CONTRIBUTION

การคำนวณของอะตอมเมื่อมีค่า Z เข้าสู่อนันต์

นางสาวจริน โอษะคลัง

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

สาขาฟิสิกส์

มหาวิทยาลัยเทคโนโลยีสุรนารี

ปีการศึกษา 2542

ISBN 974-7359-45-6

DERIVATION OF THE $Z \to \infty$ LIMIT FOR ATOMS

Miss Jarin Osaklung

A Thesis Submitted In Partial Fulfillment of the Requirements
For the Degree of Master of Science in Physics
Suranaree University of Technology
Academic Year 1999

ISBN 974-7359-45-6

Thesis Title

Derivation of the $Z \to \infty$ Limit for Atoms

Suranaree University of Technology Council has approved this thesis submitted in partial fulfillment of the requirements for a Master's Degree

Thesis Examining Committee

Prasart Suebka

(Assoc. Prof. Dr. Prasat Suebka)
Chairman

(Prof. Dr. Edouard B. Manoukian)
Thesis Advisor

(Dr. Yupeng Yan)
Member

K. Prabriputaloong

(Assoc. Prof. Dr. Kasem Prabriputaloong)
Vice rector for Academic Affairs

Tassanee Sukosol

(Assoc. Prof. Dr. Tassanee Sukosol)
Dean / Institute of Science

นางสาวจริน โอษะคลัง: การคำนวณของอะตอมเมื่อมีค่า Z เข้าสู่อนันต์ (DERIVATION OF THE $Z \to \infty$ LIMIT FOR ATOMS) อ.ที่ปรึกษา : ศ. ดร. เอ็ดเวิร์ด บี มาโนเขียน, 74 หน้า.
ISBN 974-7359-45-6

วิทยานิพนธ์ฉบับนี้ได้ศึกษาเชิงทฤษฎีของการแก้ปัญหาที่ซับซ้อนเกี่ยวกับพลังงานสถานะพื้นที่แม่นตรงของอะตอมที่เป็นกลางสำหรับค่าเลขอะตอม Z ที่เข้าสู่อนันต์โดยหาขอบเขตบนและขอบเขตล่างที่ชัดแจ้งเกี่ยวกับพลังงานสถานะพื้นที่แม่นตรงของอะตอมที่เป็นกลางโดยใช้กรีนฟังก์ชันสำหรับอนุภาคเดี่ยว พบว่าเมื่อเลขอะตอมเข้าสู่อนันต์ผลที่ได้ทั้งขอบเขตบนและล่างจะสอดคล้องกับอะตอมของทอมัส-เฟร์มี หลักการที่สำคัญคือ การเขียนแฮมิลโตเนียนของอะตอมที่เป็นกลางให้เป็นแฮมิลโตเนียนของอนุภาคเดี่ยวและแฮมิลโตเนียนแผนเดิมที่สอดคล้องกับสมบัติของอะตอม การวิเคราะห์ทั้งระบบจึงศึกษาจากกรีนฟังก์ชันของอนุภาคเดี่ยวเท่านั้น

สาขาวิชาฟิสิกส์ ลายมือชื่อนักศึกษา.จริน โอษะคลัง.....
ปีการศึกษา 2542 ลายมือชื่ออาจารย์ที่ปรึกษา.....

MISS JARIN OSAKLUNG: DERIVATION OF THE $Z \to \infty$ LIMIT FOR ATOMS THESIS ADVISOR: PROF. Dr. EDOUARD B. MANOUKIAN, Ph. D. 74 PP. ISBN 974-7359-45-6

This thesis is involved, a priori, with the very complex problem of the exact ground-state energy of neutral atoms for $Z \to \infty$. Explicit upper and lower bounds are derived for the exact ground-state energy of neutral atoms, involving one-body Green functions, and which for $Z \to \infty$ are shown both to coincide with the ground-state energy of the Thomas-Fermi atom. The basic idea of our strategy is to rewrite the exact Hamiltonian of neutral atoms as one-body Hamiltonians and c-functions with readily established properties. This analysis is then followed by a systematic study of scaling properties of integrals involving the respective one-body Green functions.

สาขาวิชาฟิสิกส์ ลายมือชื่อนักศึกษา.จริน โอชะคลัง.....

ปีการศึกษา 2542 ลายมือชื่ออาจารย์ที่ปรึกษา.....

Acknowledgments

First I would like to thank to my supervisor Professor Dr. E. B. Manoukian for his guidance and for making many extensive and valuable comments throughout the entire thesis. I am also very thankful for his patience in reading the thesis and especially for his constant encouragement, which always kept me going, and for his support throughout the writing of this thesis.

This thesis has been funded by the Institute for the Promotion of Teaching Science and Technology, to which I am grateful.

I should also thank Dr. Prapun Manyum for pointing out a reference.

I am grateful for the help of Mr. Songrit Kamyod for showing me the computer programs, which generated the figures displaced in the thesis.

Finally, I wish to extend my appreciation and thanks to all the lecturers who have taught me graduate courses in the School of Physics at Suranaree University of Technology.

Jarin Osaklung

Contents

Contents (continued)

Page

List of Figures

Figure **Page**

Chapter I

Introduction

The Thomas-Fermi atom was born over seventy years ago through the work of Thomas (1927) and Fermi (1927, 1928) when quantum mechanics was still in its infancy. It has captivated the hearts of physicists ever since and continues to do so into the twenty-first century due to its extreme simplicity and remarkable success (Dreizler and Gross, 1990; Morgan and Drake (ed), 1996). The literature on the Thomas-Fermi atom is quite vast. The very remarkable property of atoms is that in the limit $Z \to \infty$ the Thomas-Fermi theory becomes exact (Lieb and Simon, 1973, 1977; Lieb, 1976, 1981; Baumgartner, 1976), where Z is the atomic number. That is, for $Z \to \infty$ the ground state energy of atoms is given by the ground-state energy of the Thomas-Fermi one. Unfortunately, the very ingenious proofs of this beautiful result are somehow quite complex. The difficulty of the proof of this important result has prevented the presentation of its intricacies even in most advanced treatments of the subject (Dreizler and Gross, 1990). The importance of this result in physics cannot be over emphasized. It provides the initial stage (Dreizler and Gross, 1990; Lieb, 1981; Morgan and Drake, 1996; Schwinger, 1980, 1981; Englert and Schwinger, 1984a, 1984b; Manoukian and Bantitadawit, 1999) for the evaluation of the ground-state energy of the atoms in our world, as appearing in the periodic table. Also It

participates in explaining through a rigorous investigation, in part, of the Thomas-Fermi theory for large number of electrons, the stability of matter (Dyson, 1967; Dyson and Lenard ,1967, 1968; Lieb, 1976, 1991) and of our very own existence.

The Thomas-Fermi (TF) atom, introduced originally as a means of calculating electron distributions and fields in heavy atoms (Thomas, 1927; Fermi, 1927, 1928), has proved to be of very considerable value in tackling many-body problems in quantum mechanics (Lieb, 1981) and by now has been applied to molecules, solids and nuclei.

The original idea of the Thomas–Fermi model is to exploit the density–functional theory of the electronic structure in which one replaces the complicated N–electron wave function $\psi(x_1, x_2, ..., x_N)$ and the associated Schrödinger equation by the much simpler electron density $n(\boldsymbol{r})$ and its associated calculational scheme (Parr and Yang, 1989).

