DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

ELECTRONIC STRUCTURE OF MANY ELECTRON QUANTUM DOTS

by

Zeynep DEMİR

July, 2010
İZMİR

ELECTRONIC STRUCTURE OF MANY ELECTRON QUANTUM DOTS

A Thesis Submitted to the
Graduate School of Natural and Applied Sciences of
Dokuz Eylül University
In Partial Fulfillment of the Requirements for
the Degree of Master of Science in Physics

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July, 2010
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M.Sc. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"ELECTRONIC STRUCTURE OF MANY ELECTRON QUANTUM DOTS"** completed by **ZEYNEP DEMİR** under supervision of **PROF. DR. İSMAİL SÖKMEN** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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ACKNOWLEDGEMENTS

I am particularly grateful to my supervisor Prof. Dr. Ismail SOKMEN for his scientific contribution and supervision.

I would express my thanks to Assit. Prof. Dr. Kadir AKGÜNGÖR for his advice and especially technical support.

Also I want to thank Dr. Serpil SAKIROGLU for her help during writing procedure of my thesis.

I would express my thanks to Dr. Aylin YILDIZ. Without her encouragement and support the days would never pass on this journey.

Finally, I want to thank my mother and sister for all their support and encouragement.

Zeynep DEMİR

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ABSTRACT

In this thesis we have studied the ground state energies of two dimensional ($2D$) disc-like parabolic quantum dots up to seven electrons by using Spin Adapted Configuration Interaction (SACI) package. This package is written in Mathematica by R. D. Muhandiramge and J. Wang and calculates the energies and wavefunctions of a parabolic quantum dot under the influence of a magnetic field.

The ground state energies of a six electron quantum dot for different electron densities at zero angular momentum and magnetic field with total spin quantum number number $S = 0$ and $S = 3$ have been calculated by using the SACI package. Comparison SACI results with the Density Functional Theory and the conventional Configuration Interaction results has proved the accuracy of the method especially for the fully polarized states which correspond to the spin quantum number $S = 3$.

Atomic-like properties of quantum dots have been reviewed by the investigation the addition energy spectrum in parabolic quantum dots at zero magnetic field up to six electrons. Addition energy has showed the maximums for two and six electrons which proves the shell structure of the quantum dots.

Moreover in order to examine the magnetic transitions in the ground state of quantum dots electrochemical energy versus magnetic field plots have been reproduced for two, three and four electrons. It has been observed that the total spin and the angular momentum of the system changes with the increasing magnetic field.

Keywords: quantum dot, spin eigenfunctions, Configuration Interaction method.

ÇOK ELEKTRONLU KUANTUM NOKTALARIN ELEKTRONİK YAPISI

ÖZ

Bu tezde Spin Uyarlanmış Şekillenimli Etkileşim (SACI) paketini kullanarak yedi elektrona kadar iki boyutlu disk-benzeri parabolik kuantum noktaların taban durum enerjilerini hesapladık. Bu paket R. D. Muhandiramge ve J. Wang tarafından Mathematica dilinde yazılmıştır ve manyetik alan etkisindeki parabolik bir kuantum noktanın enerjilerini ve dalga fonksiyonlarını hesaplar.

Altı elektronlu bir kuantum noktanın farklı elektron yoğunlukları için sıfır açısal momentum ve manyetik alanda $S = 0$ ve $S = 3$ toplam spin kuantum sayıları durumunda taban durum enerjileri SACI paketi kullanılarak hesaplandı. SACI sonuçlarının Yoğunluk Fonksiyoneli Teorisi ve Şekillenimli etkileşim yöntemleriyle karşılaştırılması yöntemin özellikle tam polarize durumlar için güvenirliğini ispatladı.

Sıfır manyetik alan altında parabolik bir kuantum noktanın altı elektrona kadar ekleme enerjisi spektrumu elde edilerek kuantum noktaların atom benzeri-özellikleri yeniden incelendi. Ekleme enerjisinin iki ve altı elektron için en büyük değerleri alması kuantum noktaların tabakalı yapısını ispatlamış oldu.

Bundan başka kuantum noktaların taban durumlarındaki manyetik geçişlerin incelenmesi için elektrokimyasal enerjiye karşı manyetik alan grafikleri iki, üç ve dört elektron için tekrar elde edildi. Manyetik alanın artmasıyla sistemin sahip olduğu toplam spin ve toplam açısal momentumunun değiştiği gözlendi.

Anahtar sözcükler: kuantum nokta, spin özfonksiyonları, şekillenimli etkileşim yöntemi

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CHAPTER ONE
INTRODUCTION

Since the beginning of 1970s research on semiconductor structures with lower dimensions has been born. First low dimensional system was quantum well (Dingle, Wiegmann, & Henryn, 1974) which is two dimensional layer sandwiched between semiconductor with different band gaps. Because of different band gabs a triangular potential is formed which confines the electrons in one direction forming a thin layer. Extraordinary properties of this two dimensional systems has been studied in research laboratories like the the discovery of the Quantum Hall Effect (Klitzing, Dorda, & Pepper, 1980).

The rapid progress in lithographic and self organized techniques made it possible to confine electrons in one dimension. This low dimensional system is called as quantum wires. Quantization in three dimensions can be formed by trapping electrons in a quasi-zero-dimensional quantum dot. The term quantum dot was coined by Mark Reed and suggests an exceedingly small region of space. Quantum dot is formed from roughly a million atoms with all their electrons tightly bound to the nuclei however free electrons in the dot can be one and a few hundreds. Since de-Broglie wavelength of these electrons is comparable to the size of the dot, electrons occupy discrete energy levels (like real atoms) and have a discrete energy spectrum. Also it is possible to control the size, shape, energy levels and number of confined electrons of quantum dots. The energy spectrum of the few-electron quantum dot is expected to be extremely rich since the single-electron confinement energy, the cyclotron energy for modest fields and the electron-electron interaction energy can all be of similar magnitude (typically a few meV), and they scale differently as far as one varies dot parameters (Rontani, 1999). Therefore especially for small number of electrons it is appropriate to investigate electronic correlation such as formation of Wigner

molecule (Egger, Hasuler, Mak & Grabert, 1998).

However electron-electron interaction in quantum dots is not a simple many body problem. Analytic solutions for more than two electrons is impossible to obtain. Solving Schrödinger equation becomes exponentially more difficult when the number of particles increases (Helle, 2006). It is traditional to use Configuration Interaction (CI) method (Bryant, 1987; Pfannkuche, Gerhardts, & Maksym, 1993). One of the first study has been done by Pfannkuche et al who applied Hartree, Hartree Fock and exact diagonalization for quantum dot-helium (Pfannkuche, Gerhardts, & Maksym, 1993) and indicated the lack of electron correlation in the Hartree Fock method. However numerical diagonalization methods can be used only small number of electrons and not too low densities. The advantage of CI calculations is excited states can be calculated besides ground state (Reimann & Manninen, 2002; Rontani, Cavazzoni, Bellucci, & Goldoni, 2006). Also Density Functional Theory (DFT) have been applied to quantum dots (Macucci, Hess, & Iafrate, 1995) as well as Quantum Monte Carlo techniques (Bolton, 1996).

Spin Adapted Configuration Interaction (SACI) approach is an exact diagonalisation technique which reduces the time independent Schrödinger equation to matrix eigenvalue problem (Muhandiramge & Wang, 2006). In this approach many electron wavefunctions are antisymmetric products of spatial and spin wavefunctions. Spatial functions are individual products of one electron wave functions which builds an orthonormal set and spin functions are mutual eigenfunctions of total spin operator and its z component. Approximating spatial and spin functions with this properties results with a many electron wavefunction which is eigenfunction of total spin operator. This approach has an advantage over mean field approaches such as DFT and Hartree Fock because multi-electron wavefunciton is an exact wave function which describes the particles accurately and it gives excited states besides ground state while by

mean field approaches one can only get ground state. However SACI approach have an disadvantage because with this approach small number of particles can be examined because of insufficient computational resources (Wang, Hines, & Muhandiramge, n.d.).

In this thesis SACI package (Muhandiramge & Wang, 2006) written in Mathematica developed by Ranga D. Muhandiramge and Jingbo Wang is used. This program calculates the energy levels and wavefunctions of a many-electron parabolic quantum dot under the influence of perpendicular magnetic field using SACI method (Muhandiramge, 2003). Using this program ground state energies of parabolic quantum dots for different confinement potentials and spin states are calculated in order to compare the SACI results with other studies in the literature and also review electronic properties of quantum dots.

Contrary to natural atoms, in semiconductor quantum dots the Coulomb-to-kinetic-energy ratio can be rather large even larger than one order of magnitude, the smaller the carrier density the larger the ratio (Rontani et al., 2006). In order to test the accuracy of SACI method for different densities ground state energies of a six electron quantum dot at zero magnetic field with total spin quantum number number $S = 0$ and $S = 3$ is calculated. It is seen that SACI results are in good agreement with Exact diagonalization and Local Density Approximation results given in Ref. Reimann & Manninen, (2002) even in low density limit.

As mentioned above since quantum dots resemble real atoms in many respects such as shell structure and obey Hund's rule they are often called as artificial atoms (Kastner, 1993; Ashoori, 1996). Similar to $3D$ shell structure of real atoms which can be understood from peaks of atomic ionization energies $2D$ shell structure of quantum dots in the case of two dimensional parabolic potential at zero magnetic field have been proved experimentally for different number of electrons by observing Coulomb

oscillations (Tarucha, Austing, Honda, Hage, & Kouwenhoven, 1996; Tarucha et al., 1998). In this thesis addition energy of the ground states at zero magnetic up to six electrons is calculated by using results of SACI package. Maxima of addition energy for certain electron numbers prove the $2D$ shell structure of parabolic quantum dots as in Ref. Lee, Rao, Martin, & Leburton, 1998; Reimann, Koskinen, Kolehmainen, Austing, Manninen, & Tarucha, (1999)

Experimentally transitions which have never seen in natural atoms can be observed by applying external fields in quantum dots (Kouwenhoven et al., 1997). In this thesis changing of electrochemical potential by magnetic field is reproduced for two, three and four electrons. Transitions in the ground states observed and also in four electron case a manifestation of Hund's rule (Tarucha et al., 1998) is observerd.

This thesis is organized as follows. In order to understand the physical system we give a brief discussion about properties of quantum dots in Chapter 2. In Chapter 3 information about electronic structure methods are given. Constructing spin eigenfunctions and many electron wave functions is described in Chapter 4. Properties spin adapted basis are discussed in detail in Chapter 5. Numerical results and conclusion are presented in Chapter 6 and Chapter 7, respectively.

CHAPTER TWO
QUANTUM DOTS

2.1 Two Dimensional Electron Gas

Recent work on mesoscopic conductors has largely been based on GaAs-AlGaAs heterojuctions where a thin two-dimensional conducting layer is formed at the interface between GaAs and AlGaAs. To understand why this layer is formed consider the conduction and valence band line-up in z direction when we first bring the layers contact. The Fermi energy in E_f in the widegap AlGaAs layer is higher than that in the narrow gap GaAs layer. Consequently electrons spill over from AlGaAs leaving behind positively charged donors. This space charge gives rise to an electrostatic potential that causes the bands to bend. At equilibrium the Fermi energy is constant everywhere. The electron density is sharply peaked near the GaAs-AlGaAs interface (where the Fermi energy is inside the conduction band) forming a thin conducting layer which is usually referred to as the two-dimensional electron gas (2DEG).

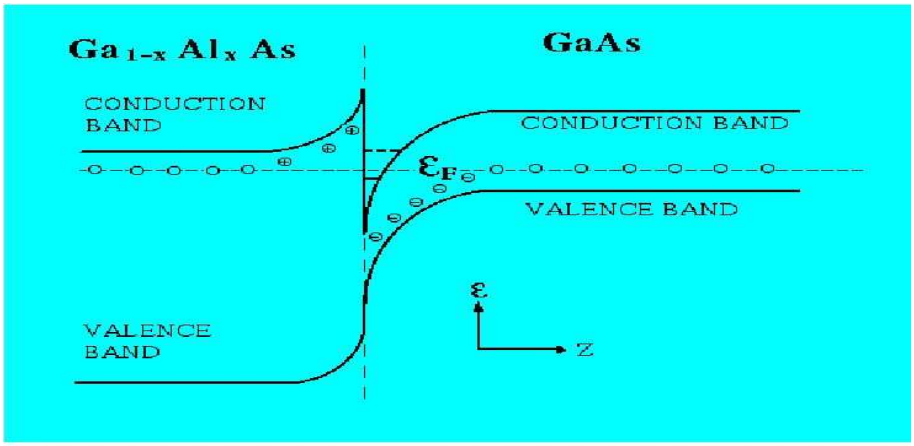

Figure 2.1 Conduction and valence band line-up at a junction between *AlGaAs* and *GaAs* after charge transfer has been occured.

The carrier concentration in a 2DEG is typically ranges from $2 \times 10^{11} cm^2$

to $2 \times 10^{12} cm^2$ and can be depleted by applying a negative voltage on the surface. The practical importance of this structure lies in its use as a field effect transistor which goes under a variety of names such as MODFET (MODulation Doped Field Effect Transistor) or HEMT (High Electron Mobility Transistor) (Datta, 2003). Therefore one can say that in 2DEG electrons are free to move in two dimensions, but they are confined in third having discrete energy levels. In most problems confinement in the third direction is neglected.

This principle can be developed by further reducing the dimensionality of the electron's environment. Confinement in two direction, gives one dimensional systems called quantum wires. The confinement on all three dimensions creates $0D$ quantum dots (Harrison, 2001). Figure 2.2 illustrates the different systems in a general way, and Figure 2.3 shows how the expected density of states varies with dimensionality. Passing from three dimensions to two dimensions the density N(E) of states changes from a continuous dependence N(E) $\propto E^{1/2}$ to a step like dependence. Being zero dimensional, quantum dots have a sharper density of states than higher-dimensional structures. As a result, they have superior transport and optical properties, and are being researched for many technological applications (Yildiz, 2009).

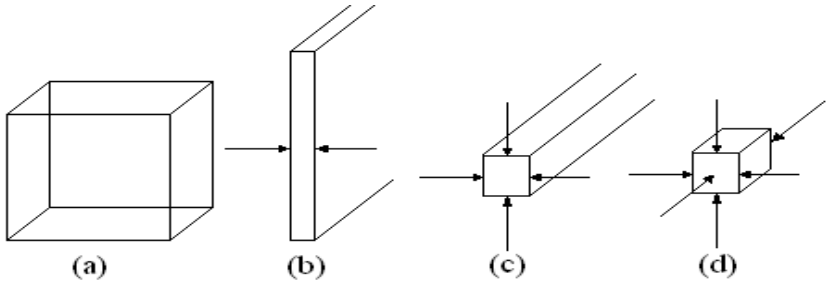

Figure 2.2 (a) bulk semiconductors, 3D; (b) thin films, layer structures, quantum wires, 2D; (c) linear chain structures, quantum wires, 1D; (d) clusters, colloids, microcrystallites, quantum dots, 0D. (from Ref. (Yildiz, 2009))

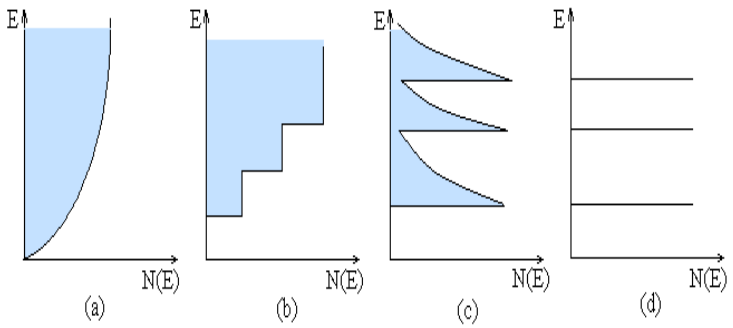

Figure 2.3 Densities of states N(E) for (a) 3D, (b) 2D, (c) 1D and (d) 0D systems (corresponding to ideal cases). (from Ref. (Yildiz, 2009))

2.2 Quantum Dots as Artifical Atoms

Quantum dots are man-made objects in which charge carriers are confined in all three dimensions. As a result they have discrete energy levels just like real atoms and usually quantum dots are called as *artifical atoms*. Quantum dots with different sizes and properties can be produced, and the number of electrons in the dot can be changed by external gate electrodes.

Besides having common properties with real atoms, quantum dots differ from real atoms in many respects: in quantum dots the electrons are usually confined to a much larger volume than the electrons in a real atom. In addition, the shape of the confining potential in the quantum dots is quite different from the one in a real atom. Typically a quantum dot structure resembles a two-dimensional box with a side length of $100\,nm$ whereas in the solids the spacing between the atoms is of the order of a few Angstroms. A single semiconductor quantum dot consists of the order of 10^6 atoms. Most of the electrons in the material are bound to atoms but some of the electrons can be made to move freely in the quantum dot region. The other difference, besides the huge size difference, between real atoms and quantum dots is in the form of the potential.

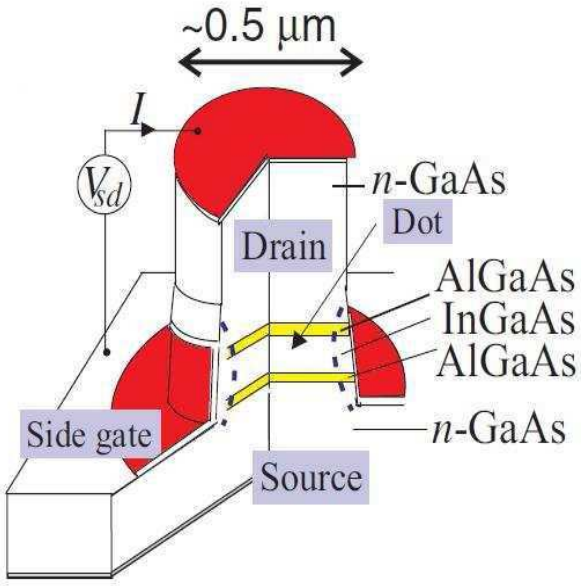

Figure 2.4 Schematic diagram of a disk shaped dot. (from Ref. (Tarucha et al., 1998))

In real atoms the strong Coulomb attraction of the nucleus restricts the electron motion into a small volume in the proximity of the nucleus. In quantum dots the potential is not a central attractive, but resembles more a harmonic trap defined by the external electrodes (lateral quantum dot) or by the physical dimensions (vertical quantum dot). Yet another interesting feature is that there exists a class of semiconductor quantum dots that can be considered effectively two-dimensional which gives rise to some interesting physics (Helle, 2006).

2.3 Fabrication of Quantum Dots

There are many ways to confine electrons in semiconductors. One way to produce a quantum dot is to isolate a small piece of metal with insulating material, for example to grow a small island of metal on an insulating substrate (e.g. Al island on Si). Metallic quantum dots tend to be rather large and the energy levels

lie close to each other, thus approaching the continuum limit.

The two other approaches create the quantum dots at or near the surface of a semiconductor crystal. Originally such quantum dots are performed by growing a semiconductor structure. In the early method lithographic process was used to create a two dimensional structure that could be than attach down to isolate a quantum dot. However, these quantum dots were only nanometer scale in one dimension-the thickness of the semiconductor were used to trap the electrons. The other two dimensions were limited by the resolution of the lithography, and could be as big as a micron. This meant that electrical studies performed in this dots had to be carried out in the extremely low temperatures to freeze out thermal effects.

Later (third method) researchers began to grow self-assembled quantum dots by depositing a semiconductor material with a larger lattice constant onto a semiconductor with a smaller lattice constant. Typical systems were germanium on silicon and indium arsenide on gallium arsenide. It is this quantum dots that have been used to fabricate quantum dot lasers (Cientifica Ltd., 2003).

2.4 Applications

Initially targeted at biotechnology applications, such as biological reagents and cellular imaging, quantum dots are being eyed by producers for eventual use in light-emitting diodes (LEDs), lasers, and telecommunication devices such as optical amplifiers and waveguides. The strong commercial interest has renewed fundamental research and directed it to achieving better control of quantum dot self-assembly in hopes of one day using these unique materials for quantum computing (Ouellette, 2003). By applying small voltages to the leads, one can control the flow of electrons through the quantum dot and thereby

make precise measurements of the spin and other properties therein. With several entangled quantum dots, or qubits, plus a way of performing operations, quantum calculations might be possible.

