correlation energy is given by,

$$\mathcal{E}_{corr} = \sum_{a<b, r<s} c_{ab}^{rs} \langle \Psi_0 | \mathcal{H} | \Psi_{ab}^{rs} \rangle \quad (2.60)$$

This does not mean that only double excitations need to be included for an exact CI description of the ground state, the coefficients of double excitations are affected by the presence of other excitations.

In almost all practical scenarios, full CI is a computationally impractical procedure. The expansion must be truncated somehow. A systematic procedure for accomplishing this is to consider only those configurations which differ from the ground state by no more than a given number of spin orbitals. The resulting ground state energy obtained from a singly and doubly excited CI (SDCI) calculation, for small molecules, gives the major fraction of the correlation energy. Here, in order to keep the formalism as simple as possible, I am ignoring single excitations. The intermediate normalized DCI is given by,

$$|\Phi_{DCI}\rangle = |\Phi_0\rangle + \sum_{c<d, t<u} c_{cd}^{tu} \langle\Psi_0|\mathcal{H}|\Psi_{cd}^{tu}\rangle \quad (2.61)$$

$$(\mathcal{H}-\mathcal{E}_0) \left( |\Psi_0\rangle + \sum_{c<d, t<u} c_{cd}^{tu} \langle\Psi_0|\mathcal{H}|\Psi_{cd}^{tu}\rangle \right) = \mathcal{E}_{corr} \left( |\Psi_0\rangle + \sum_{c<d, t<u} c_{cd}^{tu} \langle\Psi_0|\mathcal{H}|\Psi_{cd}^{tu}\rangle \right) \quad (2.62)$$

Left multiplying by  $\langle\Psi_0|$  and  $\langle\Psi_{ab}^{rs}|$ ,

$$\begin{bmatrix} 0 & B^\dagger \\ B & D \end{bmatrix} \begin{bmatrix} 1 \\ c \end{bmatrix} = \mathcal{E}_{corr} \begin{bmatrix} 1 \\ c \end{bmatrix} \quad (2.63)$$

where,

$$(B)_{rsab} = \langle\Psi_{ab}^{rs}|\mathcal{H}|\Psi_0\rangle \quad (2.64)$$

$$(D)_{rsab,tucd} = \langle\Psi_{ab}^{rs}|\mathcal{H}|\Psi_{cd}^{tu}\rangle \quad (2.65)$$

$$(c) = c_{ab}^{rs} \quad (2.66)$$

The correlation energy is the lowest eigenvalue of this matrix. It can be solved perturbatively,

$$E_{corr} \approx \sum_{a<b, r<s} \frac{\langle\Psi_0|\mathcal{H}|\Psi_{ab}^{rs}\rangle \langle\Psi_{ab}^{rs}|\mathcal{H}|\Psi_0\rangle}{\langle\Psi_{ab}^{rs}|\mathcal{H}-\mathcal{E}_0|\Psi_{ab}^{rs}\rangle} \quad (2.67)$$

This is the contribution of the double excitation to the correlation energy.

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