There is a long history of such theories, which until 1964 only had status simply as models. The history begins with the work of Thomas and Fermi in the 1920s (Thomas, 1927; Fermi 1927, 1928; Gombas, 1949; March, 1957; Teller, 1962; cf., Parr and Yang, 1989; Dreizler and Gross, 1990; Bransden and Joachain, 1995). What these authors realized was that statistical considerations can be used to approximate the distribution of electrons in an atom. The assumptions stated by Thomas (1927) are that: "Electrons are distributed uniformly in the six-dimensional phase space for the motion of n electrons at the rate of two for each h^3 of volume" and that there is as effective potential field " which is itself determined by the nuclear charge and this

distribution of electrons." The Thomas-Fermi formula for electron density can be derived from these assumptions. We give in Chapter II a slightly different, but equivalent, derivation of the Thomas-Fermi theory.

The Thomas-Fermi theory was the first method to propose using the electronic charge density as its fundamental variable instead of the wave-function. The model can be understood with reference to Figure **1.1**. Although the charge density is that of a non–uniform electron gas, the number of electrons in a given volume element, $d^3\mathbf{r}$, can be expressed as $n(\mathbf{r})d^3\mathbf{r}$, where $n(\mathbf{r})$ is the charge density for a uniform electron gas at that point. It is then possible to express the energy as a function of $n(\mathbf{r})$. The density $n(\mathbf{r})$ is just the three-dimensional single-particle density and the quantum theory for the ground-state can be put in terms of it. Density-functional theory has its roots in the papers of Thomas and Fermi in the 1920s, but became a more accurate theory (as opposed to a model) only with the publications in the early 1960s of Kohn, Hohenberg, and Sham (Hohenberg and Kohn, 1964; Kohn and Sham, 1965).

Density Functional Theory (DFT) was born over 35 years (cf., Dreizler and Gross, 1990). It is applicable to several branches of physics and chemistry (solids, liquids, plasma, molecule, nuclei, and surface physics)

DFT was originally developed by Hohenberg and Kohn (1964) and later developed by Kohn and Sham (1965). The crux of this work is the proof that it is valid to use the charge density and becomes a unique functional of the charge density and the energy E is uniquely defined by n.

DFT is a way of simplifying the many body problems by working with the electronic charge density as a fundamental variable rather than the wave function. It is a ground-state theory that incorporates both exchange and correlation effects.

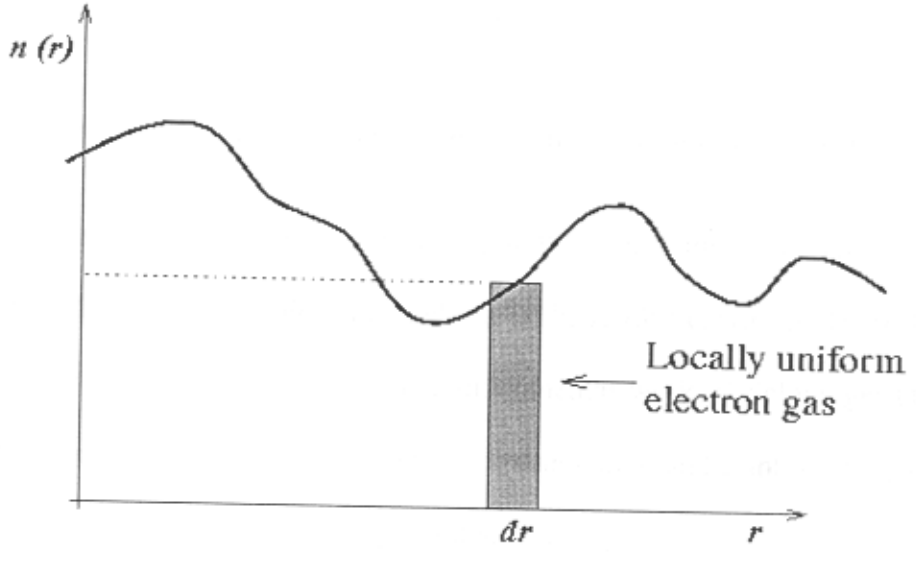

Figure 1.1. Schematic diagram showing the principle of the local density approximation, as done in the Thomas Fermi theory, namely that for a given radial slab, dr, the local density can be considered to be $n(r)$, the density of an equivalent uniform homogeneous electron gas.

The Hamiltonian of a multi-electron neutral atom consists of the kinetic energy part, the potential due to the nucleus and the potential due to electron-electron interactions. In detail it is given in a standard notation by

$$H = \sum_{\alpha=1}^{Z}\left(\frac{\mathbf{p}_\alpha^2}{2m} - \frac{Z}{r_\alpha}\right) + \sum_{\alpha<\beta}^{Z}\frac{e^2}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|} \qquad (1.1)$$

We recall that the Thomas-Fermi atom is a model and does not follow from the exact Hamiltonian. The ground state energy of the Thomas-Fermi atom is given by

$$E_{TF} = -0.7687 Z^{7/3} \tag{1.2}$$

and this will be worked out in detail in Chapter II as it is relevant to our work.

Much work has been done to improve upon the expression of the ground-state energy as given by the Thomas-Fermi model (cf. Lieb, 1973; Schwinger, 1980, 1981; Englert and Schwinger, 1984a, 1984b). The monumental work of Schwinger (1980, 1981; Englert and Schwinger, 1984a, 1984b; cf., Manoukian and Bantitadawit, 1999) gives the remarkable expression for the ground-state energy

$$E(Z) = Z^{7/3}\left[-0.785745 + \frac{1}{2}\frac{1}{Z^{1/3}} - 0.26996\frac{1}{Z^{2/3}}\right]\frac{e^2}{a_0} \tag{1.4}$$

where $a_0 = \hbar^2/me^2$ is the Bohr radius. As an improvement over the Thomas-Fermi model, equation (1.4) still represents a model and is not directly obtained from the exact Hamiltonian H given in (1.1). The second term $Z^{-1/3}/2$, in the square brackets in (1.4), is due to the electrons tightly bound to the atom and is referred to as the Scott factor (Scott, 1952). The last term $-0.26996Z^{-2/3}$ in the square brackets in (1.4) is due to "exchange" and includes a quantum correction.

The purpose of this thesis is to provide an accessible derivation of the $Z \to \infty$ limit of the exact ground-state energy E_Z for neutral problem. We use, in the process,

basic scaling properties we derive for one-body Green functions. Green functions are widely used in quantum physics and quantum field theory (e.g., Schwinger, 1961, 1993; Fitter and Walecka, 1971; Rickayzen, 1980; Manoukian and Bantitadawit, 1999). Our derivation follows by deriving upper and lower bounds, involving one-body Green functions, for the exact ground-state energy E_Z for neutral atoms, which for $Z \to \infty$ are shown both to coincide with the ground-state energy of the Thomas-Fermi atom.

The plan of the thesis is as follows. Chapter II is devoted to the Thomas-Fermi theory and a detailed derivation of its ground-state energy. In Chapter III, we develop the machinery of taking expectation values of one-body and two-body interactions with respect to determinantal functions. These results will be quite important in Chapter V. In Chapter IV, we derive and study the structure of a lower bound for the electron-electron repulsive Coulomb potential. This result is subsequently used in Chapter VI. Chapter V is devoted to the derivation of an upper bound for the exact ground-state energy E_Z of neutral atoms for $Z \to \infty$. Chapter VI is devoted to the derivation of a lower bound for E_Z for $Z \to \infty$. In the concluding Chapter VII, our method of investigation is summarized concerning the upper and lower bounds for E_Z derived, respectively, in the two earlier chapters. The comparison of these derived bounds finally establishes our main result. The research investigation carried out in this work is being published (Manoukian and Osaklung, 2000).