Quantum dots have quickly found their way into homes in many electronics. The new PlayStation 3 and DVD players to come out all use a blue laser for data reading. The blue laser up until only a few years ago was beginning to be seen as something of an impossibility, until the synthesis of a blue quantum dot laser (Nanofm Ltd., n.d.). In modern biological analysis, various kinds of organic dyes are used. However, with each passing year, more flexibility is being required of these dyes, and the traditional dyes are simply unable to meet the necessary standards at times. To this end, quantum dots have quickly filled in the role, being found to be superior to traditional organic dyes on several counts, one of the most immediately obvious being brightness (owing to the high quantum yield) as well as their stability. Currently under research as well is tuning of the toxicity. (Deak Lam Ltd., n.d.)

Sharper density of states, superior transport and optical properties and are being researched for use in diode lasers, amplifiers, and biological sensors. use in solid-state quantum computation . By applying small voltages to the leads, one can control the flow of electrons through the quantum dot and thereby make precise measurements of the spin and other properties Another cutting edge application of quantum dots is also being researched as potential artificial fluorophore for intra-operative detection of tumors using fluorescence spectroscopy. Quantum dots may have the potential to increase the efficiency and reduce the cost of todays typical silicon photovoltaic cells .

CHAPTER THREE
THEORETICAL BASIS

3.1 Introduction

Since de Broglie wavelength of an electron in quantum dot is comparable with confinement region, electron behavior can be described by their quantum mechanical properties. In quantum mechanics non-relativistic Schrodinger equation describes how the quantum state changes with time:

$$\hat{H}\psi = i\hbar\frac{\partial\psi}{\partial t} \tag{3.1.1}$$

where $\hat{H}$ is the Hamiltonian operator, ψ is the system wavefunction. Stationary states of this equation as considered in this thesis are found by solving the eigenvalue-eigenfunction (time-independent) form of the Schrödinger equation:

$$\hat{H}\psi = E\psi \tag{3.1.2}$$

Solving the Schrödinger equation analytically, or even numerically, becomes intractable for systems with more than a few particles, and therefore different levels of approximations must be introduced. This results in a variety of computational methods with different levels of accuracy.

3.1.1 Quantum Dot Hamiltonian

In previous chapter we have discussed properties of electron in quantum dots. Although an electron is effectively free to move, its motion is affected by the surrounding semiconductor material. One can rather accurately describe electron motion in a quantum dot by substituting the mass of a free electron with the effective mass of electrons of the host semiconductor material in the Hamiltonian

($m \to m^*$). This is called the effective-mass approximation (Helle, 2006). We use effective mass approximation throughout this thesis. The effective permittivity ϵ^* is also different from the vacuum permittivity ϵ_0 due to screening effect in the semi-conductor. For gallium arsenide, the effective mass m^* is approximately $0.067m_e$ and the effective permittivity ϵ^* is approximately $12.4\epsilon_0$. Under this assumptions quantum dot Hamiltonian take the form:

$$\begin{aligned} \hat{H} &= \sum_{i=1}^{N} \left\{ \frac{1}{2m^*}(\vec{P}_i - \frac{e}{c}\vec{A}_i)^2 + V_c(\vec{r}_i) \right\} + \sum_{i<j}^{N} \frac{e^2}{\epsilon^*|\vec{r}_i - \vec{r}_j|} \\ &= \sum_{i=1}^{N} \hat{H}_{0i} + \sum_{j>i} \hat{H}(i,j) \\ &= \hat{H}_0 + \hat{H}_I \end{aligned} \tag{3.1.3}$$

where N is the number electrons in the quantum dot. e, m^* and ϵ^* are, respectively, the electron charge, effective mass, and relative dielectric constant of the host semiconductor, $\vec{r}_i$ is the position of the i. electron, $\vec{P}_i$ is its canonically conjugated momentum, and $\vec{A}_i$ is the vector potential associated with an external magnetic field. The potential $V_c(\vec{r}_i)$ describes the quantum dot confinement. In this Hamiltonian spin-spin and spin orbit interaction is neglected. The first part $\hat{H}_0$, shows the sum over N electrons in the quantum dot and the second interaction part, $\hat{H}_I$ represents the total Coulomb repulsion between electron pairs. In this thesis we ignore relativistic effects such as spin-spin and spin orbit interaction which are small in comparison with Coulomb energy.

3.1.2 Single Electron Quantum Dot

The confinement in the two-dimensional semiconductor interface is created by the external electrodes which define the shape and size of the quantum dot. In many cases the confinement potential of a single quantum dot can be assumed to be parabolic. Since confinement in z direction is much stronger than in plane

region confinement potential is given by:

$$V_c(\vec{r_i}) = \frac{1}{2}m^* w_0^2(x^2 + y^2) + V(z) \tag{3.1.4}$$

where w_0 gives the strength of confinement. In the case of large quantum dots ($diameter \sim 100nm$) $\hbar w_0$ is typically of the order of a meV (Helle, 2006.) The confinement potential in z direction $V(z)$ is narrow triangular well. The energy level in z direction is generally hundreds of greater than many of the low energy states in the $x - y$ plane. This property allows us to model electron motion in a quantum dot as two dimensional as the electrons are tightly confined in z direction as they only occupy the ground state in this direction (Wang, Hines, & Muhandiramge, n.d.). There is analytical solution for two-dimensional single-electron quantum dot systems which was first established by Fock, (1928) and later independently by Darwin, (1930). Following Fock's work, Hamiltonian of the system can be written as the following:

$$\hat{H} = \frac{1}{2m^*}(\vec{P} - \frac{e}{c}\vec{A})^2 + \frac{1}{2}m^*\omega_0^2\hat{r}^2 \tag{3.1.5}$$

where vector potential in symmetric gauge: $\vec{A} = (+\frac{1}{2}B\hat{y}, -\frac{1}{2}B\hat{x}, 0)$ as $\nabla X \hat{A} = (0, 0, -B)$. Then the Hamiltonian becomes:

$$\begin{aligned}
\hat{H}\psi &= \frac{1}{2m^*}\left(i\hbar\frac{\partial}{\partial x} + \frac{1}{2}\frac{e}{c}B\hat{y}, i\hbar\frac{\partial}{\partial y} - \frac{1}{2}\frac{e}{c}B\hat{x}, 0\right)^2\psi + \frac{1}{2}m^*\omega_0^2(\hat{x}^2 + \hat{y}^2)\psi \\
&= \frac{1}{2m^*}\left(-\hbar^2\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) - \frac{B^2e^2}{4c^2}(x^2 + y^2) + \frac{i\hbar eB}{c}\left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right)\right)\psi \\
&\quad + \frac{1}{2}m^*\omega_0^2(\hat{x}^2 + \hat{y}^2)\psi \\
&= -\frac{\hbar^2}{2m^*}\left(\frac{\partial^2\psi}{\partial r^2} + \frac{1}{r}\frac{\partial\psi}{\partial r} + \frac{1}{r^2}\frac{\partial^2\psi}{\partial\theta^2}\right) + \frac{i\hbar eB}{2m^*c}\frac{\partial\psi}{\partial\theta} + \left(\frac{B^2e^2r^2}{8m^*c^2+} + \frac{1}{2}m^*\omega_0^2\right)\psi
\end{aligned} \tag{3.1.6}$$

To study in polar coordinates in the last step we have used $x = rsin\theta \quad y = rcos\theta$ and also

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} = \frac{\partial^2\psi}{\partial r^2} + \frac{1}{r}\frac{\partial\psi}{\partial r} + \frac{1}{r^2}\frac{\partial^2\psi}{\partial\theta^2} \tag{3.1.7}$$

$$y\frac{\partial\psi}{\partial x} - x\frac{\partial\psi}{\partial y} = \frac{\partial\psi}{\partial\theta} \tag{3.1.8}$$

Cyclotron frequency is defined as :

$$\omega_c = \frac{eB}{m^*c} \tag{3.1.9}$$

Then equation (3.1.6) becomes:

$$\hat{H}\psi = -\frac{\hbar^2}{2m^*}\left(\frac{\partial^2\psi}{\partial r^2} + \frac{1}{r}\frac{\partial\psi}{\partial r} + \frac{1}{r^2}\frac{\partial^2\psi}{\partial\theta^2}\right) + \frac{i\omega_c\hbar}{2}\frac{\partial\psi}{\partial\theta} + \left(\frac{m^*\omega_c^2r^2}{8} + \frac{1}{2}m^*\omega_0^2r^2\right) \tag{3.1.10}$$

If we insert

$$\psi = \frac{1}{\sqrt{2}}f(r)e^{im\theta} \tag{3.1.11}$$

into the Schrödinger equation we get:

$$-\frac{\hbar^2}{2m^*}\left(f''(r) + \frac{1}{r}f'(r) - \frac{m^2}{r^2}f(r)\right) + (\frac{1}{8}m^*(\omega_c^2 + 4\omega_0^2)r^2 - E - \frac{m\omega_c\hbar}{2})f(r) = 0 \tag{3.1.12}$$

$$-\frac{1}{2}\left(f''(r) + \frac{1}{r}f'(r) - \frac{m^2}{r^2}f(r)\right) + \left(\frac{m^{*2}}{2\hbar^2}(\frac{1}{4}\omega_c^2 + \omega_0^2)r^2 - \frac{Em^*}{\hbar^2} - \frac{mm^*\omega_c}{2\hbar}\right)f(r) = 0 \tag{3.1.13}$$

$$\left(\frac{-1}{2r}\frac{\partial}{\partial r}(r\frac{\partial}{\partial r}) + \frac{m^2}{2r^2} + \frac{\Omega^2m^{*2}}{2\hbar^2}r^2 - \frac{Em^*}{\hbar^2} - \frac{mm^*w_c}{2\hbar}\right)f(r) = 0 \tag{3.1.14}$$

where $\Omega^2 = \frac{1}{4}w_c^2 + w_0^2$. If $r \to 0$ differential equation simplifies to:

$$\left(-\frac{1}{2r}\frac{\partial}{\partial r}(r\frac{\partial}{\partial r}) + \frac{m^2}{2r^2}\right)f(r) = 0 \tag{3.1.15}$$

Inserting $f(r) = r^p$ we obtain:

$$\frac{1}{2}(m^2 - p^2)r^{p-2} = 0 \tag{3.1.16}$$

Solution must be finite at the origin so it must be $p = |m|$.

$$\begin{aligned} \frac{m^*\Omega}{2\hbar} &= \frac{m^*\sqrt{\frac{1}{4}w_c^2 + w_0^2}}{2\hbar} \\ &= \frac{m^* w_c\sqrt{1 + 4\frac{w_0^2}{w_c^2}}}{2\hbar} \\ &= \frac{m^* eBb}{2\hbar m^* c} \\ &= \frac{b}{2l_0^2} \\ &= k \end{aligned} \tag{3.1.17}$$

where $b = \sqrt{\frac{1}{4}w_c^2 + w_0^2}$, $l_0 = \sqrt{\frac{\hbar c}{eB}}$ and $k = \frac{b}{2l_0^2}$. If $r \to \infty$ equation (3.1.14) becomes:

$$\left(-\frac{1}{2r}\frac{\partial}{\partial r}(r\frac{\partial}{\partial r}) + \frac{k^2}{2}r^2\right) f(r) = 0 \tag{3.1.18}$$

The solution of this differential equation is

$$f(r) = d_1 I_0(\frac{kr^2}{2}) + d_2 J_0(\frac{kr^2}{2}) \tag{3.1.19}$$

d_1 and d_2 are constants, I_0 and J_0 are modified Bessel functions. If $r \to \infty$, $I_0(\frac{kr^2}{2})$ diverges. K_0 has the value $e^{-\frac{kr^2}{2}}$ for large r. If we use a trial wavefunction:

$$f(r) = r^{|m|}e^{-\frac{m^*\Omega r^2}{2\hbar}}g(r) \tag{3.1.20}$$

and

$$\frac{\gamma^2}{2} = \frac{Em^*}{\hbar^2} + \frac{mm^* w_c}{2\hbar} \tag{3.1.21}$$

Therefore a differential equation is obtained:

$$(\gamma^2 - 2k(|m|+1))g(r) + (-2kr^2 + 2|m|+1)g^{'}(r) + rg^{''}(r) = 0 \tag{3.1.22}$$

which has a solution:

$$g(r) = e_1\ {}_1F_1(\frac{1}{4}(-\frac{\gamma^2}{k} - 2|m|+2); 1-|m|; kr^2) + e_2\ {}_1F_1(\frac{1}{4}(-\frac{\gamma^2}{k}+2|m|+2); |m|+1; kr^2) \tag{3.1.23}$$

where e_1 and e_2 are constants and ${}_1F_1$ is the hypergeometric function. To be able to normalize the solution, the hypergeometric function must terminate. This implies that for ${}_1F_1(c, z, a) = -n$ and $c \neq -n$ where $n = 0, 1, 2, 3, ...$ This condition is satisfied by the second hypergeometric function since $c = |m|+2 \leq 1$.

$$-n = \frac{1}{4}(-\frac{\gamma^2}{k} + 2|m| + 2) \tag{3.1.24}$$

Substituting γ and k in equation (3.1.24) we can find the energy equation:

$$E = (2n + |m| + 1)\hbar\Omega - \frac{m}{2}\hbar w_c \tag{3.1.25}$$

Generalized Laguerre Polynomials are related to Hypergeometric functions as:

$$L_n^m(kr^2) = \begin{pmatrix} n+m \\ n \end{pmatrix}\ {}_1F_1(-n, m+1; kr^2) \tag{3.1.26}$$

$$f(r) = N_{n,|m|} r^{|m|} e^{-\frac{1}{2}kr^2} L_n^m(kr^2) \tag{3.1.27}$$

where $N_{n,|m|}$ is a normalization constant. Using orthogonality relations of Laguerre polynomials, one electron wavefunction is found as:

$$\psi_{nm}(r, \theta) = k^{(|m|+1)/2} \sqrt{\frac{n!}{\pi(n+m)!}} r^{|m|} e^{-kr^2/2} L_n^{|m|}(kr^2) e^{-im\theta} \tag{3.1.28}$$

In Figure 3.1 lowest ten energy levels (n, m) as a function of magnetic field

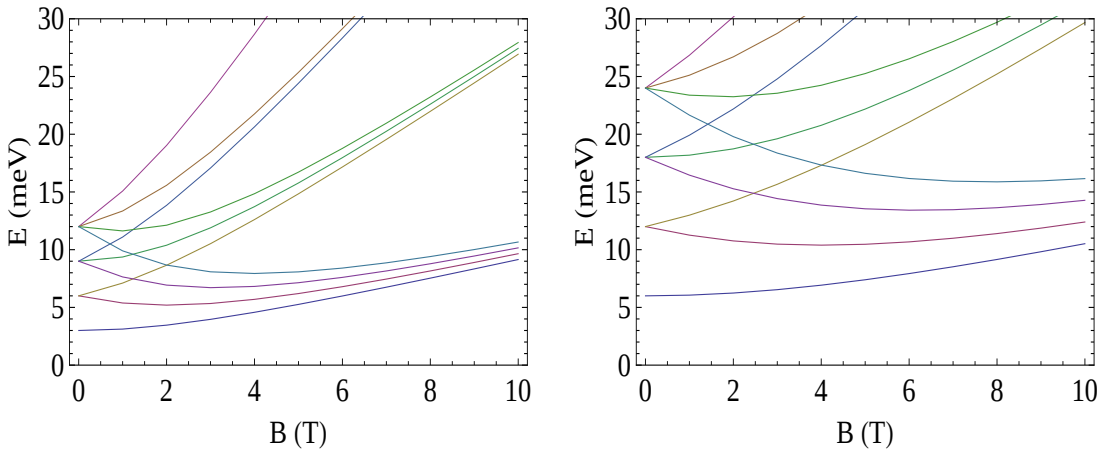

Figure 3.1 Fock Darwin energy levels as a function of magnetic field with external confinement $\hbar w_0 = 3meV$ in the left panel and $\hbar w_0 = 6meV$ in the right panel

is plotted in confinement $\hbar w_0 = 3meV$ in the left panel. For a comparison, the single-particle energy levels of $\hbar w_0 = 6meV$ parabolic quantum dot are plotted in the right panel of Fig. 3.1. As the magnetic field strength increases, energy levels shift and split. In high magnetic fields energy equation becomes:

$$E(n,m) = (2n + |m| - m + 1)\frac{\hbar w_c}{2} \tag{3.1.29}$$

with energy levels $\frac{\hbar w_c}{2}, \frac{3\hbar w_c}{2}, \frac{5\hbar w_c}{2}$ forming Landau levels. The most obvious advantage for choosing single particle basis as Fock-Darwin solutions is that they represent a natural and simple starting point with regards to physics of problem (Rontani, Cavazzoni, Bellucci, & Goldoni, 2006). Also, two dimensional Coulomb matrix elements are known analytically in the case of using single particle basis as Fock-Darwin solutions (derivation can be found in Appendix Two).

3.1.3 Hartree Fock Method

Hartree method is a mean-field model in which it is assumed that electrons move in an averaged potential formed by other electrons in the system (Hartree, 1928). In this case Schrödinger equation for many electrons in the system is reduced to a single electron Hartree equation :

$$\left(\hat{H}_i + \sum_{j=1}^{N} \int \Psi_j^*(\mathbf{r}_j) \frac{1}{r_{ij}} \Psi_j(\mathbf{r}_j)\right) \Psi_i(\mathbf{r}_i) = E_i \Psi_i(\mathbf{r}_i) \tag{3.1.30}$$

where $\hat{H}_i$, is the single-electron Hamiltonian acting only on the ith electron as defined in Equation (3.1.5), $\Psi_i(\mathbf{r}_i)$ is the single-electron wavefunction for the ith electron, and E_i is the corresponding eigenenergy. In Hartree theory wavefunction of the system is described as products of single electron spin orbitals. However this wavefunction doesn't include the antisymmetry requirement. In order to include this requirement Fock and Slater (Fock, 1930) established Hartree Fock Method which estimates the many electron wave function as a single Slater determinant:

$$\Phi_D(\mathbf{q_1}, \mathbf{q_2}, ..., \mathbf{q_n}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_\alpha(\mathbf{q_1}) & \psi_\beta(\mathbf{q_1}) & \dots & \psi_\gamma(\mathbf{q_1}) \\ \psi_\alpha(\mathbf{q_2}) & \psi_\beta(\mathbf{q_2}) & \dots & \psi_\gamma(\mathbf{q_2}) \\ \vdots & \vdots & \vdots & \vdots \\ \psi_\alpha(\mathbf{q_n}) & \psi_\beta(\mathbf{q_n}) & \dots & \psi_\gamma(\mathbf{q_n}) \end{vmatrix} \tag{3.1.31}$$

where $\frac{1}{\sqrt{N!}}$ is normalization constant. $\mathbf{q_i} = (\mathbf{r_i}, \sigma_i)$, represents the spatial and the spin coordinate of the ith electron, $\psi_\lambda(\mathbf{q_i}) = u_\lambda(\mathbf{r_i})\chi_\lambda$ is spin orbital of the i. electron with a quantum number λ and $u_\lambda(\mathbf{r_i})$ and χ_λ the spatial and the spin coordinate of the ith electron (Wang, Hines, & Muhandiramge, n.d.). Spin orbitals are orthogonal to each other:

$$\langle \psi_\mu | \psi_\lambda \rangle = \delta_{\mu,\lambda} \tag{3.1.32}$$

Slater determinant can be written in a more compact form:

$$\Phi_D(\mathbf{q_1}, \mathbf{q_2}, ..., \mathbf{q_n}) = \frac{1}{\sqrt{N!}} \sum_P (-1)^p \hat{P} \psi_\alpha(\mathbf{q_1}) \psi_\beta(\mathbf{q_2}) ... \psi_\gamma(\mathbf{q_n}) = \hat{A}\Phi \tag{3.1.33}$$

where Φ is the product of individual spin orbitals:

$$\Phi = \psi_\alpha(\mathbf{q_1}) \psi_\beta(\mathbf{q_2}) ... \psi_\gamma(\mathbf{q_n})$$

$\hat{P}$ is permutation operator which interchanges both spatial and spin coordinates of electron pairs. $\hat{A}$ is an operator which makes a wave function of N identical fermions antisymmetric under the exchange of the coordinates of any pair of fermions. After application of the wave function satisfies the Pauli principle.

$$\hat{A} = \frac{1}{\sqrt{N!}} \sum_P (-1)^p \hat{P} \tag{3.1.34}$$

According to variational principle

$$E_0 \leq \langle \Phi | \hat{H} | \Phi \rangle \tag{3.1.35}$$

If variational principle is applied, one can get a set of equations called Hartree Fock equations (McCarthy, Wang, & Abbott, 2001):

$$\left(\hat{H}_i + V_\lambda^c(\mathbf{q_i}) - V_\lambda^{exc}(\mathbf{q_i}) \right) \psi_\lambda(\mathbf{q_i}) = E_\lambda \psi_\lambda(\mathbf{q_i}) \tag{3.1.36}$$

$$V_\lambda^c(\mathbf{q_i}) = \sum_{\mu \neq \lambda} \int \frac{|\psi_\mu(\mathbf{r_j})|^2}{\mathbf{r_{ij}}} d\mathbf{r_j} \tag{3.1.37}$$

$$V_\lambda^{exc}(\mathbf{q_i}) \psi_\lambda(\mathbf{q_i}) = \sum_{\mu \neq \lambda} \left(\int \frac{\psi_\mu(\mathbf{r_j}) \psi_\lambda(\mathbf{r_j})}{\mathbf{r_{ij}}} d\mathbf{r_j} \right) \psi_\mu(\mathbf{r_i}) \tag{3.1.38}$$

where $V_\lambda^c(\mathbf{q_i})$ is called as Coulomb term and $V_\lambda^c(\mathbf{q_i})$ exchange term. Coulomb term is averaged Coulomb potential (-e) charged particle feels. It depends on average positions of electrons in the system. The essence of Hartree Fock approximation is to replace complicated many electron problem by one electron problem in which electron-electron repulsion is treated in an averaged way. Hartree Fock equation is nonlinear and must be solved iteratively. The procedure for solving Hartree Fock equation is called the self-consistent-field (SCF). The basic idea of the SCF method is simple. By making a initial guess at the spin orbitals, one can calculate the average field seen by each electron an then solve eigenvalue equation for a new set of spin orbitals. For this new orbitals one can obtain new orbitals and repeat the process until self-consistency reached.(i,e. until the fields no longer change and the spin orbitals are the same as Fock operators eigenfunctions) (Szabo, 1996). Deficiency in the Hartree Fock approximation is that it is an independent particle approximation, i.e. an electron moves in an averaged field of the other electrons and it does not actually feel the instantaneous repulsion. The Hartree Fock wavefunction do not minimise the actual electronic repulsion energy and, in reality, the electrons are further away from each other reducing the repulsion energy. (Lehtonen, 2007).