Chapter II

The Thomas–Fermi Atom and Its Ground–State Energy

2.1 The Fermi Electron Gas

Before we analyze the theory developed by Thomas and Fermi for the ground-state energy of multi-electron atoms, it is convenient to consider the simpler problem of the Fermi electron gas, that is a system consisting of a large number N of free electrons confined to a certain region of space. We shall suppose that the N free electrons of our system are confined to a large cube of sides each of length L. Each one of the electrons is therefore moving independently in a potential which is assumed to be a constant (we may take this constant to be zero) inside the cube, and is assumed to be infinite at the boundary. Thus, the spatial part of the wave function describing the motion of an electron satisfies the free particle Schrödinger equation

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(\mathbf{r})=E\psi(\mathbf{r}) \tag{2.1}$$

inside the cube, while $\psi = 0$ at the boundary.

Since the equation (2.1) is separable, in particular, in Cartesian coordinates, we may use the results for the one-dimensional infinite square well potential. Generalizing these results to three dimensions, and choosing the origin of our coordinate system to be at one of the corners of the box we find that the eigenfunctions of (2.1) which vanish at the boundary (i.e., the wave-functions for a spinless particle in a cubical box each of side L) are given by

$$\psi_{n_x n_y n_z}(\mathbf{r}) = C \sin\left(\frac{n_x \pi}{L} x\right) \sin\left(\frac{n_y \pi}{L} y\right) \sin\left(\frac{n_z \pi}{L} z\right) \tag{2.2}$$

where $C = \left(8/L^3\right)^{1/2}$ is a normalization constant and n_x, n_y, n_z are positive integers. The corresponding allowed values of the energy E of an electron are

$$E = \frac{\pi^2 \hbar^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right.$$

$$= \frac{\pi^2 \hbar^2}{2mL^2} n^2 \tag{2.3}$$

where

$$n^2 = n_x^2 + n_y^2 + n_z^2 \tag{2.4}$$

We remark that each energy level in (2.3) can in general be obtained from a number of different sets of values of $\left(n_x, n_y, n_z\right)$, and E, for a given n, is generally degenerate.

Since electrons have spin $1/2$, we must multiply the spatial part (2.2) of their wave-functions by the spin functions $\chi_{1/2,m_s}$, with $m_s = \pm 1/2$. The individual electron wave-functions are therefore the spin orbitals

$$\psi_{n_x n_y n_z m_s} = \psi_{n_x n_y n_z}(\mathbf{r})\chi_{1/2,m_s} \tag{2.5}$$

and the quantum states of an electron are specified by the three spatial quantum number (n_x, n_y, n_z) and the spin quantum numbers m_s. We note that for each energy level (2.3) labeled by the quantum numbers (n_x, n_y, n_z), there are two spin-orbitals, one corresponding to spin up $m_s = +1/2$ and one to spin down $m_s = -1/2$, so that the degeneracy of the individual energy level (2.3) is multiplied by two.

Because energy spacing is very small for any reasonable macroscopic box of sides L, it is a good approximation to consider that the energy levels are distributed nearly continuously. We may then introduce the density of states or density of orbitals $D(E)$, which is defined as the number of electron quantum states (i.e., the number of spin orbitals) per unit energy range. Thus $D(E)\,dE$ is the number of electron states for which the energy of an electron lies between E and $E + dE$.

In order to obtain the quantity $D(E)$, we consider the space formed by the axes corresponding to the values taken by n_x, n_y, n_z (see Fig. 2.1). Since n_x, n_y, n_z are positive integers, we are interested only in the octant for which $n_x > 0, n_y > 0, n_z > 0$. As seen from Fig. 2.1, each set of spatial quantum numbers (n_x, n_y, n_z) corresponds

to a point of a cubical lattice, and every elementary cube of the lattice has unit volume.

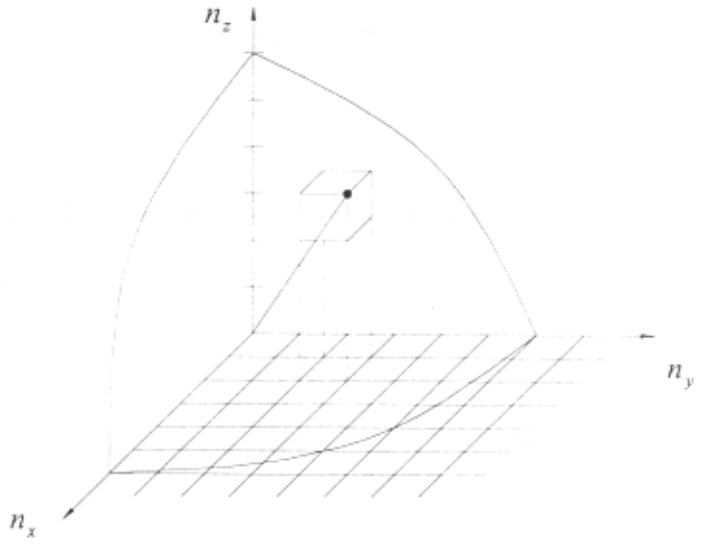

Fig. 2.1. Three-dimensional ***n***-space used in the calculation of $D(E)$. To each state (n_x, n_y, n_z), is associated a cube of unit volume. For fairly large values of some or all of the components of (n_x, n_y, n_z) the total number of states within a sphere of radius of size $n = (n_x^2 + n_y^2 + n_z^2)^{1/2}$ equals the volume of one octant of a sphere of radius n in ***n***–space.

Thus, for fairly large values of the quantum triplet (n_x, n_y, n_z), the total number of spin orbitals for all energies up to a certain value E is closely equal to the number of individual electron states for energies up to E and is therefore given approximately by

$$N_s = 2\frac{1}{8}\frac{4}{3}\pi n^3 = \frac{1}{3}\pi n^3 \tag{2.6}$$

where the factor 2 is due to the two spin states per spatial orbital. Using (2.3) and setting $V = L^3$, we may also rewrite this result as

$$N_s = \frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} VE^{3/2} \tag{2.7}$$

The number $D(E)\,dE$ of electron states within the energy range $(E, E+dE)$ is then obtained by differentiating (2.7), namely

$$dN_s = D(E)dE = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} VE^{1/2}dE \tag{2.8}$$

so that

$$D(E) = \frac{dN_s}{dE} = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} VE^{1/2} \tag{2.9}$$

According to the Pauli exclusion principle, the total wave-function describing the entire system of N electrons must be fully anti-symmetric in the (spatial and spin) coordinates of the electrons, and will therefore, for the free electron gas, be a Slater determinant constructed from the individual spin orbitals (2.5). The corresponding total energy is the sum of the individual electron energies. Assuming that the system is in the ground state (i.e., our Fermi electron gas, in particular, is at absolute zero temperature T = 0 K), the lowest total energy is then obtained when the N electrons

fill all the spin orbitals up to an energy E_F, called the *Fermi energy*, the remaining orbitals (with energies $E > E_F$) being vacant. This is illustrated in Fig. 2.2, which shows the density of states $D(E)$ as a function of E, the occupied orbitals corresponding to the ground state of the Fermi electron gas being represented by the shaded area.

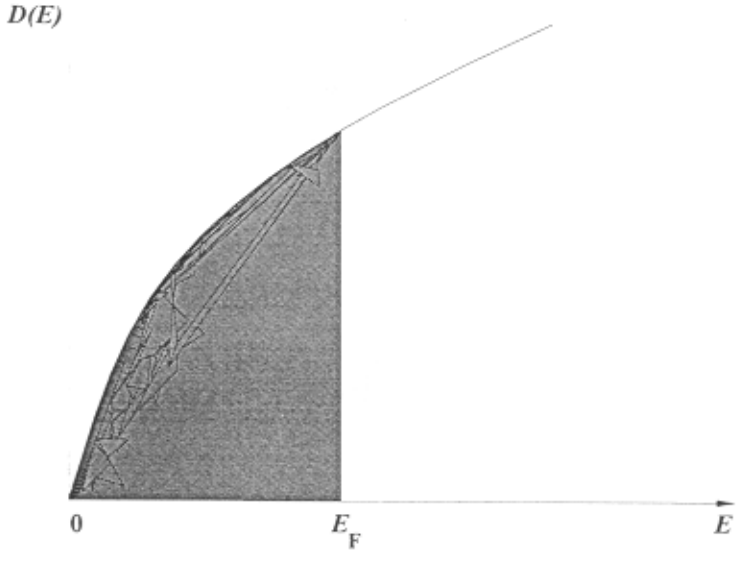

Fig. 2.2. The density of states $D(E)$ as a function of the energy E. The occupied orbitals corresponding to the ground state of the Fermi electron gas are represented by the shaded area

The Fermi energy may be evaluated by requiring that the total number N of electrons in the system should be equal to

$$N = \int_0^{E_F} D(E)\, dE \tag{2.10}$$

In writing this equation we have used the fact that the system contains many electrons, so that the integral (2.10) is a good approximation to the corresponding sum over discrete states. Moreover, since N is large, it does not matter whether the last level contains one or more electrons. Using the result (2.9), we have

$$N = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} V \int_0^{E_F} E^{1/2} dE$$

$$= \frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} V E_F^{3/2} \tag{2.11}$$

so that

$$E_F = \frac{\hbar^2}{2m}\left(3\pi^2 \rho\right)^{2/3} \tag{2.12}$$

where

$$\rho = \frac{N}{V} \tag{2.13}$$

is the number of electrons per unit volume, i.e., the density of electrons. We note that the total energy of a Fermi electron gas in the ground state (at absolute zero) is

$$E_{tot} = \int_0^{E_F} E\, D(E)\, dE$$

$$= \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} V \int_0^{E_F} E^{3/2} dE$$

$$= \frac{1}{5\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} V E_F^{5/2}$$

$$= \frac{3}{5} N E_F \qquad (2.14)$$

where we have used (2.9) and (2.11) . The average electron energy at $T = 0$ K is therefore

$$\overline{E} = \frac{E_{tot}}{N} = \frac{3}{5} E_F \qquad (2.15)$$

It is also instructive to study the problem of the Fermi electron gas by imposing periodic boundary conditions on the (spatial) wave-functions of the electrons, i.e., by requiring these wave-functions to be periodic in x, y and z with period L. Instead of the standing waves (2.2) we then have travelling wave solutions of the Schrödinger equation (2.1), having the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \qquad (2.16)$$

The allowed components of the wave vector **k** are then given by

$$k_x = \frac{2\pi}{L} n_x, \qquad k_y = \frac{2\pi}{L} n_y, \qquad k_z = \frac{2\pi}{L} n_z \qquad (2.17)$$

where n_x, n_y, n_z are positive or negative integers, or zero. The number of spatial orbitals in the volume element $d\mathbf{k} = dk_x dk_y dk_z$, about $\mathbf{k}$, is $(L/2\pi)^3 dk_x dk_y dk_z$, and this number must be multiplied by 2 to take into account the two possible spin states. A unit volume of **k**-space will therefore accommodate $V/4\pi^3$ electrons (with $V = L^3$). Thus, the individual electron states having energies up to $E = \hbar^2 k^2/2m$ will be contained within a sphere in **k**-space, of radius k, the number N_s of these states being given by

$$N_s = \frac{V}{4\pi^3}\frac{4}{3}\pi k^3 = \frac{1}{3\pi^2}Vk^3$$

$$= \frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} VE^{3/2} \qquad (2.18)$$

in agreement with (2.7)

We have seen above that for the ground state of our Fermi electron gas, the N electrons fill all the states up to the Fermi energy E_F. Thus in **k**-space all states up to a maximum value of radius k equals to k_F are filled, while the states for which $k>k_F$ are empty. In other words all occupied orbitals of a Fermi electron gas at T=0 K fill a sphere in **k**-space having radius k_F. This sphere, which is called the Fermi sphere, obviously contains

$$\frac{1}{3\pi^2}Vk_F^3 = N_s \qquad (2.19)$$

orbitals, so that

$$k_F = \left(3\pi^2 \rho\right)^{1/3} \tag{2.20}$$

At the surface of the Fermi sphere, known as the *Fermi surface*, the energy is the Fermi energy

$$E_F = \frac{\hbar^2}{2m} k_F^2 \tag{2.21}$$

and we note that the result in (2.12) immediately follows upon substitution of the expression (2.20) in (2.21). It is also convenient to introduce the Fermi momentum p_F, the Fermi velocity υ_F and the Fermi temperature T_F, such that

$$E_F = \frac{p^2}{2m} = \frac{1}{2} m \upsilon_F^2 = kT_F \tag{2.22}$$

where k is Boltzmann's constant.

2.2 The Thomas-Fermi Theory

The theory developed independently by Thomas (1927) and Fermi (1927, 1928) for the ground-state of complex atoms (or ions) having a large number of electrons is based on statistical and semi-classical considerations. For many years the Thomas-Fermi theory was considered as an uncertain approximation to the N-particle Schrödinger equation. Lieb and Simon in 1973 have then shown that the Thomas-

Fermi theory is really a large Z theory - to be precise it is exact in the limit $Z \to \infty$. The N electrons of the system are treated as an electron gas in the ground state, confined to a region of space by a central potential $V(r)$ which vanishes at infinity. It is assumed that this potential is slowly varying over a distance which is large compared to the de Broglie wavelength of the electrons, so that enough electrons are present in a volume where $V(r)$ is nearly constant, and the statistical approach used in studying the Fermi electron gas can be applied. In addition, since the number of electrons is large, many of them have high principal quantum numbers, so that semi-classical methods may be used.

The aim of the Thomas-Fermi model is to provide a method of calculating the potential $V(r)$ and the electron density $n(r)$. These two quantities can first be related by using the following argument. The total energy of an electron is written as $p^2/2m + V(r$, and this energy must be non-positive, so that the electron be bound to the atom. Since the maximum kinetic energy of an electron in a Fermi electron gas at T = 0 K is the Fermi energy E_F, we write for the total energy of the most energetic electrons of the system, the classical equation

$$E_{\max} = E_F + V(r) \tag{2.23}$$

where $V(r)$ includes the external potential $v(r) = -Ze^2 \sum_i 1/r_i$, due to the nucleus and the electrostatic potential produced by the electronic charge density.

It is clear that $E_{\max}$ must be independent of r, because if this were not the case electrons would migrate to that region of space where $E_{\max}$ is smallest, in order to lower the total energy of the system. Furthermore, we must have $E_{\max} \leq 0$. We note from (2.21) and (2.23) that the quantity k_F is now a function of r. That is,

$$k_F^2 = \frac{2m}{\hbar^2}[E_{\max} - V(r)] \tag{2.24}$$

Using (2.12) and (2.24) we then have

$$n(r) = \frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}[E_{\max} - V(r)]^{3/2} \tag{2.25}$$

where we have denoted ρ in (2.12) by $n(r)$ and we see that n vanishes when $V = E_{\max}$. In the classically forbidden region $V > E_{\max}$ we must set $n = 0$, since otherwise (2.23) would yield a negative value of the maximum kinetic energy E_F. Let us denote by

$$\varphi(r) = -\frac{V(r)}{e} \tag{2.26}$$

the electrostatic potential, and by $\varphi_0 = -E_{\max}/e$ a non-negative constant.