3.1.4 Density Functional Theory

Another mean-field approach to solve the many electron Schrödinger equation is Density Functional Theory (DFT). However, in DFT electron density distribution $n(r)$ is used in stead of many electron wavefunction In this method systems with large number of electrons can be examined while in wavefunction based approaches one can deal with small number of electrons. At the heart of the Density functional theory is the self-consistent single-electron Kohn-Sham

equation (Kohn & Sham, 1965)

$$-\frac{\hbar^2}{2m^*}\nabla^2\psi_i(\mathbf{r}) + [V_{ext} + V_c(\mathbf{r}) + V_{xc}(\mathbf{r})]\,\psi_i(\mathbf{r}) \tag{3.1.39}$$

developed from the Hohenberg-Kohn theorems (Hohenberg & Kohn, 1964). V_{ext} represents the external electric potential imposed by, for example, external electrodes. ψ_i is the wavefunction for the ith electron, which is solved from the Kohn-Sham equation to provide the electron density distribution n(r) defined as

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2 \tag{3.1.40}$$

The Coulomb potential is then given by

$$V_c(\mathbf{r}) = \frac{e^2}{4\pi\epsilon^*}\int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}' \tag{3.1.41}$$

while the exchange-correlation potential $V_{xc}\mathbf{r}$ depends functionally on the electron density distribution $n(r)$. If the exact exchange-correlation functional $E_{xc}[n(\mathbf{r})]$ is used, the Kohn-Sham equation incorporates all many-particle effects. However, exchange effects come directly from the antisymmetrisation of wavefunctions as required by the Pauli's exclusion principle. In the density function theory, this is a major problem since the mathematical object is the electron density distribution function rather than the electron wavefunction, making evaluation of the exchange interaction intrinsically difficult. For many quantum systems, this functional cannot be exactly defined and recent work has involved a considerable amount of empirical parameterization. The simplest and the most widely used representation for $E_{xc}[n(\mathbf{r})]$ is the so-called local-density approximation (LDA), i.e.

$$E_{xc}^{LDA} = \int e_{xc}(\zeta)n(\mathbf{r}')d\mathbf{r}' \tag{3.1.42}$$

where ζ represents the spin polarization and e_{xc} is the exchange-correlation energy. LDA for homogeneous two-dimensional electrons and also for systems with small

variation in e density. The exchange-correlation energy can be parameterized as

$$e_{xc}(\zeta) = \frac{a_0(\zeta)(1 + a_1(\zeta))\sqrt{(}x)}{1 + a_1(\zeta)\sqrt{(}x) + a_2(\zeta)x + a_3(\zeta)x^{1/3}} \tag{3.1.43}$$

where x relates to the electron density and is defines as the radius of a sphere containing one electron. The coefficients $a_i(0)$ and $a_i(1)$ were determined by Tanatar and Ceperley (Tanatar & Ceperley, 1989) for the ground state of 2D electron gas using the Green's function Monte Carlo method. For other values of ζ one can use,

$$e_{xc}(\zeta) = e_{xc}(0) + \frac{(1+\zeta)^{3/2} + (1-\zeta)^{3/2} - 2}{2^{3/2} - 2}(e_{xc}(1) - e_{xc}(0)) \tag{3.1.44}$$

The Kohn-Sham equations are solved iteratively. This is similar to the Hartree method. The wavefunction of each electron is solved taking into account a potential field determined by the average position of all other electrons. After a solution is obtained, the potential field is recalculated and the Kohn-Sham equation is solved for a new solution. The calculation is thus iterated until both the potential field and the solution tend to change (Wang, Hines, & Muhandiramge, n.d.).

3.1.5 Electron Correlation Methods

The energy difference between the exact nonrelativistic solution of the Schrödinger equation and the Hartree Fock energy is called the correlation energy. The difference is due to that the Hartree Fock approximation restricts the ground state wavefunction to be described by a single determinant with doubly occupied orbitals, but the many-body wavefunction cannot be represented in such a way (Lehtonen, 2007)

A certain amount of electron correlation is already considered within the HF

approximation, found in the electron exchange term describing the correlation between electrons with parallel spin. This basic correlation prevents two parallel-spin electrons from being found at the same point in space and is often called Fermi correlation. Coulomb correlation, on the other hand, describes the correlation between the spatial position of electrons with opposite spin due to their Coulomb repulsion.

How can we build a wave function that contains electron correlation? We could expand the exact wave function as a linear combination of approximate wave functions, provided these approximate wave functions form a complete set. For example, we could expand the exact wave function in terms of a linear combination of Slater determinants. This approach is called the Configuration Interaction (CI) method. CI method is discussed in detail in the next section.

3.1.6 Configuration Interaction Approach

Both Hartree Fock and local (spin) density functional approximation (LDA) have an advantage in treating large number of particles. However, Hartree Fock and LDA cannot treat properly a sort of correlation effect and have relatively poor information on the excited states. In CI method, electron correlation is taken into account by taking wavefunction as a linear combination of Slater determinants which is formed from orthogonal spin orbitals. CI wavefunction can be written as:

$$\Psi = \sum_{i=1}^{N_{det}} d_i \Phi_D \tag{3.1.45}$$

where Φ_D is Slater determinant defined as equation (3.1.31). N_{det} is the number of Slater determinants included in the expansion.

$$N_{det} = \begin{pmatrix} \aleph \\ N^{\uparrow} \end{pmatrix} \begin{pmatrix} \aleph \\ N^{\downarrow} \end{pmatrix} \tag{3.1.46}$$

where ℵ is the number of available spin-orbitals to be used in the expansion,$N^{\uparrow}$ and $N^{\downarrow}$ are the number of electrons with up and down spin, respectively, and $N^{\downarrow} + N^{\uparrow} = N$ is the total number of electrons in the system. In other words $N^{\uparrow}$ and $N^{\downarrow}$ electrons can ocuppy ℵ spin orbitals in N_{det} different ways. According to Pauli principle there can be only two electron with opposite spins in a spin orbital (Wensauer, Korkusinski, & Hawrylak, 2004):

$$\frac{N}{2} \leq max(N^{\uparrow}, N^{\downarrow}) \leq \aleph \leq N$$

Slater determinants in equation (3.1.45) can be formed by exciting electrons from occuppied to unoccupied orbitals. Therefore each Slater determinant corresponds to a different configuration.

Expansion coefficients in equation (3.1.31) can be determined by the variational principle. The linear Rayleigh-Ritz variation principal can be used to determine the expansion coefficients d_i, namely by solving the eigenvalue problem of an Hamitonian:

$$\overline{H}\,\overline{C} = E\,\overline{C} \tag{3.1.47}$$

where $\overline{H}$ is a matrix having the expectation values $\langle \Phi_D | \hat{H} | \Phi_D^j \rangle$ between different Slater determinats, $\overline{C}$ has the eigenvectors as columns and E the eigenvalues on its diagonal. The matrix elements of Hamiltonian can be expressed in terms of one and two-electron integrals using Slater-Condon rules (Slater, 1931). As the Hamiltonian contains only one and two electron operators, all the expectation values between Slater determinants which differ by more than two orbitals are zero. Additionally, all the matrix elements between the Hartree Fock reference and singly excited Slater determinants are zero due to Brillouins theorem. According to (3.1.47) equation to solve energy-eigenvalue problem we

must find Hamiltonian matrix elements (Lehtonen, 2007):

$$\begin{aligned}\langle\Phi_D|\hat{H}|\Phi_D^{'}\rangle &= \langle\hat{A}\Phi|\hat{H}|\hat{A}\Phi^{'}\rangle \\ &= \langle\Phi|\hat{H}|\hat{A}^{\dagger}\hat{A}\Phi^{'}\rangle \\ &= \sqrt{N!}\langle\Phi|\hat{H}|\hat{A}\Phi^{'}\rangle\end{aligned} \tag{3.1.48}$$

The matrix elements of Hamiltonian can be expressed in terms of one and two-electron integrals using Slater-Condon rules which allow us to reduce the N-electron integral to a sum of one or two-electron integrals, and furthermore, to identify zero Hamiltonian matrix elements.

For completeness, the derivation of these rules which are taken from Wang, Hines, & Muhandiramge, (n.d.) are given below. Note that the standard Slater-Condon rules are only applicable if the two Slater determinants applicable Φ_D and $\Phi_D^{'}$ are lined up in maximum coincidence. For example if we have $\Phi = \psi_1\psi_2\psi_3\psi_4\psi_6$ and $\Phi^{'} = \psi_1\psi_3\psi_4\psi_5\psi_6$ would need be be aligned up by pairwise permutation to $\Phi^{'} = \psi_1\psi_5\psi_3\psi_4\psi_6$. Also the formulas derived below require the one electron wavfunctions to be an orthogonal set.

Rule-1: $\hat{H} = h_0$ is constant which is independent of electron coordinates. If $\Phi_D = \Phi_D^{'}$ then $\langle\Phi_D|h_0|\Phi_D^{'}\rangle = h_0$ and otherwise $\langle\Phi_D|h_0|\Phi_D^{'}\rangle = 0$

$$\begin{aligned}\langle\Phi_D|h_0|\Phi_D^{'}\rangle &= \sqrt{N!}\langle\Phi|h_0|\hat{A}\Phi^{'}\rangle \\ &= h_0\sum_P(-1)^p\langle\Phi|P\Phi^{'}\rangle \\ &= h_0\sum_P(-1)^p\langle\psi_1|\psi_{p1}^{'}\rangle\langle\psi_2|\psi_{p2}^{'}\rangle...\langle\psi_N|\psi_{pN}^{'}\rangle\end{aligned} \tag{3.1.49}$$

Because of orthogonality of one electron integrals unless $\psi_i = \psi_{pi}^{'}$ above expression is zero. For this case Φ and $\Phi^{'}$ must have identity elements. This can be obtained only with one permutation i.e. identity permutation which have the property

$(-1)^p = 1$. Assuming that $h_0 = 1$, one can get the orthogonality of Slater determinants.

Rule-2: $\hat{h}_i$ is one electron operator which contains one electron coordinates. If we have $\hat{H} = \sum_{i=1}^{N} \hat{h}_i$:

a. $\langle \Phi_D | \hat{H} | \Phi_D^{'} \rangle = 0$, if Φ and $\Phi^{'}$ differ by more than one orbital.

b. $\langle \Phi_D | \hat{H} | \Phi_D^{'} \rangle = (-1)^{|l-m|} \langle \psi_l | \hat{h}_l | \psi_m^{'} \rangle$ if Φ and $\Phi^{'}$ differ by one orbital ψ_l versus $\psi_m^{'}$, where l is the position of ψ_l in Φ and m is the position of $\psi_m^{'}$ in $\Phi^{'}$.

c. $\langle \Phi_D | \hat{H} | \Phi_D^{'} \rangle = \sum_{i=1}^{N} \langle \psi_i | \hat{h}_i | \psi_i \rangle$, if $\Phi = \Phi^{'}$.

$$\begin{aligned} \langle \Phi_D | \hat{h}_i | \Phi_D^{'} \rangle &= \sum_P (-1)^p \langle \psi_1 | \psi_{p1}^{'} \rangle \langle \psi_2 | \psi_{p2}^{'} \rangle ... \langle \psi_i | \hat{h}_i | \psi_{pi}^{'} \rangle ... \langle \psi_N | \psi_{pN}^{'} \rangle \\ &= \sum_P (-1)^p \langle \psi_i | \hat{h}_i | \psi_{pi}^{'} \rangle \prod_{j \neq i} \langle \psi_j | \psi_{pj}^{'} \rangle \end{aligned} \tag{3.1.50}$$

which is equals to zero if for $\psi_j \neq \psi_{pj}^{'}$. If there exits two orbitals which occurs in Φ but not in $\Phi^{'}$, no permutation can provide equation (3.1.50) therefore $\langle \Phi_D | \hat{h}_i | \Phi_D^{'} \rangle = 0$ when Φ and $\Phi^{'}$ differ by more than one orbital. ψ_l is an orbital which appears in Φ but not $\Phi^{'}$. There is one $i = l$ which provides $\prod_{j \neq i} \langle \psi_j | \psi_{pj}^{'} \rangle$.

$$\begin{aligned} \langle \Phi_D | \hat{H} | \Phi_D^{'} \rangle &= \sum_{i=1}^{N} \langle \Phi_D | \hat{h}_i | \Phi_D^{'} \rangle \\ &= \sum_P (-1)^p \langle \psi_l | \hat{h}_l | \psi_{pl}^{'} \rangle \prod_{j \neq i} \langle \psi_j | \psi_{pj}^{'} \rangle \\ &= \sum_P (-1)^p \langle \psi_l | \hat{h}_l | \psi_{pl}^{'} \rangle \end{aligned} \tag{3.1.51}$$

where $(-1)^p = (-1)^{|l-m|}$ since we need $|l-m|$ permutations to have the same orbitals in the same order. Finally we consider the case $\Phi = \Phi^{'}$. Every value of j provides $\prod_{j\neq i}\langle\psi_j|\psi^{'}_{pj}\rangle$ so equation (3.1.50) becomes:

$$\langle\Phi_D|\hat{H}|\Phi_D\rangle = \sum_{i=1}^{N}\langle\psi_i|\hat{h}_i|\psi_i\rangle \tag{3.1.52}$$

Rule-3: $\hat{H} = \sum_{j>i}^{N}\hat{h}_{i,j}$ is two electron operator depending on coordinates of ith and jth electrons.

a. $\langle\Phi_D|\hat{H}|\Phi^{'}_D\rangle = 0$, if Φ and $\Phi^{'}$ differ by more than two orbitals.

b. $\langle\Phi_D|\hat{H}|\Phi^{'}_D\rangle = (-1)^{|l-m|+|s-t|}(\langle\psi_l\psi_s|\hat{h}_{i,j}|\psi^{'}_m\psi^{'}_t\rangle - \langle\psi_l\psi_s|\hat{h}_{i,j}|\psi^{'}_t\psi^{'}_m\rangle)$ if $\Phi^{'}$ and Φ differ by two orbitals ψ_l and ψ_s in Φ and $\psi^{'}_m$ and $\psi^{'}_t$ in $\Phi^{'}$.

c. $\langle\Phi_D|\hat{H}|\Phi^{'}_D\rangle = (-1)^{|l-m|}\sum_{i\neq l}(\langle\psi_l\psi_i|\hat{h}_{i,j}|\psi^{'}_m\psi_i\rangle - \langle\psi_l\psi_i|\hat{h}_{i,j}|\psi_i\psi^{'}_m\rangle)$, if Φ differs by one orbital, ψ_l in position l from $\Phi^{'}$ which has $\psi^{'}_m$ in position m instead.

d. $\sum_{j>i}^{N}(\langle\psi_i\psi_j|\hat{h}_{i,j}|\psi_i\psi_j\rangle - \langle\psi_i\psi_j|\hat{h}_{i,j}|\psi_j\psi_i\rangle)$, if $\Phi = \Phi^{'}$.

$$\begin{aligned}\langle\Phi_D|\hat{H}|\Phi^{'}_D\rangle &= \sum_{j>i}^{N}\sum^{P}(-1)^P\langle\psi_1|\psi^{'}_{p1}\rangle\langle\psi_2|\psi^{'}_{p2}\rangle...\langle\psi_i\psi_j|\hat{h}_{i,j}|\psi^{'}_{pi}\psi^{'}_{pj}\rangle...\langle\psi_N|\psi^{'}_{pN}\rangle \\ &= \sum_{j>i}^{N}\sum^{P}(-1)^P\langle\psi_i\psi_j|\hat{h}_{i,j}|\psi^{'}_{pi}\psi^{'}_{pj}\rangle\prod_{k\neq i,j}\langle\psi_k|\psi^{'}_{pk}\rangle\end{aligned} \tag{3.1.53}$$

If we do not have $\psi_k = \psi^{'}_{pk}$ for $\forall k \neq i,j$ equation (3.1.53) is zero. Asuming

that Φ and $\Phi^{'}$ differ by more than two orbitals there is not any permutation which provides $\prod_{k\neq i,j}\langle\psi_k|\psi^{'}_{pk}\rangle = 1$ thus $\langle\Phi_D|\hat{H}|\Phi^{'}_D\rangle = 0$ If Φ and $\Phi^{'}$ differ by two orbitals, ψ_l and ψ_s in Φ and $\psi^{'}_m$, $\psi^{'}_t$ in $\psi^{'}_m$, there are only two possible permutations. $\hat{P}$ and$\hat{L} = \hat{P}_{l,s}\hat{P}$ satisfying these conditions, where:

$$\begin{aligned}\psi_k &= \psi^{'}_{Pk}\\ \psi^{'}_m &= \psi^{'}_{Pl}\\ \psi^{'}_t &= \psi^{'}_{Ps}\end{aligned} \tag{3.1.54}$$

and

$$\begin{aligned}\psi_k &= \psi^{'}_{Lk}\\ \psi^{'}_m &= \psi^{'}_{Ll}\\ \psi^{'}_t &= \psi^{'}_{Ls}\end{aligned} \tag{3.1.55}$$

$$\begin{aligned}\langle\Phi_D|\hat{H}|\Phi^{'}_D\rangle &= (-1)^p\langle\psi_l\psi_s|\hat{h}_{i,j}|\psi^{'}_{Pl}\psi^{'}_{Ps}\rangle + (-1)^l\langle\psi_l\psi_s|\hat{h}_{i,j}|\psi^{'}_{Ll}\psi^{'}_{Ls}\rangle\\ &= (-1)^p\langle\psi_l\psi_s|\hat{h}_{i,j}|\psi^{'}_m\psi^{'}_t\rangle + (-1)^l\langle\psi_l\psi_s|\hat{h}_{i,j}|\psi^{'}_t\psi^{'}_m\rangle\\ &= (-1)^p(\langle\psi_l\psi_s|\hat{h}_{i,j}|\psi^{'}_m\psi^{'}_t\rangle - \langle\psi_l\psi_s|\hat{h}_{i,j}|\psi^{'}_t\psi^{'}_m\rangle)\end{aligned} \tag{3.1.56}$$

where $(-1)^L =_(-1)^P$ is used. Also $|l-m|$ permutations is used to line-up ψ_l and $\psi^{'}_m$, $|s-t|$ permutations for ψ_s and $\psi^{'}_t$. Therefore $(-1)^p = (-1)^{|l-m|+|s-t}$. If Φ and $\Phi^{'}$ differ by only one orbital, ψ_l in Φ and $\psi^{'}_m$ in $\Phi^{'}$, the conditions can be satisfied when $i = l$. But j can take on any value allowed by the original definition of H. For any given value of j, there are two possible permutations which give non-zero results, so again we have:

$$\langle\Phi_D|\hat{H}|\Phi^{'}_D\rangle = \sum_{j\neq l}^{N}(-1)^{|l-m|}(\langle\psi_l\psi_s|\hat{h}_{i,j}|\psi^{'}_m\psi^{'}_t\rangle - \langle\psi_l\psi_s|\hat{h}_{i,j}|\psi^{'}_t\psi^{'}_m\rangle) \tag{3.1.57}$$

Finally if Φ and $\Phi^{'}$ are identical all permutations provides the condition so we

have:

$$\langle \Phi_D | \hat{H} | \Phi_D^{'} \rangle = \sum_{j>i}^{N} (\langle \psi_i \psi_j | \hat{h}_{i,j} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \hat{h}_{i,j} | \psi_j \psi_i \rangle \quad (3.1.58)$$

CHAPTER FOUR
SPIN EIGENFUNCTIONS

4.1 One Electron Spin Eigenfunctions

In quantum mechanics spin is the essential property of elementary particles. Every elementary particle has a specific and immutable spin quantum number S. If one measures spin angular momentum of an electron along an axis usually denoted by z, the result is either $\hbar/2$ or $-\hbar/2$ where $\hbar$ is the Plancks constant. z component of spin operator $\hat{S}_z$ has two eigenvalues: α and β represents spin up and spin down, respectively.

$$\hat{S}_z\alpha = \frac{\hbar}{2}\alpha$$

$$\hat{S}_z\beta = -\frac{\hbar}{2}\beta$$

Spin angular momemntum compenents of a system for example electron cannot measured be simultaneously because they don't commute and they have commutation relations as follows:

$$[\hat{S}_x, \hat{S}_y] = i\hat{S}_z$$

$$[\hat{S}_y, \hat{S}_z] = i\hat{S}_x$$

$$[\hat{S}_z, \hat{S}_x] = i\hat{S}_y$$

However square of spin angular momentum operator $\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$ commutes with $\hat{S}_z$ so we can construct common eigenfunctions of this operators.

$$\hat{S}^2\alpha = S(S+1)\alpha = \frac{3}{4}\hbar^2\alpha$$

$$\hat{S}^2\beta = S(S+1)\beta = \frac{3}{4}\hbar^2\beta$$

This formation brief information about one electron spin operators and their eigenfunctions will be basis for many electron case.