Setting

$$\phi(r) = e[\ \varphi(r) - \varphi_0\ ] \tag{2.27}$$

we see that $n(r)$ and $\phi(r)$ are related by

$$n(r) = \frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \phi^{3/2}(r) \qquad \phi \geq 0 \tag{2.28}$$

$$= 0 \qquad \phi < 0 \tag{2.29}$$

For a neutral atom $(N = Z)$ the electrostatic potential $\varphi(r)$ vanishes at infinity and we will set $\varphi_0 = 0$.

A second relation between $n(r)$ and $\phi(r)$ may be obtained as follows. The sources of the electrostatic potential $\varphi(r)$ are:

(i) the point charge Ze of the nucleus, located at the origin

(ii) the charge density distribution due to the N electrons.

Treating the charge density $-en(r)$ of the electrons as a continuous function of r, we may use Poisson's equation of electrostatics to write

$$\nabla^2 \phi(r) = \frac{1}{r}\frac{d^2}{dr^2}[r\phi(r)] = 4\pi e^2 n(r) \tag{2.30}$$

The equation (2.28) and (2.30) are two simultaneous equations for $n(r)$ and $\phi(r)$. Eliminating $n(r)$ from these equations, we find that for $\phi \geq 0$

$$\frac{1}{r}\frac{d^2}{dr^2}[r\phi(r)] = \frac{4e^2}{3\pi\hbar^3}(2m)^{3/2}\phi^{3/2}(r), \qquad \phi \geq 0 \tag{2.31}$$

On the other hand, when $\phi < 0$ we see from (2.29) and (2.30) that

$$\frac{d^2}{dr^2}[r\phi(r)] = 0, \qquad \phi < 0 \tag{2.32}$$

For $r \to 0$ the leading term of the electrostatic potential must be due to the nucleus, so that the boundary condition at $r = 0$ reads

$$\lim_{r\to 0} r\phi(r) = Ze^2 \tag{2.33}$$

On the other hand, we also have the normalization condition

$$\int d^3\mathbf{r}\, n(r) = N \tag{2.34}$$

In order to simplify the above equations, it is convenient to introduce the new dimensionless variable x and the function $\Phi(x)$ such that

where

$$r = xb, \qquad r\phi(r) = Ze^2\Phi(x) \tag{2.35}$$

$$b = \left[\left(\frac{3\pi}{4}\right)^{2/3}\left(\frac{\hbar^2}{2me^2}\right)\frac{1}{Z^{1/3}}\right] \quad = \quad 0.0885\, a_0 Z^{-1/3} \tag{2.36}$$

and $a_0 = \dfrac{\hbar^2}{me^2}$ is the Bohr radius.

From (2.30) and (2.36) we will have

$$n(r) \equiv Z^2 \rho_{TF}(R) = Z^2 \left[\frac{1}{4\pi b^3} \frac{\Phi^{3/2}(x)}{x^{3/2}} \right] \tag{2.37}$$

where we have introduced the vector $\mathbf{R}$ defined by

$$\mathbf{R} = Z^{1/3}\mathbf{r} \tag{2.38}$$

The important equation (2.31) may be then rewritten in dimensionless from as

$$\frac{d^2\Phi}{dx^2} = \frac{\Phi^{3/2}}{x^{1/2}} \tag{2.39}$$

This is the famous " Thomas – Fermi" equation.

The boundary conditions are:

$$\Phi(0) = 1, \qquad \Phi(\infty) = 0 \tag{2.40}$$

The following well know numerical value is to be noted (e.g., Dreizler and Gross 1990, p.129)

$$\Phi'(0) = -1.5881 \tag{2.41}$$

for the slope of $\Phi(x)$ near the origin, and

$$\Phi'(\infty) = 0 \tag{2.42}$$

2.3 Some Properties of the Thomas-Fermi Function.

The Thomas-Fermi equation (2.39) and the boundary conditions in (2.40): $\Phi(0)=1, \Phi(\infty)=0$, define a universal function $\Phi(x)$ for all neutral atoms. Values of this function are obtained by numerical integration. At $x=0$ one has from (2.41) that in the vicinity of the origin

$$\Phi(x) \underset{x\to 0}{\sim} 1-1.5881x+\cdots \tag{2.43}$$

From (2.37) we then conclude that we have the following power law behavior for $\rho_{TF}(R)$:

$$\rho_{TF}(R) \underset{R\to 0}{\sim} \frac{1}{R^{3/2}} \tag{2.44}$$

By direct substitution in (2.39) we readily check that $\Phi(x)==144/x^3$ is a solution of this differential equation. Since the latter solution in not valid for $x=0$ $(\Phi(0)=1)$, we may infer from (2.37) that

$$\rho_{TF}(R) \underset{R\to\infty}{\sim} \frac{1}{R^6} \tag{2.45}$$

The knowledge of the behavior of $\rho_{TF}(R)$ for $R\to 0$ and $R\to\infty$ as given, respectively, in (2.44) and (2.45) turns out to be quite important in establishing our lower bound for the exact ground-state energy of neutral atoms for $Z\to\infty$ in Chapter VI.

2.4 Derivation of the Ground-State Energy

From (2.25) we may write

$$n(r) = \frac{1}{3\pi^2\hbar^3} p^3 \tag{2.46}$$

or

$$dn = \frac{p^2 dp}{\pi^2\hbar^3} \tag{2.47}$$

and thus, we have the following explicit expressions for the kinetic energy per unit volume:

$$\int \frac{p^2}{2m} dn = \frac{\left(3\pi^2\right)^{5/3}\hbar^2 n^{5/3}(r)}{10\pi^2 m} \tag{2.48}$$

and for total kinetic energy we have

$$\frac{\left(3\pi^2\right)^{5/3}\hbar^2}{10\pi^2 m} \int n^{5/3}(\mathbf{r}) d^3\mathbf{r} \tag{2.49}$$

The potential energy between the electrons and the nucleus is

$$-Z\int \frac{e^2}{r} n(\mathbf{r}) d^3\mathbf{r} \tag{2.50}$$

The potential energy due to electron-electron interactions is

$$\frac{e^2}{2}\int\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}\,d^3\mathbf{r}' \tag{2.51}$$

Accordingly, for the ground-state energy of the Thomas-Fermi atom we have the expression:

$$E_{TF}=\frac{(3\pi^2)^{5/3}\hbar^2}{10\pi^2 m}\int n^{5/3}(\mathbf{r})d^3\mathbf{r}-Z\int\frac{e^2}{r}n(\mathbf{r})d^3\mathbf{r}+\frac{e^2}{2}\int\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}\,d^3\mathbf{r}' \tag{2.52}$$

with the subscript "*TF*" referring to the Thomas-Fermi atom. We will evaluate each of the three terms above separately. The Thomas-Fermi density $n(r)$ actually minimizes the expression (2.52) (Lieb, 1981).

The first term is the kinetic energy part:

$$E_k=\frac{(3\pi^2)^{5/3}\hbar^2}{10\pi^2 m}\int_0^{2\pi}d\phi\int_0^{\pi}\sin\theta\,d\theta\int_0^{\infty}dx\,\frac{1}{(3\pi^2)^{5/3}}\frac{(2m)^{5/2}}{\hbar^5}\frac{Z^{5/2}e^5\Phi(x)^{5/2}b^3}{(xb)^{5/2}}$$

$$=\frac{(2m)^{5/2}}{10\pi^2 m}\frac{e^5}{\hbar^2}Z^{5/2}b^{1/2}(4\pi)\int_0^{\infty}\frac{\Phi^{5/2}(x)}{x^{1/2}}dx$$

$$=\frac{2}{5}\frac{(2m)^{5/2}}{\pi m}\frac{e^5}{\hbar^3}Z^{5/2}\left(\frac{3\pi}{4}\right)^{1/3}\left(\frac{\hbar^2}{2me^2}\right)^{1/2}\frac{1}{Z^{1/6}}\int_0^{\infty}\frac{\Phi^{5/2}(x)}{x^{1/2}}dx$$

$$=\frac{2}{5}\frac{(2m)^2}{\pi m}\frac{e^4}{\hbar^2}\left(\frac{3\pi}{4}\right)^{1/3}Z^{7/3}\int_0^{\infty}\frac{\Phi^{5/2}(x)}{x^{1/2}}dx$$

$$= \frac{8}{5\pi}\left(\frac{3\pi}{4}\right)^{1/3}\frac{e^2}{a_0}Z^{7/3}\int_0^{\infty}\frac{\Phi^{5/2}(x)}{x^{1/2}}dx$$

$$= \frac{8}{5\pi}\left(\frac{3\pi}{4}\right)^{1/3}\frac{e^2}{a_0}Z^{7/3}\left(-\frac{5}{7}\Phi'(0)\right)$$

$$= 0.7687\frac{e^2}{a_0}Z^{7/3} \tag{2.53}$$

where

$$\int_0^{\infty}\frac{\Phi^{5/2}(x)}{x^{1/2}}dx = -\frac{5}{7}\phi'(0) \tag{2.54}$$

and $\Phi'(0) = -1.5881$

$$d^3r = r^2\sin\theta\,d\theta\,d\phi = (xb)^2\sin\theta\,d\theta\,d\phi\,bdx = x^2b^3dx\sin\theta\,d\theta\,d\phi$$

The second term in (2.52) may be rewritten as

$$E_{N-e} = -Ze^2\int\frac{n(\mathbf{r})}{r}d^3\mathbf{r}$$

$$= -Ze^2\int_0^{2\pi}d\phi\int_0^{\pi}\sin\theta\,d\theta\int_0^{\infty}dx\,\frac{1}{3\pi^2}\frac{(2m)^{3/2}}{\hbar^3}e^3Z^{3/2}\frac{\Phi^{3/2}(x)}{(xb)^{5/2}}x^2b^3dx$$

$$= -\frac{4(2m)^{3/2}}{3\pi}\frac{e^5}{\hbar^3}Z^{5/2}b^{1/2}\int_0^{\infty}\frac{\Phi^{3/2}(x)}{x^{1/2}}dx$$

$$= -\frac{4(2m)^{3/2}}{3\pi}\frac{e^5}{\hbar^3}Z^{5/2}\left(\frac{3\pi}{4}\right)^{1/3}\left(\frac{\hbar^2}{2me^2}\right)^{1/2}\frac{1}{Z^{1/6}}\int_0^\infty \frac{\Phi^{3/2}(x)}{x^{1/2}}dx$$

$$= -\frac{8m}{3\pi}\left(\frac{3\pi}{4}\right)^{1/3}\frac{e^4}{\hbar^2}Z^{7/3}\int_0^\infty \frac{\Phi^{3/2}(x)}{x^{1/2}}dx$$

$$= -\frac{8}{3\pi}\left(\frac{3\pi}{4}\right)^{1/3}\frac{e^2}{a_0}Z^{7/3}\int_0^\infty \frac{\Phi^{3/2}(x)}{x^{1/2}}dx$$

$$= -\frac{8}{3\pi}\left(\frac{3\pi}{4}\right)^{1/3}\frac{e^2}{a_0}Z^{7/3}\int_0^\infty \Phi''(x)dx$$

$$= -\frac{8}{3\pi}\left(\frac{3\pi}{4}\right)^{1/3}\frac{e^2}{a_0}Z^{7/3}\,\Phi'(0)$$

$$= -1.7937\frac{e^2}{a_0}Z^{7/3} \qquad (2.55)$$

For the third term in (2.52) we have

$$E_{e-e} = \frac{e^2}{2}\int\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}\,d^3\mathbf{r}'$$

$$= \frac{e^2}{2}\frac{1}{(3\pi^2)^2}\frac{(2m)^3}{\hbar^6}e^6Z^3\int_0^{2\pi}d\phi\int_0^{\pi}\sin\theta\,d\theta\int_0^{\infty}dx\frac{\Phi^{3/2}(x)}{(xb)^{3/2}}b^3x^2$$

$$\times\int_0^{2\pi}d\phi'\int_0^{\pi}\sin\theta\,d\theta'\int_0^{\infty}dx'\frac{\Phi^{3/2}(x')}{(x'b)^{3/2}}\frac{b^3x'^2}{\sqrt{r^2-r'^2-2rr'\cos\theta}}$$

$$= \frac{1}{2}\frac{(2m)^3}{(3\pi^2)^2}\frac{e^8}{\hbar^6}Z^3b^2\int_0^{2\pi}d\phi\int_0^{\pi}\sin\theta\,d\theta\int_0^{\infty}dx\;x^{1/2}\Phi^{3/2}(x)$$

$$\times\int_0^{2\pi}d\phi'\int_0^{\pi}\sin\theta' d\theta'\int_0^{\infty}dx'\frac{x'^{1/2}\Phi^{3/2}(x')}{\sqrt{x^2+x'^2-2xx'\cos\theta}}$$

$$\equiv \frac{1}{2}\frac{(2m)^3}{(3\pi^2)^2}\frac{e^8}{\hbar^6}Z^3\left(\frac{3\pi}{4}\right)^{4/3}\left(\frac{\hbar^2}{2me^2}\right)^2\frac{1}{Z^{2/3}}I$$

$$= \frac{1}{(3\pi^2)^2}\left(\frac{3\pi}{4}\right)^{4/3}\frac{e^2}{a_0}Z^{7/3}I \qquad (2.56)$$

where the integral I is defined by

$$I = \int_0^{2\pi}d\phi\int_0^{\pi}\sin\theta\,d\theta\int_0^{\infty}dx\;x^{1/2}\Phi^{3/2}(x)\times\int_0^{2\pi}d\phi'\int_0^{\pi}\sin\theta' d\theta'\int_0^{\infty}dx'\frac{x'^{1/2}\Phi^{3/2}(x')}{\sqrt{x^2+x'^2-2xx'\cos\theta}} \qquad (2.57)$$

Consider the expansion in terms of Legendre polynomials (e.g., Arfken and Weber, 1995, p. 695)

$$\left(x^2+x'^2-2xx'\cos\theta\right)^{-1/2} = \frac{1}{x}\sum_{l=0}^{\infty}f^l P_l\cos\theta \qquad for \quad x'<x$$

$$= \frac{1}{x'}\sum_{l=0}^{\infty}\frac{P_l(\cos\theta)}{f^l} \qquad for \quad x'>x$$

where $f = x'/x$.