4.2 Many Electron Spin Eigenfunctions

In this section we will give information about building eigenfunctions of many electron spin operators. Initially constructing eigenfunctions of z component of total spin operator $\hat{S}_z$ is discussed, then a straightforward method for constituting eigenfunctions of square of total spin operator $\hat{S}^2$ is explained which are derived originally in Pauncz, (1979).

4.2.1 $\hat{S}_z$ Eigenfunctions

$\hat{S}_z$ operator is the sum of one electron operators:

$$\hat{S}_z = \sum_{i=1}^{N} \hat{S}_z(i) \tag{4.2.1}$$

where $\hat{S}_z(i)$ represents one electron operator. As the operator $\hat{S}_z$ is the sum of one electron operators, the eigenfunctions are products of one-electron spin functions; we shall call them *primitive spin functions* and denote them by θ_i:

$$\theta_i = \theta_1(1)\theta_2(2)...\theta_N(N) \tag{4.2.2}$$

Each $\theta(j)$, can be either α or β. If we have N electrons, dimension of the spin space must be equal to 2^N. This space can be decomposed into subspaces according to the eigenvalues of $\hat{S}_z$:

$$S_z\theta_i(\mu,\gamma) = \frac{1}{2}(\mu-\gamma)\theta_i(\mu,\gamma) \qquad i = 1,2,...,\begin{pmatrix} N \\ \mu \end{pmatrix} \tag{4.2.3}$$

$\theta_i(\mu,\gamma)$ is a primitive spin eigenfunction with μ α's and γ β's. The number of these functions:

$$\begin{pmatrix} N \\ \mu \end{pmatrix} = \begin{pmatrix} N \\ \gamma \end{pmatrix} = \frac{N!}{\mu!\gamma!}$$

Evidently:

$$\sum_{\gamma=0}^{N} \begin{pmatrix} N \\ \gamma \end{pmatrix} = 2^N$$

4.2.2 Construction of $\hat{S}^2$ Eigenfunctions by the Diagonalization Method

In N electron case $\hat{S}^2$ operator take the form:

$$\hat{S}^2 X = \sum_{j>i} \hat{P_{ij}} X + \frac{N}{4}(4-N)X \tag{4.2.4}$$

where $\hat{P_{ij}}$ is the permutation operator which changes the positions of $i.$ and $j.$ electron. This equation is called as *Dirac Identity* and derivation can be found in Appendix One. Our goal is to find eigenfunctions of this operator. There are many ways to do this. In this section we will discuss a straightforward procedure in which all we need to do is to write $\hat{S}^2$ operator in matrix form using primitive spin functions.

Since $\hat{S}^2$ and $\hat{S}_z$ operators commute we can build simultaneous eigenfunctions of this operators. However primitive spin functions in general are not eigenfunctions of $\hat{S}^2$ operator. But it can be obtained by using proper linear combinations of primitive spin functions $X = \sum_k c_k\theta_k$ which belongs to same eigenvalue.

If there is one function with a given $\hat{S}_z$ eigenvalue, then this must be eigenfunction of both of these operators. For example the primitive function

$\alpha(1)\alpha(2)...\alpha(N)$, is an eigenfunction of $\hat{S}^2$ with eigenvalue $M = N/2$. If there is more than one function with a given $\hat{S}_z$ eigenvalue, then one can set up matrix representation of $\hat{S}^2$ in the space spanned by $\begin{pmatrix} N \\ \mu \end{pmatrix}$ primitive spin functions. Matrix elements of $\hat{S}^2$ operator can be found by using Dirac identity. As an example consider the case electron number is 3 and $M = 1/2$. Primitive spin functions must be $\theta_1 = \alpha\alpha\beta, \quad \theta_2 = \alpha\beta\alpha, \quad \theta_3 = \beta\alpha\alpha$.

$$\begin{aligned} \hat{S}^2|\theta_1\rangle &= \sum_{j>i} \hat{P_{ij}}|\theta_1\rangle + \frac{N}{4}(4-N)|\theta_1\rangle \\ &= P_{12}|\alpha\alpha\beta\rangle + P_{13}|\alpha\alpha\beta\rangle + P_{23}|\alpha\alpha\beta\rangle + \frac{3}{4}(4-3)|\alpha\alpha\beta\rangle \\ &= |\alpha\alpha\beta\rangle + |\beta\alpha\alpha\rangle + |\alpha\beta\alpha\rangle + \frac{3}{4}|\alpha\alpha\beta\rangle \\ &= \frac{7}{4}|\theta_1\rangle + |\theta_2\rangle + |\theta_3\rangle \end{aligned} \tag{4.2.5}$$

In a similar way

$$\hat{S}^2|\theta_2\rangle = |\theta_1\rangle + \frac{7}{4}|\theta_2\rangle + |\theta_3\rangle \tag{4.2.6}$$

$$\hat{S}^2|\theta_3\rangle = |\theta_1\rangle + |\theta_2\rangle + \frac{7}{4}|\theta_3\rangle \tag{4.2.7}$$

Therefore $\{\hat{S}^2\}$ matrix:

$$\begin{pmatrix} \frac{7}{4} & 1 & 1 \\ 1 & \frac{7}{4} & 1 \\ 1 & 1 & \frac{7}{4} \end{pmatrix} \tag{4.2.8}$$

Eigenvalues of this matrix $\frac{15}{4}$ and $\frac{3}{4}$ corresponding to spin quantum numbers $S = \frac{3}{2}$ and $S = \frac{1}{2}$, respectively. Eigenvectors are $(1,1,1)$,$(-1,0,1)$,$(-1,1,0)$. Because $\hat{S}^2$ is an hermitian operator different eigenvalues correspond to different eigenfunctions must be orthogonal. $S = 1/2$ case is degenerate so eigenvalues are not orthogonal to each other. Therefore the orthonormalised spin eigenfunctions are obtained by applying the Gram- Schmidt orthonormalization procedure. New eigenfunctions are $(\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}})$, $(-\frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}})$, $(-\frac{1}{\sqrt{6}}, \frac{2}{\sqrt{6}}, -\frac{1}{\sqrt{6}})$. For $N = 3$ and

$M = 1/2$ spin eigenfunctions are:

$$\begin{aligned} X(3, \tfrac{3}{2}, \tfrac{1}{2}; 1) &= \frac{1}{\sqrt{3}}(\alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha) \\ X(3, \tfrac{1}{2}, \tfrac{1}{2}; 1) &= \frac{1}{\sqrt{2}}(-\alpha\alpha\beta + \beta\alpha\alpha) \\ X(3, \tfrac{1}{2}, \tfrac{1}{2}; 2) &= \frac{1}{\sqrt{6}}(-\alpha\alpha\beta + 2\alpha\beta\alpha - \beta\alpha\alpha) \end{aligned} \tag{4.2.9}$$

$X(N, S, M; k)$, are eigenfunctions of $\hat{S}^2$ operator. N is electron number, S spin quantum number, M magnetic quantum number and k is an integer represents different eigenfunctions in a multidimensional spin eigenspace (Wang, Hines, & Muhandiramge, n.d.). Diagonalization of $\hat{S}^2$ matrix is a straight forward procedure. The drawback of this method lies in the fact that the dimension of subspace is usually quite large (Pauncz, 1979).

CHAPTER FIVE
SPIN ADAPTED BASE

5.1 Combination of Spatial and Spin Functions

So far we have discussed constructing spin eigenfunctions. In this section we will discuss to construct spin adapted basis (Muhandiramge, 2003) formed from antisymmetric N electron wavefunctions that contain both spatial and spin coordinates and also eigenfunctions of $\hat{S}^2$ operator. The derivations given below can be found originally in Ruedenberg & Poshusta, (1972); Salmon & Ruedenberg, (1972); Pauncz, (1979); Pauncz, (1979); Muhandiramge, (2003).

As we know total wavefunction of N electron wavefunction must be antisymmetric, i,.e., it must change sign if we interchange the coordinates of two electrons. Let's start with a spatial wavefunction $\phi(r_1, r_2, .., r_n)$ which depends the spatial coordinates of electrons $1, 2, .., N$. Many electron wavefunction (Pauncz, 1979):

$$\Psi_i = \hat{A}\Phi(r_1, r_2, .., r_n)X(N, S, M; i) \quad i = 1, 2, ...f(N, S) \tag{5.1.1}$$

$\hat{A}$ is antisymmetrizer:

$$\hat{A} = \frac{1}{\sqrt{N!}} \sum_P (-1)^p \hat{P} \tag{5.1.2}$$

$X(N, S, M; i)$ is spin function which is eigenfunciton of $\hat{S}^2$ operator and spatial function:

$$\Phi(r_1, r_2, .., r_n) = \phi_1(r_1)\phi_2(r_2)...\phi_N(r_N)$$

where $\phi_i(r_i)$ represents one electron spatial wavefunction. In a given calculation N, S, M will be fixed numbers so we can show $X(N, S, M; i)$ spin eigenfunction as X_i We can show that this many electron wavefunction is eigenfunction of $\hat{S}^2$

(Pauncz, 1979):

$$\hat{S}^2\Psi_i = \hat{S}^2\hat{A}\Phi X_i = \hat{A}\Phi\hat{S}^2 X_i = S(S+1)\Psi_i \tag{5.1.3}$$

Properties of Antisymmetrizer

a) $\hat{P}\hat{A} = \hat{P}\hat{A} = (-1)^p\hat{A}$

Proof: Multiply by a given permutation, say $\hat{R}$, on the left.

$$\begin{aligned} \hat{R}\hat{A} &= \hat{R}\frac{1}{\sqrt{N!}}\sum_P (-1)^p\hat{P} \\ &= \frac{1}{\sqrt{N!}}\sum_P (-1)^p\hat{R}\hat{P} \end{aligned} \tag{5.1.4}$$

As $\hat{P}$ runs over all permutations, $\hat{R}\hat{P} = \hat{Q}$ also runs over all permutations (in a different order). We can therefore replace sum over $\hat{P}$ by a summation over $\hat{Q}$:

$$(-1)^r(-1)^p = (-1)^{rp}$$

$$\begin{aligned} \hat{R}\hat{A} &= \frac{1}{\sqrt{N!}}\sum_Q (-1)^{q+r}\hat{Q} \\ &= (-1)^r\hat{A} \end{aligned} \tag{5.1.5}$$

b) Antisymmetrizer is a hermitian operator:$(\hat{A}^\dagger = \hat{A})$

Proof:

$$\begin{aligned} \hat{A}^\dagger &= \frac{1}{\sqrt{N!}}\sum_p (-1)^p\hat{P}^\dagger \\ &= \frac{1}{\sqrt{N!}}\sum_P (-1)^p\hat{P}^{-1} \end{aligned} \tag{5.1.6}$$

P ve P^{-1} have the same parity.

$$\begin{aligned} \hat{A}^{\dagger} &= \frac{1}{\sqrt{N!}} \sum_{P^{-1}} (-1)^{p^{-1}} \hat{P}^{-1} \\ &= \hat{A} \end{aligned} \tag{5.1.7}$$

c) The antisymmetrizer is an essentially idempotent operator: $\hat{A}^2 = (N!)^{1/2} \hat{A} = \sum_p (-1)^p \hat{P}$

Proof:

$$\begin{aligned} \hat{A}^2 &= \frac{1}{\sqrt{N!}} \sum_P (-1)^p \hat{P} \frac{1}{\sqrt{N!}} \sum_R (-1)^r \hat{R} \\ &= \frac{1}{N!} \sum_P \sum_R (-1)^p (-1)^r \hat{P}\hat{R} \\ &= \frac{1}{N!} \sum_P \sum_R (-1)^q (-1)^r \hat{Q} \end{aligned} \tag{5.1.8}$$

The product $\hat{P}\hat{R} = \hat{Q}$ is again a permutation. If $\hat{P}$ is held constant and $\hat{R}$ runs over all the permutations, so does $\hat{Q}$ We shall replace the sum over $\hat{R}$ over sum over $\hat{Q}$:

$$\begin{aligned} \hat{A}^2 &= \sum_P (N!)^{1/2} \hat{A} \\ &= (N!)^{1/2} \hat{A} \end{aligned} \tag{5.1.9}$$

The first property is the most important one; from it follows that Ψ_i is antisymmetric. The other properties will be useful for the calculation of matrix elements (Pauncz, 2000).

5.1.1 Properties of Spin Adapted Basis

The base which is formed from antisymmetric space-spin wavefunction is called as *spin adapted base* (Muhandiramge, 2003). In the following properties of spin adapted base are given briefly. More details can be get from Salmon & Ruedenberg, (1972), Pauncz, (2000) and Muhandiramge, (2003).

Lineer Dependence: Unless special precautions are taken, some of them will be linearly dependent (Salmon & Ruedenberg, 1972).
If two of the space products Φ and Φ' are related by a permutation

$$\Phi' = \hat{P}\Phi$$

then wavefunctions containing Φ' will be linearly dependent on those containing Φ:

$$\begin{aligned} \hat{A}\Phi' X_i &= \hat{A}\hat{P}\Phi X_i \\ &= \hat{A}\hat{P}[\Phi\hat{P}^{-1}X_i] \\ &= \hat{P}\hat{A}[\Phi\hat{P}^{-1}X_i] \\ &= \epsilon(p)\hat{A}[\Phi\sum_{j=1}^{f} U(P)_{j,i}X_j] \\ &= \epsilon(p)\sum_{j=1}^{f} U(P)_{j,i}\hat{A}\Phi X_j \end{aligned} \tag{5.1.10}$$

where $\epsilon(p)$ is $+1$ when P is even and $+1$ when P is odd. Therefore in order to avoid this dependence, we must include spatial wavefunction that are not permutations of each other. In other words Φ should include only one space product for each choice of orbitals. Still, there is a linear dependence when space products are doubly occupied. Suppose that Φ contains at least one doubly occupied orbital, so that there exists a transposition $\hat{t} = \hat{t}^{-1}$ under which Φ is invariant: $\Phi = \Phi'$

$$\begin{aligned} \hat{A}\Phi X_i &= \hat{A}\hat{t}\Phi X_i \\ &= \hat{A}\hat{t}[\Phi\hat{t}^{-1}X_i] \\ &= -\hat{A}[\Phi\hat{t}^{-1}X_i] \\ &= -\hat{A}\Phi\hat{t}X_i \\ &= -\sum_{j=1}^{f} U(t)_{j,i}\hat{A}\Phi X_j \end{aligned} \tag{5.1.11}$$

$$U(t)_{j,i} = -\delta_{j,i} \tag{5.1.12}$$

This means that spin adapted wavefunctions can be linearly independent only if

their spin functions are antisymmetric with respect to every interchange of two electrons occupying the same space orbital (Salmon & Ruedenberg, 1972). Also any space orbital may not occur more than two in a space product Φ . We must define linear independent base to construct a well defined eigenvalue problem. Therefore we should make some conventions about spatial and spin functions.

Space Products: It is convenient to make some definitions about spin adapted base (Salmon & Ruedenberg, 1972). Two electrons numbered by $2i-1$ and $2i$ will be called as geminal pair. A transposition $\hat{P}_{2i-1,2i}$ interchanging electrons $2i-1$ and $2i$ will be called geminal transposition. Permutation which can be written as a product of geminal transpositions is called geminal permutation. Geminal subgroup S_Φ is a group of all permutations formed from $\{P_{1,2}, P_{3,4}, .., P_{2d-1,2d}\}$. d is the number of doubly occupied orbitals in space product. An element of this group $P = P_{1,2}^{n_1} * P_{3,4}^{n_2} * ... * P_{2d-1,2d}^{n_d}$. $(n_i = 0 \quad or \quad 1, i = 1, .., d)$. The order of this group is 2^d (Muhandiramge, 2003).

In order to have a linearly independent base in a given space product doubly occupied orbitals must be in $(1,2), (3,4), ..., (2d-1, 2d)$ positions. In other words doubly occupied orbitals are listed first in the order of ascending order (Ruedenberg, 1971). And also spatial functions of different spin adapted wave functions should not be permutations of each other.