Thus for the integral I defined above we may write

$$I = \int_0^{2\pi} d\phi \int_0^{2\pi} d\phi' \int_0^{\pi} \sin\theta' d\theta' \int_0^{\infty} dx \int_0^{x} dx' \frac{1}{x} x^{1/2} \Phi^{3/2}(x) x'^{1/2} \Phi^{3/2}(x') \sum_{l=0}^{\infty} \int_0^{\pi} P_l(\cos\theta) f^l \sin\theta \, d\theta$$

$$+ \int_0^{2\pi} d\phi' \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta \int_0^{\infty} dx' \int_{x'}^{\infty} dx \frac{1}{x'} x'^{1/2} \Phi^{3/2}(x') x^{1/2} \Phi^{3/2}(x) \sum_{l=0}^{\infty} \int_0^{\pi} \frac{P_l(\cos\theta')}{f^l} \sin\theta' \, d\theta'$$

Using the orthogonality relation (Arfken and Weber, 1995, p.709)

$$\int_0^{\pi} P_l(\cos\theta) P_m(\cos\theta) \sin\theta d\theta = \frac{2\delta_{lm}}{2l+1} \tag{2.58}$$

we may integrate over θ to obtain

$$I = 16\pi^2 \int_0^{\infty} \frac{dx}{x^{1/2}} \Phi^{3/2}(x) \int_0^{x} dx' (x')^{1/2} \Phi^{3/2}(x') + 16\pi^2 \int_0^{\infty} dx \Phi^{3/2}(x) \int_x^{\infty} \frac{dx'}{x'^{1/2}} \Phi^{3/2}(x') \tag{2.59}$$

or upon integration by parts, we obtain

$$I = 16\pi^2 \left[-\Phi'(0) - \int_0^{\infty} \frac{dx}{x^{1/2}} (\Phi(x))^{5/2} \right] \tag{2.60}$$

Upon using (2.54), the latter gives

$$I = -\frac{32}{7} \pi^2 \Phi'(0) \tag{2.61}$$

Finally we substitute (2.61) in (2.56) to obtain

$$E_{e-e} = \frac{1}{\left(3\pi^2\right)^2}\left(\frac{3\pi}{4}\right)^{4/3}\frac{e^2}{a_0}Z^{7/3}\left(-\frac{32}{7}\pi^2\Phi'(0)\right)$$

or

$$E_{e-e} = 0.2565\frac{e^2}{a_0}Z^{7/3} \tag{2.62}$$

where we have used the fact that $\Phi'(0) = -1.5881$.

The ground-state energy of the Thomas-Fermi atom in (2.52), is then obtained by adding (2.53), (2.55) and (2.62):

$$E_{TF} = (0.7687 - 1.7937 + 0.2565)\frac{e^2}{a_0}Z^{7/3}$$

$$= -0.7685\frac{e^2}{a_0}Z^{7/3} \tag{2.63}$$

Finally we note from the expression of the ground-state energy expression (2.52) we may write

$$Z^{-7/3}E_{TF} = \frac{\left(3\pi^2\right)^{5/3}\hbar^2}{10\pi^2 m}\int d^3\mathbf{R}\left(\rho_{TF}(R)\right)^{5/3} - e^2\int d^3\mathbf{R}\frac{\rho_{TF}(R)}{R}$$

$$+\frac{e^2}{2}\int d^3\boldsymbol{R}\, d^3\boldsymbol{R}'\rho_{TF}(R)\frac{1}{|\boldsymbol{R}-\boldsymbol{R}'|}\rho_{TF}(R') \tag{2.64}$$

where $\rho_{TF}(R)$ is the scaled Thomas-Fermi density in (2.37): $n(\mathbf{r}) = Z^2\rho_{TF}(R)$ and $\mathbf{R} = Z^{1/3}\mathbf{r}$.

To prove the validity of equation (2.64), we reconsider equation (2.52)

$$E_{TF} = \frac{\left(3\pi^2\right)^{5/3}\hbar^2}{10\pi^2 m}\int n^{5/3}(\mathbf{r})d^3\mathbf{r} - Z\int\frac{e^2}{r}n(\mathbf{r})d^3\mathbf{r} + \frac{e^2}{2}\int\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}d^3\mathbf{r}'$$

and introduce the following transformations:

$$n(\mathbf{r}) = Z^2\rho_{TF}(R)$$

and $$\mathbf{r} = \frac{\mathbf{R}}{Z^{1/3}}, \qquad d^3\mathbf{r} = \frac{d^3\mathbf{R}}{Z}$$

we then have

$$E_{TF} = \frac{\left(3\pi^2\right)^{5/3}\hbar^2}{10\pi^2 m}\int Z^2\rho_{TF}^{5/3}(R)\frac{d^3\mathbf{R}}{Z} - Z\int\frac{e^2}{\left(R/Z^{1/3}\right)}Z^2\rho(R)\frac{d^3\mathbf{R}}{Z}$$

$$+e^2\frac{\int d^3\mathbf{R}\,d^3\mathbf{R}'}{Z^2}\frac{Z^{1/3}}{|\mathbf{R}-\mathbf{R}'|}Z^4\rho_{TF}(R)\rho_{TF}(R')$$

$$E_{TF} = Z^{7/3}\left[\frac{\left(3\pi^2\right)^{5/3}\hbar^2}{10\pi^2 m}\int d^3\boldsymbol{R}\left(\rho_{TF}{}^{5/3}(R)\right) - e^2\int d^3\boldsymbol{R}\frac{\rho_{TF}(R)}{R}\right.$$

$$\left.+\frac{e^2}{2}\int d^3\boldsymbol{R}\,d^3\boldsymbol{R}'\rho_{TF}(R)\frac{1}{|\boldsymbol{R}-\boldsymbol{R}'|}\rho_{TF}(R')\right] \qquad (2.65)$$

which establishes the validity of equation (2.64).

Chapter III

Expectation Value of One-Body and Two-Body Interactions with respect to Determinantal Wave-Functions

The purpose of this chapter is to develop the general theory of the expectation value of operators with respect to determinantal functions - the so-called Slater determinants. This will be essential for the work done in Chapter V on the upper bound of the exact ground-state energy for $Z \to \infty$.

To the above end, we must provide first the method of calculating the matrix elements of an arbitrary operator F. Specific cases for F will be considered later. More generals cased are considered in Bethe and Jackiw (1993).

To evaluate $\langle \psi | H | \psi \rangle$, where H is the Hamiltonian of a system, and for other applications we must calculate the matrix elements of an arbitrary operator F between determinantal wave-functions

$$\psi = \begin{vmatrix} u_1(1) & u_1(2)\ldots & u_1(N) \\ u_2(1) & u_2(2)\ldots & u_2(N) \\ \vdots & \vdots & \vdots \\ u_N(1) & u_N(2)\ldots & u_N(N) \end{vmatrix} \tag{3.1}$$

where

$$u_i(j) = u_i(r_j)\chi(\sigma_j) \tag{3.2}$$

$$\int u_i^*(1)u_j(1)d\tau_1 = \delta_{ij} \tag{3.3}$$

and $\int d\tau = \sum_{\sigma} \int d^3\mathbf{r}$. We can rewrite ψ in the form

$$\psi = (N!)^{-1/2} \sum_P \varepsilon_P \prod_{i=1}^{N} u_{P_i}(i) \tag{3.4}$$

$$= (N!)^{-1/2} \sum_P \varepsilon_P \prod_{i=1}^{N} u_i(P_i) \tag{3.5}$$

where the sum extends over all permutations and ε_p is + or – depending on whether $P_1, P_2, \ldots, P_N$ is an even or odd permutation of *1, 2, ..., N*.