Spin Eigenfunctions: According to equation (5.1.12) spin eigenfunction must be antisymmetric with respect to geminal transpositions. Spin eigenfunctions must have the property:

$$\hat{P}_{2i-1,2i} = -X_i \tag{5.1.13}$$

It is certainly possible to construct such spin functions. Since geminal

permutations and spin operators commute we can construct orthonormal spin eigenfunctions which are simultaneous eigenfunctions of this operators:

$$\hat{S^2}\hat{P}X(N,S,M;k) = \hat{P}\hat{S^2}X(N,S,M;k) = S(S+1)\hat{P}X(N,S,M;k) \quad (5.1.14)$$

$$\hat{S_z}\hat{P}X(N,S,M;k) = \hat{P}\hat{S_z}X(N,S,M;k) = M\hat{P}X(N,S,M;k) \quad (5.1.15)$$

where $X(N,S,M;k)$ is eigenfunction of $\hat{S^2}$ operator. New spin function $\hat{P}X(N,S,M;k)$ belongs to the $f(N,S)$ dimensional spin space by the orthogonal set of functions, so it can be expressed as a linear combination of them:

$$\hat{P}X(N,S,M;k) = \sum_{l=1}^{f} X(N,S,M;l)U(\hat{P})_{lk} \quad (5.1.16)$$

The expansion coefficient $U(\hat{P})_{lk}$ can be obtained left by $X(N,S,M;l)$ and integrating over spin N-electron spin space. By orthogonality we should have one contribution:

$$\langle X(N,S,M;m)|\hat{P}|X(N,S,M;l)\rangle = U(\hat{P})_{mk} \quad (5.1.17)$$

Let us apply another permutation to the result of the first permutation:

$$\begin{aligned} \hat{R}\hat{P} &= \sum_{l=1}^{f} \hat{R}X(N,S,M;l)U(\hat{P})_{lk} \\ &= \sum_{l=1}^{f}\sum_{m=1}^{f} X(N,S,M;m)U(\hat{R})_{ml}U(\hat{P})_{lk} \end{aligned} \quad (5.1.18)$$

The product of two permutations $\hat{P}$ and $\hat{R}$ is again a permutation $\hat{Q} = \hat{P}\hat{R}$ and if we apply $\hat{Q}$ directly to $X(N,S,M;k)$ we then have

$$\hat{Q}X(N,S,M;k) = \sum_{m=1}^{f} X(N,S,M;m)U(\hat{Q})_{mk} \quad (5.1.19)$$

Comparing the right hand side of equations (5.1.18) and (5.1.19) we must have

the same coefficient in both equations:

$$U(\hat{Q})_{mk} = \sum_{l=1}^{f} U(\hat{R})_{ml} U(\hat{P})_{lk} \tag{5.1.20}$$

The matrix corresponding to the product of permutations $\hat{P}$ and $\hat{R}$ is equal to the matrix corresponding to $\hat{Q} = \hat{P}\hat{R}$. Therefore we can write

$$U(RP) = U(R)U(P) \tag{5.1.21}$$

satisfying the condition for a representation of the symmetric group (Pauncz, 2000). Let's show spin function which are eigenfunctions of $\hat{S}^2$ by $X^0(N, S, M; k)$. This functions in general not eigenfunctions of geminal permutations. However the orthonormalised eigenvectors of $U(P_{2i-1,2i})$ will give the linear combinations of vectors X^0 that form a new orthonormal basis. This new orthonormal basis will be eigenfunctions of geminal permutations. As an example $N = 3, S = 1/2, M = 1/2$

$$X^0(3, \frac{1}{2}, \frac{1}{2}; 1) = \frac{1}{\sqrt{2}}(-\alpha\alpha\beta + \beta\alpha\alpha) \tag{5.1.22}$$

$$X^0(3, \frac{1}{2}, \frac{1}{2}; 2) = \frac{1}{\sqrt{6}}(-\alpha\alpha\beta + 2\alpha\beta\alpha - \beta\alpha\alpha) \tag{5.1.23}$$

$$\begin{aligned} \hat{P_{12}} X^0(3, \tfrac{1}{2}, \tfrac{1}{2}; 1) &= \frac{1}{\sqrt{2}}(-\alpha\alpha\beta + \beta\alpha\alpha) \\ &= \frac{1}{\sqrt{2}}(-\alpha\alpha\beta + \alpha\beta\alpha) \\ &= \frac{1}{2} X^0(3, \frac{1}{2}, \frac{1}{2}; 1) + \frac{\sqrt{3}}{2} X^0(3, \frac{1}{2}, \frac{1}{2}; 2) \end{aligned} \tag{5.1.24}$$

$$\begin{aligned} \hat{P_{12}} X^0(3, \tfrac{1}{2}, \tfrac{1}{2}; 2) &= \frac{1}{\sqrt{6}}(-\alpha\alpha\beta + 2\alpha\beta\alpha - \beta\alpha\alpha) \\ &= \frac{1}{\sqrt{6}}(-\alpha\alpha\beta + 2\beta\alpha\alpha - \alpha\beta\alpha) \\ &= \frac{\sqrt{3}}{2} X^0(3, \frac{1}{2}, \frac{1}{2}; 1) - \frac{1}{2} X^0(3, \frac{1}{2}, \frac{1}{2}; 2) \end{aligned} \tag{5.1.25}$$

Therefore $U(\hat{P}_{12})$ matrix:

$$\begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$$

Eigenvalues of this matrix ± 1 and eigenvectors $(\frac{\sqrt{3}}{2}, \frac{1}{2})$ and $(-\frac{1}{2}, \frac{\sqrt{3}}{2})$. New spin eigenfunctions:

$$\begin{aligned} X^1(3, \tfrac{1}{2}, \tfrac{1}{2}; 1) &= \frac{\sqrt{3}}{2} X^0(3, \frac{1}{2}, \frac{1}{2}; 1) + \frac{1}{2} X^0(3, \frac{1}{2}, \frac{1}{2}; 2) \\ &= \frac{\sqrt{3}}{2} \frac{1}{\sqrt{2}} (-\alpha\alpha\beta + \beta\alpha\alpha) + \frac{1}{2} \frac{1}{\sqrt{6}} (-\alpha\alpha\beta + 2\alpha\beta\alpha - \beta\alpha\alpha) \\ &= \frac{1}{\sqrt{6}} (-2\alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha) \end{aligned} \tag{5.1.26}$$

$$\begin{aligned} X^1(3, \tfrac{1}{2}, \tfrac{1}{2}; 2) &= -\frac{1}{2} X^0(3, \frac{1}{2}, \frac{1}{2}; 1) + \frac{\sqrt{3}}{2} X^0(3, \frac{1}{2}, \frac{1}{2}; 2) \\ &= \frac{1}{2} \frac{1}{\sqrt{2}} (-\alpha\alpha\beta + \beta\alpha\alpha) + \frac{\sqrt{3}}{2} \frac{1}{\sqrt{6}} (-\alpha\alpha\beta + 2\alpha\beta\alpha - \beta\alpha\alpha) \\ &= \frac{1}{\sqrt{2}} (-\alpha\beta\alpha + \beta\alpha\alpha) \end{aligned} \tag{5.1.27}$$

This new spin functions are eigenfunctions of P_{12}. First spin eigenfunction is symmetric under permutation P_{12} while second is antisymmetric. This means that the first function will vanish if we multiply it with a spatial function with doubly occupied orbitals in positions one an two. But we can product second spin eigenfunction with a spatial function in which two orbitals are the same (Muhandiramge, 2003).

So far we have construct spin adapted basis which has elements $\hat{A}\Phi X_i$. X_i is a spin eigenfunction which is also eigenfunction of geminal transpositions. In spatial wavefunctions doubly occupied orbitals must be in sequentially in the geminal positions. Also,two representative wavefunctions for different basis elements are not permutations of each other. With this conventions orthonormal basis can be constructed. Following theorems (Wang, Hines, & Muhandiramge, n.d.) proves the orthogonality and linear independence of spin

adapted base.

Theorem-1: Let $\Phi = \phi_1\phi_2...\phi_n$ with $\phi_{2i-1,2i} = \phi_{2i}$ (i.e. there is a doubly occupied orbital at this position). Then if $\hat{A}\Phi X_k = 0$ we have $P_{2i-1,2i}X_k = -X_k$ and $U(P_{2i-1,2i})_{kk} = -1$.

Proof:

$$\begin{aligned} U(P_{2i-1,2i})_{j,i} &= \langle X_j|P_{2i-1,2i}|X_i\rangle \\ &= \langle X_j|P_{2i-1,2i}|X_i\rangle \\ &= \lambda_j\langle X_j|X_i\rangle \\ &= \lambda_j\delta_{j,i} \end{aligned} \tag{5.1.28}$$

According to equation (5.1.12)

$$\lambda_j\delta_{j,i} = -\delta_{j,i}$$

$$\lambda_j = -1$$

And also

$$\begin{aligned} \hat{P}_{2i-1,2i}X_j &= \lambda_j X_j \\ &= -X_j \end{aligned} \tag{5.1.29}$$

We can say that representations of geminal transpositions are diagonal:

$$U(P)_{kk} = (-1)^p$$

Theorem-2: $\Phi = \phi_1\phi_2...\phi_n$ with $\phi_1 = \phi_2, ..., \phi_{2d-1,2d} = \phi_{2d}$ where d is the number of doubly occupied orbitals in Φ. Then if $\hat{P}$ is element of S_Φ, with $\hat{A}\Phi X_k \neq 0$ we have $U(P)_{kk} = (-1)^p$ where $(-1)^p$ is the parity of the permutation P.

Proof:

$$\begin{aligned} U(P) &= U(P_{1,2}^{n_1}) * U(P_{3,4}^{n_2}) * ... * U(P_{2d-1,2d}^{n_d}) \\ &= U(P_{1,2})^{n_1} * U(P_{3,4})^{n_2} * ... * U(P_{2d-1,2d})^{n_d} \end{aligned} \tag{5.1.30}$$

$U(P)^0$ is identity matrix. $U(P_{2i-1,2i})$ is diagonal. $U(P)^0$ birim matristir. The parity of P is given by $(-1)^p = (-1)^{n_1+n_2+...+n_d}$ so $U(P)_{kk} = (-1)^p$.

Theorem-3: The basis functions $\hat{A}\Phi X_j$ and $\hat{A}\Psi X_k$ are orthogonal if $\Phi \neq \Psi$ for all permutations P.

Proof:

$$\begin{aligned} \langle \hat{A}\Phi X_j | \hat{A}\psi X_k \rangle &= \langle \Phi X_j | \hat{A}^\dagger \hat{A}\psi X_k \rangle \\ &= \langle \Phi X_j | \sqrt{N!}\hat{A}\psi X_k \rangle \\ &= \textstyle\sum_P (-1)^p \langle \Phi | \hat{P}\psi \rangle \langle X_j | \hat{P} X_k \rangle \\ &= \textstyle\sum_P (-1)^p \langle \Phi | \hat{P}\psi \rangle U(P)_{jk} \end{aligned} \tag{5.1.31}$$

This means basis elements are orthogonal for different spatial wavefunctions. Note that our basis does not include spatial wavefunctions that are non-invariant permutations of each other. The only case where two basis elements would have the same spatial wavefunction is when it is multiplied by a different spin eigenfunction. This case is dealt with by the next theorem.

Teorem-4: The basis elements $\hat{A}\Phi X_j$ and $\hat{A}\Phi X_k$ are orthogonal where $\hat{A}\Phi X_j, \hat{A}\Phi X_k \neq 0$ That is for $j = k$ their inner product is 0. Furthermore for $j = k$ their inner product is 2^d , where d is the number of pairs of doubly occupied orbitals in Φ.

Proof:

$$\langle \hat{A}\Phi X_j | \hat{A}\Phi X_k \rangle = \sum_P (-1)^p \langle \Phi | \hat{P}\Phi \rangle U(P)_{jk} \tag{5.1.32}$$

$$\langle \Phi | P\Phi \rangle = \begin{cases} 1, & PS_\Phi; \\ 0, & \text{otherwise} \end{cases} \tag{5.1.33}$$

In this case (5.1.32) equation:

$$\langle \hat{A}\Phi X_j | \hat{A}\Phi X_k \rangle = \sum_{P \epsilon S_\Phi} (-1)^p U(P)_{jk} \tag{5.1.34}$$

If $j = k$ then $\langle \hat{A}\Phi X_j | \hat{A}\Phi X_k \rangle = 0$ as $U(P)_{jk}$ is diagonal for $P \epsilon S_\Phi$.
If $j = k$ then

$$\begin{aligned} \langle \hat{A}\Phi X_k | \hat{A}\Phi X_k \rangle &= \sum_{P \epsilon S_\Phi} (-1)^p U(P)_{kk} \\ &= \sum_{P \epsilon S_\Phi} (-1)^p (-1)^p \\ &= |S_\Phi| \\ &= 2^d \end{aligned} \tag{5.1.35}$$

Thus $N_\Phi \hat{A}\Phi X_k$ is a properly normalised basis functions with $N_\Phi = \frac{1}{\sqrt{2^d}}$.

5.2 Hamiltonian Matrix Elements

In this section analytic derivations of Hamiltonian matrix element in the spin adapted base and special cases are discussed. These derivations are can be found originally Muhandiramge, (2003). In order to construct Hamiltonian matrix we must find $\langle N_\Phi \hat{A}\phi X_k | \hat{H} | N_\psi \hat{A}\psi X_j \rangle$ matrix elements with Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_{int}$. $\hat{H}_0 = \hat{H}_{0i}$ where is the one electron component $\hat{H}_{int} = \sum_{j>i}^{N} \hat{H}_{i,j}$ is the interaction component that acts pairwise. One electron orbitals are the eigen-functions of $\hat{H}_{0i}$ i.e. $(\hat{H}_{0i}\phi_{r_i} = E_i\phi_{r_i})$ .This is the general form of a spin- free Hamiltonian in which spin-orbit and spin-spin interactions are neglected. This

gives us:

$$\begin{aligned}\langle N_\Phi \hat{A}\phi X_j|\hat{H}|N_\psi \hat{A}\psi X_k\rangle &= \langle N_\Phi \hat{A}\phi X_j|\hat{H}_0+\hat{H}_{int}|N_\psi \hat{A}\psi X_k\rangle \\ &= \langle N_\Phi \hat{A}\phi X_j|\hat{H}_0|N_\psi \hat{A}\psi X_k\rangle + \langle N_\Phi \hat{A}\phi X_j|\hat{H}_{int}|N_\psi \hat{A}\psi X_k\rangle\end{aligned} \tag{5.2.1}$$

5.2.1 The Single Electron Integral

As one electron orbitals are eigenfuncitons of $\hat{H}_{0i}$'nin the single electron integral is straightforward.

$$\begin{aligned}\langle N_\Phi \hat{A}\Phi X_j|\hat{H}_0|N_\psi \hat{A}\psi X_k\rangle &= N_\Phi N_\psi i \sum_P^N (-1)^p \langle\Phi|\hat{H}_0|P\psi\rangle U(P)_{jk} \\ &= N_\Phi N_\psi \sum_{i=1}^N \sum_P (-1)^p \langle\Phi|\hat{H}_{0i}|P\psi\rangle U(P)_{jk} \\ &= N_\Phi N_\psi \sum_{i=1}^N \sum_P (-1)^p E_{P(i)} \langle\Phi|P\psi\rangle U(P)_{jk}\end{aligned} \tag{5.2.2}$$

where $\hat{H}_{0i}(P\psi) = E_{P(i)}(P\psi)$. $E_{P(i)}$ is the single electron energy of ith orbital in $P\psi$.

If $\Phi \neq \psi$ then $\langle\Phi|P\psi\rangle = 0$ therefore we have $\langle N_\Phi \hat{A}\Phi X_j|\hat{H}_0|N_\Phi \hat{A}\psi X_k\rangle = 0$.

But if $\Phi = \psi$ and $P\epsilon S_\phi$ according to (5.1.33) equation it must be $\langle\Phi|P\psi\rangle = 1$.

Therefore

$$\begin{aligned}
\langle N_\Phi \hat{A}\Phi X_j|\hat{H}_0|N_\Phi \hat{A}\psi X_k\rangle &= N_\Phi^2 \sum_{i=1}^{N}\sum_{P\epsilon S_\phi}(-1)^p E_{p(i)}\langle\Phi|\Phi\rangle U(P)_{jk} \\
&= N_\Phi^2 \sum_{i=1}^{N}\sum_{P\epsilon S_\phi}(-1)^p(-1)^p\delta_{j,k}E_i \\
&= N_\Phi^2 \sum_{i=1}^{N}\sum_{P\epsilon S_\phi}(-1)^{2p}\delta_{j,k}E_i \\
&= N_\Phi^2 \|S_\phi| \sum_{i=1}^{N}\delta_{j,k}E_i \\
&= \delta_{j,k}\sum_{i=1}^{N}E_i
\end{aligned} \tag{5.2.3}$$

In other words $\hat{A}\Phi X_j$ and $\hat{A}\psi X_k$ wavefunctions is same in both space and spin functions i.e. $\Phi = \psi$ and $j = k$ then $\langle N_\Phi \hat{A}\Phi X_j|\hat{H}_0|N_\psi \hat{A}\psi X_k\rangle$ expectation value is the sum of one electron energies $\sum_{i=1}^{N}E_i$, otherwise it is equal to zero.

5.2.2 Line-up Permutation

$N_\Phi \hat{A}\Phi X_j$ and $N_\psi \hat{A}\psi X_k$ are different wavefunctions with $\Phi = \phi_1\phi_2...\phi_N$ and $\Psi = \psi_1\psi_2...\psi_N$. There is a permutation called *linu-up permutation* which makes the orbitals in Ψ to bring into maximum coincidence with in Φ. If we assume that Ψ and Φ have $N - q$ orbitals in common, the remaining q orbitals of Φ will not occur in Ψ. There is a permutation like $W = \hat{L}\psi$ which has following properties.

a) $(N - q)$ common orbitals occur in same position in Ψ and Φ.

b) The remaining q orbitals occur in Φ in the same order as they occur in Ψ

There always exists a line-up permutation. However if there are doubly occupied orbitals it is not unique. Using $W = \hat{L}\psi = w_1 w_2 ... w_N$ notation the following conventions will be adopted in the presence of doubly occupied orbitals:

a) Assuming that ϕ_α occurs twice in Φ and once in Ψ if $\phi_{2i-1} = \phi_{2i} = \phi_\alpha$ then it must be $w_{2i-1} \neq \phi_{2i-1}$ and $w_{2i} = \phi_\alpha$.

b)If ϕ_β occurs twice in Ψ and once in Φ it must be $\psi_{2i} = \phi_{2i}$.

c) If the orbital is doubly occupied in both Φ and Ψ then it should be $\psi_{2i-1} = \phi_{2i-1}$ and $\psi_{2i} = \phi_{2i}$.

According to this three properties line-up permutation must be function of Φ and Ψ : $(\hat{L}(\Phi, \psi))$.

5.2.3 Interaction Integral

Interaction integral which depends on two elecron coordinates is $\hat{H}_{int} = \sum_{j>i} \hat{H}_{i,j}$ where $\hat{H}_{i,j}$ represents the interaction between two electrons.

$$\begin{aligned} \langle \Phi | \hat{H}_{i,j} | \Psi \rangle &= \langle \phi_1 \phi_2 ... \phi_N | \hat{H}_{i,j} | \psi_1 \psi_2 ... \psi_N \rangle \\ &= \langle \psi_i \psi_j | \hat{H}_{i,j} | \phi_i \phi_j \rangle \prod_{k \neq i,j}^{N} \langle | \phi_k | \psi_k \rangle \end{aligned} \tag{5.2.4}$$

Therefore expectation value of interaction integral $\langle\Phi|\hat{H}_{i,j}|\Psi\rangle = 0$ unless for $\phi_k = \psi_k \quad \forall \neq i,j$ Using this

$$\begin{aligned}\langle N_\Phi \hat{A}\phi X_j|\hat{H}_{int}|N_\Psi \hat{A}\psi X_k\rangle &= N_\phi N\Psi \sum_P (-1)^p \langle\Phi|\hat{H}_{int}|P\Psi\rangle U(P)_{jk} \\ &= N_\phi N_\Psi \sum_{j>i}\sum_P (-1)^p \langle\Phi|\hat{H}(i,j)|P\Psi\rangle U(P)_{jk} \\ &= N_\phi N_\Psi \sum_{j>i}\sum_P ((-1)^p \langle\phi_i\phi_j|\hat{H}(i,j)|(P\Psi)_i(P\Psi)_j\rangle \times \\ &\quad \textstyle\prod_{k\neq i,j}^N \langle\phi_k|(P\Psi)_k\rangle U(P)_{jk})\end{aligned} \tag{5.2.5}$$

where $(P\Psi)_i$ represents the ith orbital in $(P\Psi)$.

We can define a permutation $L_{i,j}$ which lines up Φ and Ψ such that $\phi_k = (L_{i,j}\psi_k)$ for $\forall \neq i,j$. If there is not a permutation for particular Φ, Ψ, i, j then $L_{i,j} = 0$ and $U(L_{i,j}) = 0$. For this permutation $\prod_{k\neq i,j}^{N} \langle\phi_k|(L_{i,j}\Psi)_k\rangle = 1$ However this permutation will not be unique because for $Q\epsilon S_\Phi$ $L_{i,j}Q$ and $P_{i,j}L_{i,j}Q$ are line-up permutations. It must be noticed that for the case of $i = j$ $((P\Psi)_i = (P\Psi)_j)$ $L_{i,j}Q$ and $P_{i,j}L_{i,j}Q$ will produce same integrals. Define w_i as $w_i = (L_{i,j}\Psi)_i$ and w_j as $w_j = (L_{i,j}\Psi)_j$, also

$$\langle\Phi|P\Phi\rangle = \begin{cases} 1, & w_i = w_j; \\ 0, & \text{otherwise} \end{cases} \tag{5.2.6}$$

In this case we have:

$$\langle N_\Phi \hat{A}\phi X_j|\hat{H}_{int}|N_\Psi \hat{A}\psi X_k\rangle = N_\phi N_\Psi \sum_{j>i}\sum_{Q\epsilon S_\phi} 2^{-\delta(w_i,w_j)}$$

$$((-1)^{l_{i,j}q} U(L_{i,j}Q)_{kl}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_i,w_j\rangle + (-1)^{p_{i,j}l_{i,j}q} U(P_{i,j}L_{i,j}Q)_{kl}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_j,w_i\rangle)$$

which is the reduction of interaction integral equation (5.2.5). $2^{-\delta(w_i,w_j)}$ product

is used in order to not to calculate integral twice in the case of $i = j$.

$$\begin{aligned}
\langle N_\Phi \hat{A}\phi X_j|\hat{H}_{int}|N_\Psi \hat{A}\psi X_k\rangle &= N_\phi N_\Psi \sum_{j>i}\sum_{Q\epsilon S_\phi} 2^{-\delta(w_i,w_j)}((-1)^{l_{i,j}q}(-1)^q U(L_{i,j})_{km}\times \\
&\quad U(Q)_{ml}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_i,w_j\rangle \\
&\quad -(-1)^{l_{i,j}q}(-1)^q U(P_{i,j}L_{i,j})_{km}U(Q)_{ml}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_j,w_i\rangle) \\
\langle N_\Phi \hat{A}\phi X_j|\hat{H}_{int}|N_\Psi \hat{A}\psi X_k\rangle &= N_\phi N_\Psi \sum_{j>i}\sum_{Q\epsilon S_\phi} 2^{-\delta(w_i,w_j)}((-1)^{l_{i,j}}(-1)^q\times \\
&\quad U(L_{i,j})_{kl}(-1)^q\langle\phi_i\phi_j|\hat{H}_{i,j}|w_i,w_j\rangle \\
&\quad -(-1)^{l_{i,j}}(-1)^q U(P_{i,j}L_{i,j})_{kl}(-1)^q\langle\phi_i\phi_j|\hat{H}_{i,j}|w_j,w_i\rangle) \\
\langle N_\Phi \hat{A}\phi X_j|\hat{H}_{int}|N_\Psi \hat{A}\psi X_k\rangle &= N_\phi N_\Psi \sum_{j>i}|S_\Phi|2^{-\delta(w_i,w_j)}(-1)^{l_{i,j}}U(L_{i,j})_{kl}\times \\
&\quad \langle\phi_i\phi_j|\hat{H}_{i,j}|w_i,w_j\rangle - U(P_{i,j}L_{i,j})_{kl}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_j,w_i\rangle) \\
\langle N_\Phi \hat{A}\phi X_j|\hat{H}_{int}|N_\Psi \hat{A}\psi X_k\rangle &= 2^{-\delta(w_i,w_j)}(-1)^{l_{i,j}}(U(L_{i,j})_{kl}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_i,w_j\rangle\times \\
&\quad \frac{N_\Phi}{N_\psi}\sum_{j>i} -U(P_{i,j}L_{i,j})_{kl}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_j,w_i\rangle)
\end{aligned} \tag{5.2.7}$$

So the sum of integral over all permutations is reduced because of orthogonality of orbitals. In the next section we will see that this formula can be reduce further if we know more information about Φ and Ψ

5.3 Special Cases of the Hamiltonian Elements

5.3.1 Orbital Difference Equals to Zero

It is proper to define orbital difference between two special functions Φ and Ψ. Orbital difference is the number of orbitals which appear in Ψ but not in Φ considering doubly occupied orbitals.

If orbital difference equals to one two spatial functions must be equal because in spin adapted base we do not include special functions which are permutations of each other. Therefore the line-up permutation for any pair i, j is equal to identity permutation e.

$$\begin{aligned}\langle N_\phi \hat{A}\phi X_j|\hat{H}_{int}|N_\Psi \hat{A}\psi X_k\rangle &= \frac{N_\Phi}{N_\Psi}\sum_{j>i} 2^{-\delta(w_i,w_j)}(-1)^{l_{i,j}}(U(L_{i,j})_{kl}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_i,w_j\rangle \\ &\quad -U(P_{i,j}L_{i,j})_{kl}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_j,w_i\rangle) \qquad (5.3.1)\\ \langle N_\Phi \hat{A}\phi X_j|\hat{H}_{int}|N_\Psi \hat{A}\psi X_k\rangle &= \frac{N_\Phi}{N_\Psi}\sum_{j>i} 2^{-\delta(w_i,w_j)}(-1)^{e}(U(e)_{kl}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_i,w_j\rangle \\ &\quad -U(P_{i,j}e)_{kl}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_j,w_i\rangle) \qquad (5.3.2)\\ \langle N_\Phi \hat{A}\phi X_j|\hat{H}_{int}|N_\Psi \hat{A}\psi X_k\rangle &= \frac{N_\Phi}{N_\Psi}\sum_{j>i} 2^{-\delta(w_i,w_j)}(\delta_{kl}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_i,w_j\rangle \\ &\quad -U(P_{i,j})_{kl}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_j,w_i\rangle) \qquad (5.3.3)\end{aligned}$$

5.3.2 Orbital Difference Equals to One

In this case there is one orbital which appears in Φ but not Ψ. We represent this orbital as ϕ_{dif}. This orbital can occur in Φ once. For instance if $\Phi = \phi_1\phi_2\phi_3$ and $\Psi = \phi_1\phi_4\phi_2$ then $\phi_{dif} = \phi_4$ or it can occur twice in Φ, for example if $\Phi = \phi_1\phi_1\phi_3$ and $\Psi = \phi_1\phi_2\phi_3$ then $\phi_{dif} = \phi_1$. Therefore we should take into consideration this two cases when simplifying matrix elements.

The (i, j) pairs which will not give nonzero elements are one includes ϕ_{dif} orbital. If ϕ_{dif} appears once in Φ then

$$(1,i),(2,i),...,(i-1,i),(i,i+1),...,(i,N)$$

pairs will give nonzero results. If ϕ_{dif} appears twice in position $(i, i+1)$ the pairs which will not give nonzero elements are:

$$(1,i),(2,i),...,(i-1,i),(i,i+1),...,(i,N)$$

$$(1,i+1),(2,i+1),...,(i-1,i+1),(i+1,i+2),...,(i+1,N)$$

It is important to note that $\phi_i = \phi_{i+1} = \phi_{dif}$, so the integrals in the second case are the same as the integrals in the first case except for $(i, i+1)$ pair.

If the line-up permutation is $L_{i,j}$ for the pair (i, j) then for $(i+1, j)$ it must be $P_{i,i+1}L_{i,j}$. Taking into account all this we have:

$$\begin{aligned}
\langle N_\phi \hat{A}\phi X_j|\hat{H}_{int}|N_\Psi \hat{A}\psi X_k\rangle &= \frac{N_\Phi}{N_\Psi}\sum_{j=1,j\neq i} 2^{-\delta(w_i,w_j)}(-1)^{l_{i,j}}(U(L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_i,w_j\rangle \\
&- U(P_{i,j}L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_j,w_i\rangle) + (n_{dif}-1)\frac{N_\Phi}{N_\Psi}\times \\
&(\textstyle\sum_{j=1,j\neq i+1} 2^{-\delta(w_{i+1},w_j)}(-1)^{p_{i,i+1}l_{i,j}}(U(P_{i,i+1}L_{i,j})_{jk}\times \\
&\langle\phi_{i+1}\phi_j|\hat{H}_{i+1,j}|w_{i+1},w_j\rangle - (U(P_{i,i+1}P_{i,j}L_{i,j})_{jk}\times \\
&\langle\phi_{i+1}\phi_j|\hat{H}_{i+1,j}|w_j,w_{i+1}\rangle)) - 2^{-\delta(w_{i+1},w_j)}(-1)^{l_{i,i+1}}\times \\
&(U(L_{i,i+1})_{jk}\langle\phi_i\phi_{i+1}|\hat{H}_{i,i+1}|w_i,w_{i+1}\rangle \\
&- (U(P_{i,i+1}L_{i,i+1})_{jk}\langle\phi_i\phi_{i+1}|\hat{H}_{i,i+1}|w_{i+1},w_i\rangle))
\end{aligned} \tag{5.3.4}$$

$$\begin{aligned}
\langle N_\phi \hat{A}\phi X_j|\hat{H}_{int}|N_\Psi \hat{A}\psi X_k\rangle &= \frac{N_\Phi}{N_\Psi}\sum_{j=1,j\neq i} 2^{-\delta(w_i,w_j)}(-1)^{l_{i,j}}(U(L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_i,w_j\rangle \\
&- U(P_{i,j}L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_j,w_i\rangle) + (n_{dif}-1)\tfrac{N_\Phi}{N_\Psi}\times \\
&(\sum_{j=1,j\neq i} 2^{-\delta(w_i,w_j)}(-1)(-1)^{l_{i,j}}((-1)U(L_{i,j})_{jk}\times \\
&\langle\phi_i\phi_j|\hat{H}_{i,j}|w_i,w_j\rangle - ((-1)U(P_{i,j}L_{i,j})_{jk}\times \\
&\langle\phi_i\phi_j|\hat{H}_{i,j}|w_j,w_i\rangle)) - 2^{-\delta(w_{i+1},w_j)}(-1)^{l_{i,i+1}}\times \\
&(U(L_{i,i+1})_{jk}\langle\phi_i\phi_{i+1}|\hat{H}_{i,i+1}|w_i,w_{i+1}\rangle \\
&- (U(P_{i,i+1}L_{i,i+1})_{jk}\langle\phi_i\phi_{i+1}|\hat{H}_{i,i+1}|w_{i+1},w_i\rangle))
\end{aligned} \tag{5.3.5}$$

where we have used the case $\phi_i = \phi_{i+1}$ and

$$U(P_{i,i+1}R)_{kl} = U(P_{i,i+1})_{kk}U(R)_{kl} = (-1)^{p_{i,i+1}} = -U(R)_{kl}$$

Grouping terms we have the final result:

$$\begin{aligned}
\langle N_\phi \hat{A}\phi X_j|\hat{H}_{int}|N_\Psi \hat{A}\psi X_k\rangle &= \frac{N_\Phi}{N_\Psi}n_{dif}\sum_{j=1,j\neq i} 2^{-\delta(w_i,w_j)}(-1)^{l_{i,j}}(U(L_{i,j})_{jk}\times \\
&\langle\phi_i\phi_j|\hat{H}_{i,j}|w_i,w_j\rangle - U(P_{i,j}L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_j,w_i\rangle) \\
&- \frac{N_\Phi}{N_\Psi}(n_{dif}-1)(2^{-\delta(w_{i+1},w_j)}(-1)^{l_{i,i+1}}\times \\
&(U(L_{i,i+1})_{jk}\langle\phi_i\phi_{i+1}|\hat{H}_{i,i+1}|w_i,w_{i+1}\rangle \\
&- (U(P_{i,i+1}L_{i,i+1})_{jk}\langle\phi_i\phi_{i+1}|\hat{H}_{i,i+1}|w_{i+1},w_i\rangle))
\end{aligned} \tag{5.3.6}$$

5.3.3 Orbital Difference Equals to Two

If the orbital difference is equal to two then only pairs which include orbitals appear in Φ but not in Ψ will have line-up permutation and therefore nonzero result. If ϕ_i and ϕ_j are orbitals that appear in Φ and not in Ψ. Although there is only one choice for the orbitals, this could correspond to more than one pair of i, j as each of i and j could appear up to twice in Φ. We can have $\phi_i \neq \phi_j$ and either or both of ϕ_i and ϕ_j appear twice in Φ. As an example if $\Phi = \phi_1\phi_1\phi_3\phi_3$ and $\Psi = \phi_1\phi_2\phi_3\phi_4$ then different orbitals ϕ_1 and ϕ_3 which appears twice in Φ. Taking into account all this cases:

$$\begin{aligned}
\langle N_\phi \hat{A}\phi X_j|\hat{H}_{int}|N_\Psi \hat{A}\psi X_k\rangle &= \frac{N_\Phi}{N_\Psi}2^{-\delta(w_i,w_j)}((-1)^{l_{i,j}}(U(L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_i,w_j\rangle \\
&- U(P_{i,j}L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_j,w_i\rangle) \\
&+ (n_i-1)(-1)^{l_{i,j}p_{i,i+1}}(U(P_{i,i+1}L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_i,w_j\rangle \\
&- U(P_{i,i+1}P_{i,j}L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_j,w_i\rangle) \\
&+ (n_j-1)(-1)^{l_{i,j}p_{i,i+1}}(U(P_{j,j+1}L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_i,w_j\rangle \\
&- U(P_{j,j+1}P_{i,j}L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_j,w_i\rangle) \\
&+ (n_i-1)(n_j-1)(-1)^{l_{i,j}p_{i,i+1}p_{j,j+1}} \\
&\quad (U(P_{i,i+1}P_{j,j+1}L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_i,w_j\rangle \\
&- U(P_{i,i+1}P_{j,j+1}P_{i,j}L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_j,w_i\rangle)
\end{aligned} \tag{5.3.7}$$

$$\begin{aligned}
\langle N_\phi \hat{A}\phi X_j|\hat{H}_{int}|N_\Psi \hat{A}\psi X_k\rangle &= \frac{N_\Phi}{N_\Psi} 2^{-\delta(w_i,w_j)}(-1)^{l_{i,j}}((U(L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_i,w_j\rangle \\
&- U(P_{i,j}L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_j,w_i\rangle) \\
&+ (n_i-1)(-1)((-1)U(L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_i,w_j\rangle \\
&- (-1)U(P_{i,j}L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_j,w_i\rangle) \\
&+ (n_j-1)(-1)((-1)U(L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_i,w_j\rangle \\
&- (-1)U(P_{i,j}L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_j,w_i\rangle) \\
&+ (n_i-1)(n_j-1)(-1)((-1)(-1)U(L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_i,w_j\rangle \\
&- (-1)(-1)U(P_{i,j}L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_j,w_i\rangle))) \qquad (5.3.8)
\end{aligned}$$

$$\begin{aligned}
\langle N_\phi \hat{A}\phi X_j|\hat{H}_{int}|N_\Psi \hat{A}\psi X_k\rangle &= \frac{N_\Phi}{N_\Psi} 2^{-\delta(w_i,w_j)}(-1)^{l_{i,j}}((U(L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_i,w_j\rangle \\
&- U(P_{i,j}L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_j,w_i\rangle) \\
&+ (n_i-1)(U(L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_i,w_j\rangle \\
&- U(P_{i,j}L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_j,w_i\rangle) \\
&+ (n_j-1)(U(L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_i,w_j\rangle \\
&- U(P_{i,j}L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_j,w_i\rangle) \\
&+ (n_i-1)(n_j-1)(U(L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_i,w_j\rangle \\
&- U(P_{i,j}L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_j,w_i\rangle))) \qquad (5.3.9)
\end{aligned}$$

$$\begin{aligned}
\langle N_\phi \hat{A}\phi X_j|\hat{H}_{int}|N_\Psi \hat{A}\psi X_k\rangle &= \frac{N_\Phi}{N_\Psi} 2^{-\delta(w_i,w_j)}(-1)^{l_{i,j}}((U(L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_i,w_j\rangle \\
&- U(P_{i,j}L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_j,w_i\rangle)\times \\
&(1+(n_i-1)+(n_j-1)+(n_i-1)(n_j-1)) \qquad (5.3.10)
\end{aligned}$$

$$\begin{aligned}\langle N_\phi \hat{A}\phi X_j|\hat{H}_{int}|N_\Psi \hat{A}\psi X_k\rangle &= \frac{N_\Phi}{N_\Psi}2^{-\delta(w_i,w_j)}(-1)^{l_{i,j}}(n_i n_j)((U(L_{i,j})_{jk}\times \\ &\quad \langle\phi_i\phi_j|\hat{H}_{i,j}|w_i,w_j\rangle - U(P_{i,j}L_{i,j})_{jk}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_j,w_i\rangle)\end{aligned} \tag{5.3.11}$$

Since n_i and n_j can take values 1 and 2 we can define a relation as $n_i n_j = 2^{(n_i+n_j-2)}$ Combining the conditions $\phi_i = \phi_j$ and $\phi_i \neq \phi_j$ we finally get:

$$s(\upsilon_i,\upsilon_j,\Phi) = \begin{cases} 0, & \upsilon_i = \upsilon_j; \\ n(\upsilon_i,\Phi)+n(\upsilon_j,\Phi)-2, & \upsilon_i = \upsilon_j \end{cases} \tag{5.3.12}$$

where $n_i = n(\upsilon_i,\Phi)$ and $n_j = n(\upsilon_j,\Phi)$.

$$\begin{aligned}\langle N_\phi \hat{A}\phi X_j|\hat{H}_{int}|N_\Psi \hat{A}\psi X_k\rangle &= \frac{N_\Phi}{N_\Psi}2^{-\delta(w_i,w_j)}2^{s(\upsilon_i,\upsilon_j,\Phi)}(-1)^{l_{i,j}}((U(L_{i,j})_{jk}\times \\ &\quad \langle\upsilon_i\upsilon_j|\hat{H}_{i,j}|w_i,w_j\rangle - U(P_{i,j}L_{i,j})_{jk}\langle\upsilon_i\upsilon_j|\hat{H}_{i,j}|w_j,w_i\rangle)\end{aligned} \tag{5.3.13}$$

5.3.4 Orbital Difference Equals to Three

In this case a line-up permutation does not exist for any pair i, j:

$$\begin{aligned}\langle N_\Phi \hat{A}\phi X_j|\hat{H}_{int}|N_\Psi \hat{A}\psi X_k\rangle &= \frac{N_\Phi}{N_\psi}\sum_{j>i}2^{-\delta(w_i,w_j)}(-1)^{l_{i,j}}(U(L_{i,j})_{kl}\times \\ &\quad \langle\phi_i\phi_j|\hat{H}_{i,j}|w_i,w_j\rangle - U(P_{i,j}L_{i,j})_{kl}\langle\phi_i\phi_j|\hat{H}_{i,j}|w_j,w_i\rangle) \\ &= 0\end{aligned} \tag{5.3.14}$$

In the last step we have used $U(L_{i,j}) = 0$.

CHAPTER SIX
NUMERICAL RESULTS

6.1 Addition Energy

As mentioned in Chapter 2 quantum dots resemble the real atoms in many respects. One of them is having shell structure. Experimentally two-dimensional $2D$ shell structure of the parabolic quantum dots have been proved by measuring Coulomb oscillations at zero magnetic field by Tarucha et al., (1996). They have observed $2D$ shell structure from the addition energies, analogous to $3D$ shell structure from atomic ionization energies.

In the one electron case the energy $E(n,m)$, of a a parabolic quantum dot with a radial quantum number $n = 0, 1, 2, ...$ and angular momentum quantum number $m = 0, \pm 1, \pm 2, ...$ is given by:

$$E(n,m) = (2n + |m| + 1)\hbar\omega_0 \tag{6.1.1}$$

where $\hbar\omega_0$ is the electrostatic confinement energy. Energy, has degenerate sets of states, which are separated by $h\omega_0$ from each other as seen in Figure 6.1 and are completely filled for $N = 2, 6, 12, 20$, etc. These N values are called as magic numbers since they signify the complete filling of a shell (Tarucha et al., 1996).

In this thesis addition energy $\Delta\mu(N)$, needed to place an extra electron in a system, is calculated for up to six electrons in a parabolic quantum dot with harmonic well constant $5.5\, meV$ at zero magnetic field. For this purpose initially the ground state energies of the system are found up to seven electrons. These results are used to calculate chemical energy which is defined as:

$$\mu(N) = U(N) - U(N-1) \tag{6.1.2}$$

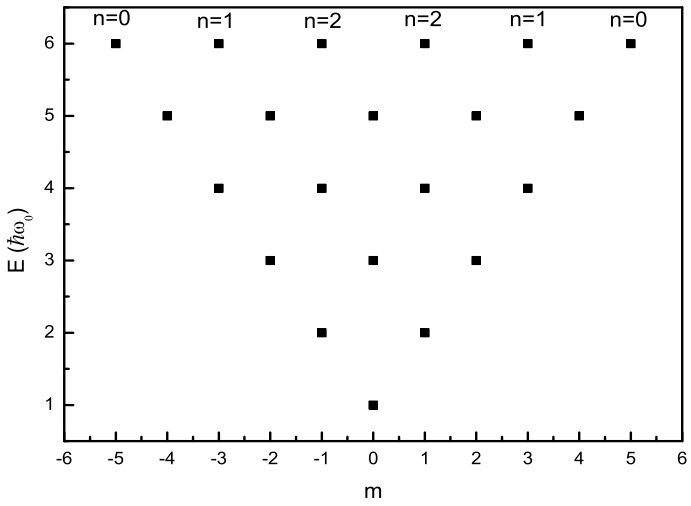

Figure 6.1 Single particle energies for $2D$ parabolic quantum dot in absence of magnetic field. n and m denotes radial and angular momentum quantum number respectively.

where $U(N)$ is the energy of N electron system. Then addition energies are calculated according to equation:

$$\Delta\mu(N) = \mu(N+1) - \mu(N) \tag{6.1.3}$$

In Figure 6.2 the addition energy spectrum is plotted from $N = 1$ to 6 electrons where labels of peaks with "N" corresponds to the energy difference $\mu(N+1) - \mu(N)$ between $(N+1)$ and N electron ground states. It is clearly seen that the addition energy is large for $2, 6$ which correspond to full filling of first and second shells. Also there is a second maximum for 4 electron which is due to the half filling of second shell with parallel spins according to the Hund's rule (Tarucha et al., 1996).

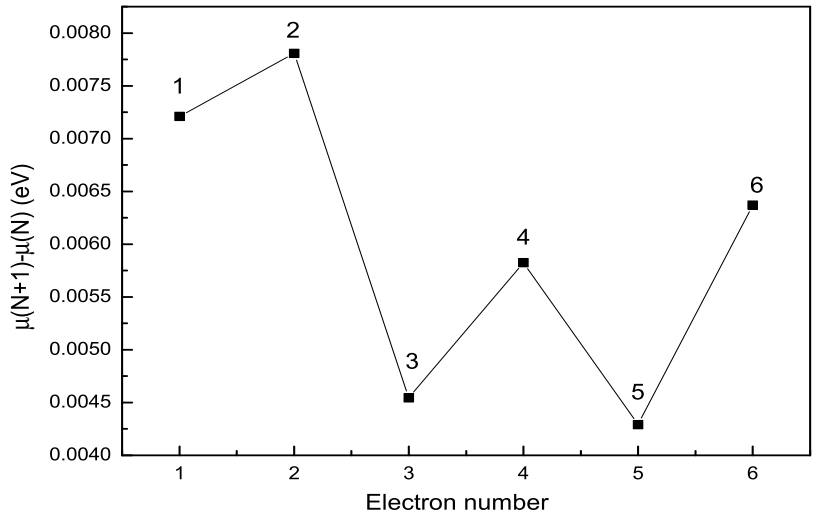

Figure 6.2 Change of addition energy calculated for $2D$ parabolic quantum dot with $\hbar w_0 = 5.5meV$

6.2 Magnetic Transitions

Tarucha et. al., (1998) have observed magnetic field induced transitions in the ground states of disk-shaped semiconductor quantum dots experimentally. Also they have discussed these transitions in the conjunction with the exact diagonalization calculations.

In this thesis in order to observe the magnetic transitions which have been observed in experiment by Tarucha et al., (1998) electrochemical energy versus magnetic field plots are reproduced for $2, 3$ end 4 electrons. For this calculations we take harmonic well constant $\hbar w_0 = 5.5meV$, relative mass $m^* = 0.67m_0$ and dielectric constant $\epsilon^* = 13.1\epsilon_0$.

In figure 6.3 electrochemical energies versus magnetic field are plotted for 2 electrons. A transition occurs at about $4\,T$ (labeled by ■) from the singlet $(S, L) = (0, 0)$ to triplet state $(S, L) = (1, 1)$ in the ground state which is in

agreement with the experiment and also the exact results done by Tarucha et. al., (1998). Also in the experiment this transition is observed at $4\,T$. With increasing magnetic field electrons will feel increasing Coulomb interaction. Because of this the increasing Coulomb interaction one electron will be forced to occupy a higher level. In this case one electron will be in $(S, L) = (0, 0)$ and the other one in $(S, L) = (1, 1)$ with a larger kinetic energy before the transition. However this transition reduces the Coulomb interaction because of larger spatial distance between electrons.The transition in angular momentum state is compensated by transition in singlet $(S = 0)$ to triplet state $(S = 1)$ (Tarucha et al., 1998).

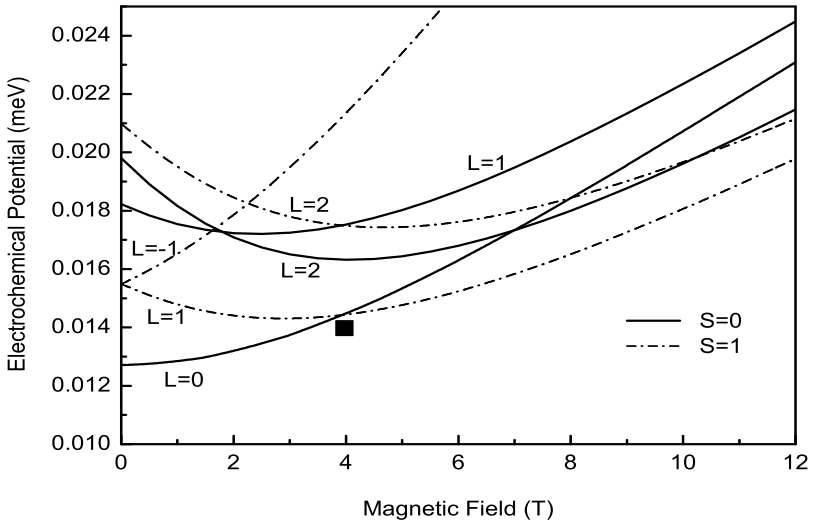

Figure 6.3 Ground state energies versus magnetic field of a 2 electron $2D$ parabolic quantum dot with $\hbar w_0 = 5.5meV$.

For 3 electron case energy spectrum versus magnetic field is plotted in Figure 6.4. Spin and angular momentum quantum numbers change from $(S, L) = (\frac{1}{2}, 1)$ to $(\frac{1}{2}, 2)$ at $4\,T$ and to $(\frac{3}{2}, 3)$ $4.8\,T$. In the experiment these transitions are observed at $4.3\,T$ and $4.8\,T$, respectively. In these transitions the angular momentum states increase meanwhile reducing the Coulomb potential of the system. On the other hand the total spin increases gaining exchange energy.

Similar to the 2 electron case reducing Coulomb energy is accompanied with the increasing exchange energy.

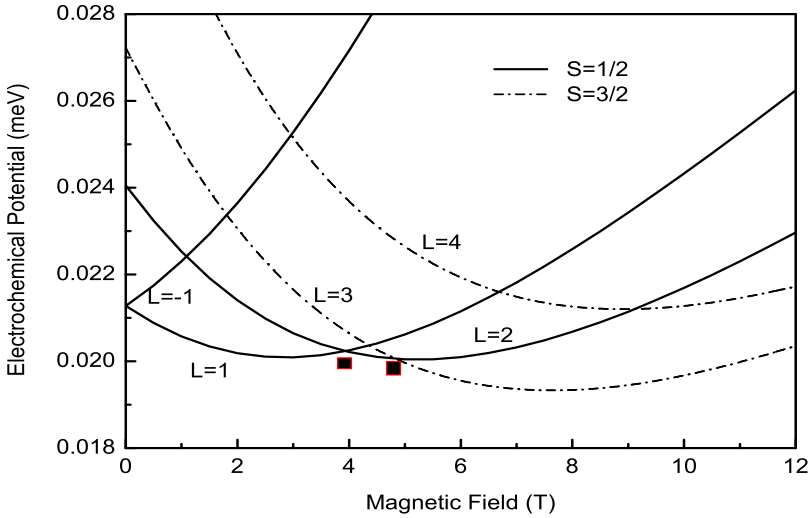

Figure 6.4 Ground state energies versus magnetic field of a 3 electron $2D$ parabolic quantum dot with $\hbar w_0 = 5.5meV$.

In four electron ground state there is a transition at $0.43\,T$ which is in agreement with the experiment and the exact result from $(S, L) = (1, 0)$ to $(0, 2)$ state as shown in Figure 6.5 which is identified as manifestation of Hund's rule (Tarucha et al., 1998). A transition from parallel spins to antiparallel spins occurs.

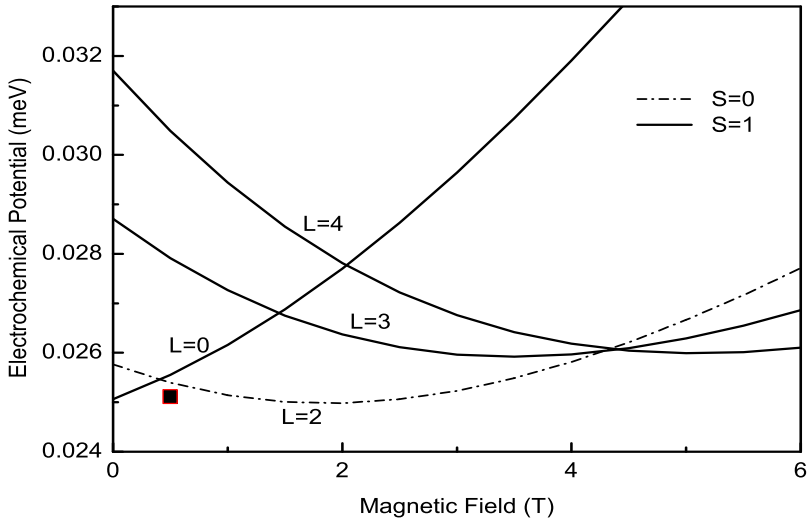

Figure 6.5 Ground state energies versus magnetic field of a 4 electron $2D$ parabolic quantum dot with $\hbar w_0 = 5.5meV$.

6.3 Comparision with Other Results

The ground state energies of six electron parabolic quantum dot with the total spin quantum numbers $S = 0$ and $S = 3$ at zero magnetic field and the total angular momentum $L = 0$ are calculated in this section. These calculations are done for different values of the the density parameter r_s , which determines the average particle density in the dot and related to the electron density as:

$$n_0 = \frac{1}{\pi r_s^2} \tag{6.3.1}$$

Harmonic well constant can be approximated in terms of r_s as (Reimann & Manninen, 2002):

$$w_0^2 = \frac{e^2}{4\pi\epsilon^* m^* r_s^3 \sqrt{N}} \tag{6.3.2}$$

For every density parameter, harmonic well constant is calculated according to equation (6.3.2). Also atomic units are used and effective mass and effective

dielectric constant are taken as $m^* = 0.67m_0$, $\epsilon^* = 12.4\epsilon_0$ respectively for which the length and energy units then scale to $a_b^* = 9.79\,nm$ and $Ha^* = 11.9\,meV$. In order to build spin space, z component of total spin operator is taken as $S_z = 0$ for both $S = 0$ and $S = 3$ because all the spin states have components with this value.

Table 6.1 and 6.2 total energy results of the ground state with spin zero and the with spin $S = 3$ with the SACI, exact and DFT results obtained by Reimann & Manninen, (2002). In the DFT they treated the exchange-correlation part of the electron-electron interactions in the Local Spin Density Approximation (LSDA). In the paramagnetic case LSDA gives lower energies than exact and CI results when $r_s > 2a_b$. However in the ferromagnetic case SACI gives the lowest energies. Figure 6.6 shows the energy difference between the fully polarized state and the ferromagnetic state versus $\frac{1}{r_s}$. The LDA gives larger energy difference than the exact and SACI.

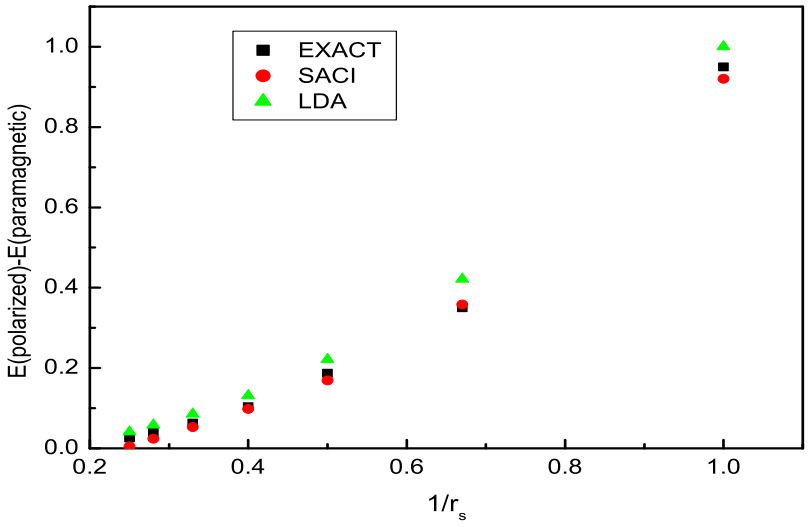

Figure 6.6 Energy difference (units of Ha^*) between ferromagnetic and paramagnetic case as a function of $\frac{1}{r_s}$

Table 6.1 Comparision between the SACI ground state energies (units of Ha^*) obtained in this thesis and the exact and LDA results taken from Ref. (Reimann & Manninen, 2002) at zero magnetic field in a six electron quantum dot for paramagnetic case.

r_s/a_B^*	$\hbar w_0/meV$	LDA	EXACT	SACI
1	7.58	14.30	14.27	14.30
1.5	4.12	8.988	8.983	9.002
2	2.68	6.503	6.508	6.522
2.5	1.92	5.073	5.084	5.085
3	1.46	4.148	4.162	4.167
3.5	1.16	3.502	3.519	3.531
4	0.94	3.027	3.045	3.048

Table 6.2 Comparision between the SACI ground state energies (units of Ha^*) obtained in this thesis and the exact and LDA results taken from Ref. (Reimann & Manninen, 2002) at zero magnetic field in a six electron quantum dot for ferromagnetic case.

r_s/a_B^*	$\hbar w_0/meV$	LDA	EXACT	SACI
1	7.58	15.30	15.22	15.22
1.5	4.12	9.409	9.363	9.360
2	2.68	6.724	6.695	6.691
2.5	1.92	5.204	5.188	5.183
3	1.46	4.233	4.225	4.220
3.5	1.16	3.560	3.559	3.555
4	0.94	3.068	3.071	3.053

For reasons of numerical feasibility it is necessary to truncate the set of basis functions to be used in the diagonalization (Reimann & Manninen, 2002). For this purpose the SACI package includes the states with the sum of occupied single particle energies less than or equal to a specified cutoff energy E_c. In this calculations for ferromagnetic case we take the cut-off energy $22\hbar w_0$ which corresponds to 1456 basis elements. Since correlation becomes stronger with increasing r_s value, for the paramagnetic case the cut-off energy is taken $24\hbar w_0$ for $r_s \leq 2.5$. Also for every calculation convergence is tested. SACI package gives the convergence plots as in Figure 6.7 in which the ground state and the first excited state energy values versus basis size is plotted for $r_s = 2$. After 2500 basis elements have been used energy value begin to be stable.

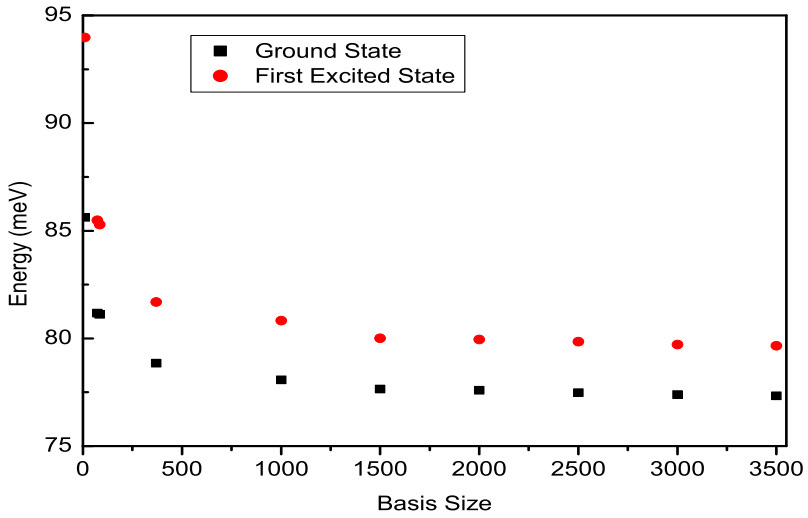

Figure 6.7 Convergence plot of six electron parabolic quantum dot for $r_s = 2$.

CHAPTER SEVEN
CONCLUSION

In this thesis we have calculated the ground state energies of two dimensional ($2D$) disc-like parabolic quantum dots up to seven electrons by using Spin Adapted Configuration Interaction (SACI) package. This package calculates the energies and wavefunctions of a parabolic quantum dot under the influence of magnetic field.

The total ground state energies with spin zero (paramagnetic state) and the state with spin $S = 3$ (ferromagnetic state) are obtained at zero magnetic field and zero angular momentum for different densities. These results are compared with the exact and the LSDA results to test the accuracy of the method. In the ferromagnetic case the SACI results are found to be lower than both the the exact and the LSDA results for all the density parameter values. In paramagnetic case the results found to be higher than both the exact and the LSDA results with a relative error %0.2 to exact results. This error could be lowered by using a larger basis. Also it is seen that for the large density parameter values larger basis must be used since correlation effects become stronger with the decreasing density.

In order to exhibit the atomic-like properties of the quantum dots we have plotted the addition energy which is the energy required to add an extra electron to the system. Just like the real atoms $2D$ parabolic quantum dot has shown maximum addition energies when the Fock-Darwin shells are full filled. Also we have examined secondary maximums when the shells are half filled with parallel spins.

Also we have plotted electrochemical energy versus magnetic field and observed magnetic transitions in the ground state of the multi-electron system which is in agreement with experiment done by Tarucha et al.. In the case of

2 electrons a transition has been ocurred at $4\,T$ from singlet to triplet state gaining the exchange energy. Similar transitions has been observed in 3 electron case. Also breaking of the Hunds rule in the case of 4 electrons for relatively low magnetic field of $0.5\,T$ have been observed.

This work could be extended for more electrons using powerful computers and using more efficient programming language such as Fortran in the future. And also this method can be applied to the systems having more complex geometry.

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APPENDIX ONE

A.1 Dirac Identity

In this appendix $\hat{S}^2$ operator for many electron case is derived following Ref. (Pauncz, 1979). $\hat{S}_x$, $\hat{S}_y$ and $\hat{S}_z$ operators

$$\hat{S}_x = \sum_{i=1}^{N} \hat{S}_x(i), \qquad \hat{S}_y = \sum_{i=1}^{N} \hat{S}_y(i), \qquad \hat{S}_z = \sum_{i=1}^{N} \hat{S}_z(i) \tag{A.1.1}$$

Similarly way we can define step-up and step-down operators:

$$\hat{S}_+ = \sum_{i=1}^{N} \hat{S}_+(i), \qquad \hat{S}_- = \sum_{i=1}^{N} \hat{S}_-(i) \tag{A.1.2}$$

$\hat{S}^2$ operator can be written in the form:

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 = \hat{S}_+\hat{S}_- + \hat{S}_z^2 - \hat{S}_z = \hat{S}_-\hat{S}_+ + \hat{S}_z^2 + \hat{S}_z \tag{A.1.3}$$

For convenience let us look at common eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$. Using equation (A.1.1) and (A.1.3):

$$\begin{aligned}
\hat{S}^2 &= \left[\sum_{i=1}^{N} \hat{S}_x(i)\right]^2 + \left[\sum_{i=1}^{N} \hat{S}_y(i)\right]^2 + \left[\sum_{i=1}^{N} \hat{S}_z(i)\right]^2 \\
&= \sum_{i=1}^{N} \hat{S}_x^2(i) + \sum_{i=1}^{N} \hat{S}_y^2(i) + \sum_{i=1}^{N} \hat{S}_z^2(i) + 2\sum_{j>i}^{N} \hat{S}_x(i)\hat{S}_x(j) \\
&\quad + 2\sum_{j>i}^{N} \hat{S}_y(i)\hat{S}_y(j) + 2\sum_{j>i}^{N} \hat{S}_y(i)\hat{S}_y(j)
\end{aligned}$$

$$= \sum_{i=1}^{N} \left[\hat{S}_x^2(i) + \hat{S}_y^2(i) + \hat{S}_z^2(i) \right] + 2 \sum_{j>i}^{N} \left[\hat{S}_x(i)\hat{S}_x(j) + \hat{S}_y(i)\hat{S}_y(j) + \hat{S}_z(i).\hat{S}_z(j) \right] \tag{A.1.4}$$

$$\hat{S}^2 = \sum_{i=1}^{N} \hat{S}^2(i) + 2 \sum_{j>i}^{N} \hat{S}(i).\hat{S}(j) \tag{A.1.5}$$

$\hat{S}(i).\hat{S}(j)$ scalar product in terms of step-up and step-down operators take the form:

$$\hat{S}(i).\hat{S}(j) = \frac{1}{2}[\hat{S}_+(i)\hat{S}_-(j) + \hat{S}_-(i)\hat{S}_+(j)] + \hat{S}_z(i)\hat{S}_z(j) \tag{A.1.6}$$

Let us apply $\hat{S}(i).\hat{S}(j)$ operator to primitive spin functions for two electron case:

$$\begin{aligned}
[\hat{S}(1).\hat{S}(2)]\alpha(1)\alpha(2) &= \{\frac{1}{2}[\hat{S}_+(1)\hat{S}_-(2) + \hat{S}_-(1)\hat{S}_+(2)] + \hat{S}_z(1)\hat{S}_z(2)\}\alpha(1)\alpha(2) \\
&= [\hat{S}_+(1)\alpha(1)\hat{S}_-(2)\alpha(2) + \hat{S}_-(1)\alpha(1)\hat{S}_+(2)\alpha(2)] \\
&\quad + \hat{S}_z(1)\alpha(1)\hat{S}_z(2)\alpha(2) \\
&= \frac{1}{2}\alpha(1)\frac{1}{2}\alpha(2) \\
&= \frac{1}{4}\alpha(1)\alpha(2)
\end{aligned} \tag{A.1.7}$$

where α and β represents spin-up and spin-down, respectively. We use following relations.

$$S_+\alpha = 0 \qquad S_-\alpha = \beta$$

$$S_+\beta = \alpha \qquad S_-\beta = 0$$

In a similar way

$$\begin{aligned}
\left[\hat{S}(1).\hat{S}(2)\right]\beta(1)\beta(2) &= \tfrac{1}{4}\beta(1)\beta(2) \\
\left[\hat{S}(1).\hat{S}(2)\right]\alpha(1)\beta(2) &= \tfrac{1}{2}\beta(1)\alpha(2) - \tfrac{1}{4}\alpha(1)\beta(2) \\
\left[\hat{S}(1).\hat{S}(2)\right]\beta(1)\alpha(2) &= \tfrac{1}{2}\alpha(1)\beta(2) - \tfrac{1}{4}\beta(1)\alpha(2)
\end{aligned} \tag{A.1.8}$$

can be written. Using permutation operator to change spin coordinates of electrons 1 and 2 we have:

$$\begin{aligned}
\hat{P}_{12}\alpha(1)\alpha(2) &= \alpha(1)\alpha(2) \\
\hat{P}_{12}\alpha(1)\beta(2) &= \beta(1)\alpha(2) \\
\hat{P}_{12}\beta(1)\alpha(2) &= \alpha(1)\beta(2) \\
\hat{P}_{12}\beta(1)\beta(2) &= \beta(1)\beta(2)
\end{aligned} \tag{A.1.9}$$

If we compare (A.1.8) and (A.1.9) equations we can define an operator which makes the same effect with $\hat{S}(1).\hat{S}(2)$ operator:

$$[\hat{S}(1).\hat{S}(2)]\theta(1,2) = (\frac{1}{2}\hat{P}_{12} - \frac{1}{4})\theta(1,2) \tag{A.1.10}$$

$\theta(1,2)$ represents the two electron spin functions or linear combination of them. (A.1.10) equation is called as *Dirac Identity*. It can be written in the form:

$$\begin{aligned}
\hat{S}^2\theta(1,2) &= \{\hat{S}^2(1) + \hat{S}^2(2) + 2[\hat{S}(1).\hat{S}(2)]\}\theta(1,2) \\
&= 2(\frac{3}{4} + \frac{1}{2}\hat{P}_{12} - \frac{1}{4})\theta(1,2) \\
&= (1 + \hat{P}_{12})\theta(1,2)
\end{aligned} \tag{A.1.11}$$

Using the form of *Dirac equation* for many electron case we can write $\hat{S}^2$ operator.

$$\hat{S}^2\theta = N\frac{3}{4}\theta + 2\sum_{j>i}(-\frac{1}{4} + \frac{1}{2}\hat{P}_{ij})\theta \tag{A.1.12}$$

$$\hat{S}^2\theta = \frac{-N(N-4)}{4}\theta + \sum_{j>i}\hat{P}_{ij}\theta \tag{A.1.13}$$

where θ is an eigenfunction in 2^N dimensional spin space

As an example let's apply Dirac Identity for two electron spin functions:

$$\begin{aligned}\hat{S}^2\alpha(1)\alpha(2) &= \frac{-2(2-4)}{4}\alpha(1)\alpha(2) + \alpha(1)\alpha(2) \\ &= 2\alpha(1)\alpha(2)\end{aligned} \tag{A.1.14}$$

$$\hat{S}^2\beta(1)\beta(2) = 2\beta(1)\beta(2) \tag{A.1.15}$$

$$\hat{S}^2\beta(1)\alpha(2) = \beta(1)\alpha(2) + \alpha(1)\beta(2) \tag{A.1.16}$$

$$\hat{S}^2\alpha(1)\beta(2) = \alpha(1)\beta(2) + \beta(1)\alpha(2) \tag{A.1.17}$$

It is clearly seen that $\alpha(1)\alpha(2)$ and $\beta(1)\beta(2)$ are eigenfunctions of $\hat{S}^2$ with eigenvalue 2 which corresponds spin quantum number $S = 1$ Adding and subtracting equations (A.1.16) and (A.1.17), we can find following relations:

$$\hat{S}^2[\beta(1)\alpha(2) + \alpha(1)\beta(2)] = 2[\beta(1)\alpha(2) + \alpha(1)\beta(2)] \tag{A.1.18}$$

$$\hat{S}^2[\beta(1)\alpha(2) - \alpha(1)\beta(2)] = 0 \tag{A.1.19}$$

We see that proper linear combinations of primitive spin functions are common eigenvectors of $\hat{S}^2$ and $\hat{S}_z$. We can summarize the results:

$$\hat{S}^2\begin{Bmatrix}\alpha(1)\alpha(2) \\ (\alpha(1)\beta(2) + \beta(1)\alpha(2))2^{-1/2} \\ \beta(1)\beta(2)\end{Bmatrix} = 1.2\begin{Bmatrix}\alpha(1)\alpha(2) \\ (\alpha(1)\beta(2) + \beta(1)\alpha(2))2^{-1/2} \\ \beta(1)\beta(2)\end{Bmatrix} \tag{A.1.20}$$

These three results belong to the triplet state with spin quantum number $S = 1$ and also eigenfunction of S_z with eigenvalues $+1, -1, 0$. Other linear combination is eigenfunction of both $\hat{S}^2$ and S_z with eigenvalue 0 and it corresponds to singlet state.

APPENDIX TWO

A.2 Coulomb Matrix Element

In this appendix analytic form of Coulomb matrix element for two dimensional parabolic quantum dot following (Rontani, 1999).

In order to evaluate Hamiltonian matrix elements we need to find expectation value of two electron operators. Wavefunction of an electron in parabolic quantum dot is:

$$\psi_{nm}(\rho,\varphi) = k^{(|m|+1)/2}\sqrt{\frac{n!}{\pi(n+m)!}}\rho^{|m|}e^{-k\rho^2/2}L_n^{|m|}(k\rho^2)e^{-im\varphi} \tag{A.2.1}$$

Coulomb interaction conserves angular momentum i.e. if (n_1,m_1),(n_2,m_2) and (n_3,m_3),(n_4,m_4) are quantum numbers before and after scattering respectively we must have $m_1+m_1=m_3+m_4=M$.

$$\langle n_1m_1,n_2m_2|\frac{e^2}{\epsilon^*|\vec{r_1}-\vec{r_2}|}|n_3m_3,n_4m_4\rangle = \int\int \psi^*_{n_1m_1}(\rho_1,\varphi_1)\psi^*_{n_2m_2}(\rho_2,\varphi_2)$$

$$\times \quad \frac{e^2}{\kappa_r|\vec{r_1}-\vec{r_2}|}\psi_{n_3m_3}(\rho_2,\varphi_2)\psi_{n_4m_4}(\rho_1,\varphi_1) \tag{A.2.2}$$

In order to work with dimensionless coordinates, we should make a $(x,y)=k^{1/2}\mathbf{r}$ transformation.

$$dx_1dy_1 = kd\vec{r_1}$$

$$dx_2dy_2 = kd\vec{r_2}$$

$$\sqrt{(x_1-x_2)^2+(y_1-y_2)^2} = k^{1/2}|\vec{r_1}-\vec{r_2}|$$

$$\rho^{'} = k^{1/2}\rho \qquad \rho^{'2} = k\rho$$

$$V_{n_1m_1,n_2m_2,n_3m_3,n_4m_4} = \frac{e^2\sqrt{k}}{\epsilon^*}\frac{1}{\pi^2}\sqrt{\frac{n_1!n_2!n_3!n_4!}{(n_1+|m_1|)!(n_2+|m_2|)!(n_3+|m_3|)!(n_4+|m_4|)!}}$$

$$\times \int dx_1 \int dy_1 \int dx_2 \int dy_2 \frac{\rho_1^{|m_1|}\rho_2^{|m_2|}\rho_2^{|m_3|}\rho_2^{|m_4|}}{\sqrt{(x_1-x_2)^2+(y_1-y_2)^2}}$$

$$\times L_{n_1}^{|m_1|}(\rho_1^2)L_{n_2}^{|m_2|}(\rho_2^2)L_{n_3}^{|m_3|}(\rho_2^2)L_{n_4}^{|m_4|}(\rho_1^2) \tag{A.2.3}$$

$$\times e^{-(\rho_1^2+\rho_2^2)}e^{im_1\varphi_1}e^{im_2\varphi_2}e^{-im_3\varphi_2}e^{-im_4\varphi_1}$$

Using the expansion of the Generalized Laguerre Polynomial:

$$L_n^{|m|}(\rho^2) = \sum_{j=0}^{n}(-1)^j \begin{pmatrix} n+|m| \\ n-j \end{pmatrix} \frac{\rho^{2j}}{j!} \tag{A.2.4}$$

$$V_{n_1m_1,n_2m_2,n_3m_3,n_4m_4} = \frac{e^2\sqrt{k}}{\epsilon^*}\frac{1}{\pi^2}\left[\prod_{i=1}^{4}\frac{n_i!}{(n_i+m_i!)}\right]^{1/2}$$

$$\times \sum_{(4)j=0}^{n} = \frac{(-1)^{j_1+j_2+j_3+j_4}}{j_1!j_2!j_3!j_4!}\prod_{i=1}^{4}\begin{pmatrix} n_l+|m_l| \\ n_l-j_l \end{pmatrix}\int dx_1\int dy_1\int dx_2\int dy_2$$

$$\times \frac{e^{-(\rho_1^2+\rho_2^2)}e^{i(m_1-m_4)\varphi_1}e^{i(m_2-m_3)\varphi_2}}{\sqrt{(x_1^2-x_2^2)^{1/2}+(y_1^2-y_2^2)^{1/2}}}\rho_1^{|m_1|+|m_4|+2j_1+2j_4}\rho_2^{|m_2|+|m_3|+2j_2+2j_3} \tag{A.2.5}$$

We make an abbreviation:

$$\sum_{(4)j=0}^{n_1} = \sum_{j_1=0}^{n_1}\sum_{j_2=0}^{n_2}\sum_{j_3=0}^{n_3}\sum_{j_4=0}^{n_4}$$

$$\begin{aligned}
\gamma_1 &= j_1 + j_4 + (|m_1| + m_1)/2 + (|m_4| - m_4)/2 \\
\gamma_2 &= j_2 + j_3 + (|m_2| + m_2)/2 + (|m_3| - m_3)/2 \\
\gamma_3 &= j_2 + j_3 + (|m_2| - m_2)/2 + (|m_3| + m_3)/2 \\
\gamma_4 &= j_1 + j_4 + (|m_1| - m_1)/2 + (|m_4| + m_4)/2
\end{aligned} \tag{A.2.6}$$

$$\gamma_1 + \gamma_4 = |m_1| + |m_4| + 2j_1 + 2j_4 \qquad \gamma_1 - \gamma_4 = m_1 - m_4$$

$$\gamma_2 + \gamma_3 = |m_2| + |m_3| + 2j_2 + 2j_3 \qquad \gamma_2 - \gamma_3 = m_2 - m_3$$

If we write equation (A.2.5) using this definitions we have:

$$\begin{aligned}
V_{n_1 m_1, n_2 m_2, n_3 m_3, n_4 m_4} &= \frac{e^2\sqrt{k}}{\epsilon^*}\frac{1}{\pi^2}\left[\prod_{i=1}^{4}\frac{n_i!}{(n_i + m_i!)}\right]^{1/2} \\
\times \quad \sum_{(4)j=0}^{n} &= \frac{(-1)^{j_1+j_2+j_3+j_4}}{j_1!j_2!j_3!j_4!}\prod_{i=1}^{4}\begin{pmatrix} n_l + |m_l| \\ n_l - j_l \end{pmatrix}\int dx_1 \int dy_1 \int dx_2 \int dy_2 \\
\times \quad & \frac{e^{-(\rho_1^2+\rho_2^2)}}{\sqrt{(x_1^2 - x_2^2)^{1/2} + (y_1^2 - y_2^2)^{1/2}}}(\rho_1 e^{i\varphi_1})^{\gamma_1}(\rho_2 e^{i\varphi_2})^{\gamma_2}(\rho_2 e^{-i\varphi_2})^{\gamma_3}(\rho_1 e^{-i\varphi_1})^{\gamma_4}
\end{aligned} \tag{A.2.7}$$

Separating integral integral I:

$$\begin{aligned}
I &= \int dx_1 \int dy_1 \int dx_2 \int dy_2 \frac{e^{-(\rho_1^2+\rho_2^2)}}{\sqrt{(x_1^2 - x_2^2)^{1/2} + (y_1^2 - y_2^2)^{1/2}}} \\
&\times \quad (\rho_1 e^{i\varphi_1})^{\gamma_1}(\rho_2 e^{i\varphi_2})^{\gamma_2}(\rho_2 e^{-i\varphi_2})^{\gamma_3}(\rho_1 e^{-i\varphi_1})^{\gamma_4}
\end{aligned} \tag{A.2.8}$$

We now separate integration variables into center of $\mathbf{R}$ and ρ relative motion coordinates:

$$\mathbf{R} = (\mathbf{r_1} + \mathbf{r_2})/2, \quad \rho = (\mathbf{r_1} - \mathbf{r_2}) \tag{A.2.9}$$

and making transformation to complex plane, namely:

$$(x_1, y_1) = \rho_1 e^{i\varphi_1} = z_1 = Z + z/2 \qquad (x_2, y_2) = \rho_1 e^{i\varphi_2} = z_2 = Z - z/2$$

$$Z = (z_1 + z_2)/2 \quad z = z_1 - z_2$$

$$\int dx_1 \int dy_1 \int dx_2 \int dy_2 = \int dz_1 \int dz_2$$

$$J = \begin{vmatrix} \frac{\partial z_1}{\partial z} & \frac{\partial z_1}{\partial Z} \\ \frac{\partial z_2}{\partial z} & \frac{\partial z_2}{\partial Z} \end{vmatrix} = \begin{vmatrix} 1/2 & 1 \\ -1/2 & 1 \end{vmatrix} = 1$$

$$\int dz_1 \int dz_2 = \int dz \int dZ$$

Equation A.2.8 transforms into:

$$\begin{aligned} I &= \int dZ e^{-2Z^2} \int dz |z|^{-1} e^{-|z|^2/2} (Z + z/2)^{\gamma_1} \\ &\times (Z - z/2)^{\gamma_2} (Z^* - z^*/2)^{\gamma_3} (Z^* + z^*/2)^{\gamma_4} \end{aligned} \tag{A.2.10}$$

Making use of the binomial theorem

$$(a+b)^n = \sum_{i=0}^{n} \begin{pmatrix} n \\ i \end{pmatrix} a^i b^{n-i} \tag{A.2.11}$$

Equation (A.2.10) turns into:

$$\begin{aligned} I &= \sum_{(4)\ell=0} \begin{pmatrix} \gamma_1 \\ \ell_1 \end{pmatrix} \begin{pmatrix} \gamma_2 \\ \ell_2 \end{pmatrix} \begin{pmatrix} \gamma_3 \\ \ell_3 \end{pmatrix} \begin{pmatrix} \gamma_4 \\ \ell_4 \end{pmatrix} \int dZ e^{-2Z^2} \int dz |z|^{-1} e^{-|z|^2/2} \\ &\times Z^{\ell_1+\ell_2} (Z^*)^{l_3+l_4} (z/2)^{\gamma_1-\ell_1} (-z^*/2)^{\gamma_3-\ell_3} (z^*/2)^{\gamma_4-\ell_4} \end{aligned} \tag{A.2.12}$$

If we write equation (A.2.12) using following definitions:

$$G = \gamma_1 + \gamma_2 + \gamma_3 + \gamma_4 \qquad \Lambda = \ell_1 + \ell_2 + \ell_3 + \ell_4 \tag{A.2.13}$$

$$
\begin{aligned}
I &= \sum_{(4)\ell=0}^{\gamma} \prod_{i=1}^{4} \left(\begin{array}{c} \gamma_i \\ \ell_i \end{array} \right) (-1)^{\gamma_2+\gamma_3-\ell_2-\ell_3} 2^{\Lambda-G} \int dZ e^{-2Z^2} \int dz |z|^{-1} e^{-|z|^2/2} \\
&\times |z|^{(G-\Lambda)} expi\varphi_{rm}(\gamma_1+\gamma_2-\gamma_3-\gamma_4-\ell_1-\ell_2+\ell_3+\ell_4) \\
&\times |Z|^{\Lambda} exp(\ell_1+\ell_2-\ell_3-\ell_4)
\end{aligned}
\tag{A.2.14}
$$

$$
dz = d|z||z|d\varphi \qquad \int dz = \int d|z||z| \int d\varphi
$$

$$
\int d\varphi_{rm} \exp \varphi_{rm}(\gamma_1+\gamma_2-\gamma_3-\gamma_4-\ell_1-\ell_2+\ell_3+\ell_4) = 2\pi\delta_{m_1+m_2,m_3+m_4}
$$

$$
\int d\varphi_{cm} \exp \varphi_{cm}(\ell_1+\ell_2-\ell_3-\ell_4) = 2\pi\delta_{\ell_1+\ell_2,\ell_3+\ell\ell_4}
$$

$$
\begin{aligned}
I &= \delta_{m_1+m_2,m_3+m_4} 4\pi^2 \sum_{(4)\ell=0}^{\gamma} \delta\ell_1+\ell_2,\ell_3+\ell_4 \prod_{i=1}^{4} \left(\begin{array}{c} \gamma_i \\ \ell_i \end{array} \right) (-1)^{\gamma_2+\gamma_3-\ell_2-\ell_3} 2^{\Lambda-G} \\
&\times \int d|Z||Z|^{\Lambda+1} e^{-2|Z|^2} \int d|z||z|^{G-\Lambda} e^{|z|^2/2}
\end{aligned}
\tag{A.2.15}
$$

Making use of gamma functions:

$$
\Gamma(z) = \int_0^{\infty} = t^{z-1} e^{-t} dt
$$

$$
\int d|Z|Z|Z|^{\Lambda} e^{-2|Z^2|} = \frac{1}{42^{\Lambda/2}} \int du u^{k/2} e^{-u} = \frac{1}{2^{\Lambda/2}} \Gamma(\Lambda/2+1)
$$

$$
(2|Z|^2 = u)
$$

$$
\int d|z||z|^{G-\Lambda} e^{-|z|^2/2} = \int du u^{G-\Lambda-1/2} e^{-u} = \Gamma\left(\frac{G-\Lambda+1}{2}\right)
$$

$$
(|z^2|/2 = u)
$$

$$
\begin{aligned}
I &= \delta_{m_1+m_2,m_3+m_4} \pi^2 2^{-G/2-1/2} \sum_{(4)\ell=0}^{\gamma} \delta_{\ell_1+\ell_2,\ell_3+\ell_4} \prod_{i=1}^{4} \left(\begin{array}{c} \gamma_i \\ \ell_i \end{array} \right) (-1)^{\gamma_2+\gamma_3-\ell_2-\ell_3} \\
&\times \Gamma(\Lambda/2+1)\Gamma([G-\Lambda+1]/2)
\end{aligned}
\tag{A.2.16}
$$

Finally we find Coulomb matrix element:

$$
\begin{aligned}
Vn_1m_1, n_2m_2, n_3m_3, n_4m_4 = \delta_{m_1+m_2,m_3+m_4} \frac{e^2\sqrt{k}}{\epsilon^*} \frac{1}{\pi^2} \left[\prod_{i=1}^{4} \frac{n_i!}{(n_i+m_i!)} \right]^{1/2} \\
\times \quad \sum_{(4)j=0}^{n} \frac{(-1)^{j_1+j_2+j_3+j_4}}{j_1!j_2!j_3!j_4!} \prod_{i=1}^{4} \begin{pmatrix} n_l + |m_l| \\ n_l - j_l \end{pmatrix} \\
\times \quad 2^{-G/2-1/2} \sum_{(4)\ell=0}^{\gamma} \delta_{\ell_1+\ell_2,\ell_3+\ell_4} \prod_{i=1}^{4} \begin{pmatrix} \gamma_i \\ \ell_i \end{pmatrix} (-1)^{\gamma_2+\gamma_3-\ell_2-\ell_3} \\
\times \quad \Gamma(\Lambda/2+1)\Gamma([G-\Lambda+1]/2)
\end{aligned}
\tag{A.2.17}
$$