To evaluate expectation values, we assume that the orbitals corresponding to ψ_b are $u_i(j)$, and ψ_a correspond to $v_i(j)$ then

$$\langle F \rangle = \frac{1}{N!} \int \sum_Q \varepsilon_Q \prod_{i=1}^{N} u_i^*(Q_i) F \sum_P \varepsilon_P \prod_{j=1}^{N} \left[v_{P_j}(j) d\tau_j \right] \tag{3.6}$$

For the initial wave function we permute the states, and for the final wave function we permute the electrons. F must be symmetric in the coordinates of all the electrons, since these electrons are identical. To simplify, we group the terms referring to the same electron coordinates together and set $j = Q_i$

$$\langle F \rangle = \frac{1}{N!} \int \sum_Q \sum_P \varepsilon_Q \varepsilon_P \prod_{i=1}^{N} u_i^*(Q_i) F v_{PQ_i}(Q_i) d\tau_{Q_i} \tag{3.7}$$

where $\varepsilon_P \varepsilon_Q = \varepsilon_{PQ}$.

Now Q_i is only a dummy variable in the integral, and we may set $Q_i = i$, this does not change the integral in question:

$$\langle F \rangle = \frac{1}{N!} \sum_Q \sum_{PQ} \varepsilon_{PQ} \int \prod_{i=1}^{N} u_i^*(i) F v_{PQ_i}(Q_i) d\tau_i \tag{3.8}$$

Now the integral and ε_{PQ} are independent of Q, each Q gives the same contribution and the total contribution is $N!$ times the contribution of $P = I$. This eliminates the normalization factor $\frac{1}{N!}$. Replacing PQ by P, then

$$\langle F \rangle = \sum_P \varepsilon_P \int \prod_{i=1}^{N} u_i^*(i) F v_{P_i}(i) d\tau_i \tag{3.9}$$

Consider particular forms of F:

1. $F = 1$. Because of the orthogonality of the one-electron wave functions, we obtain $\langle F \rangle = 0$, unless for some one P, $v_{P_i} = u_i$ for all i. Only $u_i = v_i$ for all i and v must be arranged in the same order with u (u, v are for identical particles) then

$$\langle F \rangle = 1 \tag{3.10}$$

2. $F = \sum_{j=1}^{N} f_j$, where f_j = a one-electron operator operating on electron j

$$\langle F \rangle = \sum_{j=1}^{N} \sum_{P} \varepsilon_P \int \prod_{i=1}^{N} u_i^*(i) f_j v_{p_i}(i) \, d\tau_i \tag{3.11}$$

For $u_j = v_j$ for all j except $j = i$ and $u_i \neq v_i$ for some one i we get

$$\langle F \rangle = \langle i | f | i \rangle = \int u_i^*(1) f_1 v_i(1) d\tau_1 \tag{3.12}$$

where $P = I$ is the identity permutation.

If $u_i = v_i$ for all i,

$$\langle F \rangle = \sum_i \langle i | f | i \rangle \tag{3.13}$$

Only the identity permutation $P = I$ contributes to (3.12) and (3.13).

For example if

$$F = \sum_i f_i \qquad f_i = -\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}$$

then

$$\langle F \rangle = \sum_i \int d\tau u_i^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 - \frac{Z}{r} \right) u_i(\mathbf{r}) \tag{3.14}$$

3. $F = \sum_{i<j} g_{ij}$, g_{ij} is an operator operating on electrons i and j:

$$\langle F \rangle = \sum_{i<j} \sum_{P} \varepsilon_P \int\prod_{i=1}^{N} u_i^*(i) g_{ij} v_{P_i}(i)\, d\tau_i \tag{3.15}$$

If $u_i \neq v_i$ for more than two i's

$$\langle F \rangle = 0 \tag{3.16}$$

If $u_i = v_i$ for all i

$$\langle F \rangle = \sum_{i<j} \left[\langle ij|g|ij \rangle - \langle ij|g|ji \rangle \right] \tag{3.17}$$

where

$$\langle ij|g|kl \rangle = \int u_i^*(1) u_j^*(2) g_{12} v_k(1) v_l(2) d\tau_1 d\tau_2 \tag{3.18}$$

If for some i, $u_i \neq v_i$ but for all j except $j = 1$, $u_i = v_i$

$$\langle F \rangle = \sum_{j \neq i} \left[\langle ij|g|ij \rangle - \langle ij|g|ji \rangle \right] \tag{3.19}$$

If for some i and j, $u_i \neq v_i$ and $u_j \neq v_j$, but for all k except $k = i$, $k = j$ we have $u_k = v_k$ and

$$\langle F \rangle = \langle ij|g|ij \rangle - \langle ij|g|ji \rangle \tag{3.20}$$

For example if

$$F = \sum_{i<j} g_{ij} \qquad g_{ij} = \frac{1}{r_{ij}}$$

then

$$\langle F\rangle = \sum_{i<j}\Bigg[\sum_{\sigma_1,\sigma_2}\int d\tau_1 d\tau_2 u_i^*(\mathbf{r}_1)u_j^*(\mathbf{r}_2)g_{12}u_i(\mathbf{r}_1)u_j(\mathbf{r}_2)\times|\chi_i(\sigma_1)|^2|\chi_j(\sigma_2)|^2$$

$$-\sum_{\sigma_1,\sigma_2}\int d\tau_1 d\tau_2 u_i^*(\mathbf{r}_1)u_j^*(\mathbf{r}_2)g_{12}u_i(\mathbf{r}_2)u_j(\mathbf{r}_1)$$

$$\times\chi_i^*(\sigma_1)\chi_j^*(\sigma_2)\chi_i(\sigma_2)\chi_j(\sigma_1)\Bigg] \qquad (3.21)$$

and where we have taken $u_i(j)=u_i(\mathbf{r}_j)\chi_i(\sigma_j)$, and used the orthogonality relation, with *i, j* corresponding, respectively, to m_{s_i}, m_{s_j}

$$\sum_{\sigma}\chi^*_{m_{s_i}}(\sigma)\chi_{m_{s_j}}(\sigma)=\delta(m_{si},m_{sj})$$

Chapter IV

Detailed Derivation of a Lower Bound for the Coulomb Potential

Before deriving the lower bound for the exact ground-state energy for atoms for large Z, we first provide a detailed derivation of a lower bound for the Coulomb potential. This result will be used later on in Chapter VI.

4.1 Lower Bound for Interactions of Positive Type

Let $V(\mathbf{r})$ be a real potential function of positive type (i.e., with a Fourier transform $\widetilde{V}(\mathbf{k}) \geq 0, V(0) < \infty$). A known result by Thirring(1981), that will be needed in Chapter VI, is

$$\sum_{n>m}^{Z} V(\mathbf{r}_n - \mathbf{r}_m) \geq \sum_{n=1}^{Z} \Phi(\mathbf{r}_n) - \frac{1}{2} \int \frac{d^3\mathbf{k}}{(2\pi)^3} \left[\frac{\left|\widetilde{\Phi}(\mathbf{k})\right|^2}{\widetilde{V}(\mathbf{k})} + Z\widetilde{V}(\mathbf{k}) \right] \tag{4.1}$$

provided the integrals on the right-hand side exist and where $\Phi(\mathbf{r})$ is an arbitrary real function. We provide a detailed proof of (4.1).

Proof:

It follows from the positivity of the following expression:

$$0 \le \int d^3\mathbf{r} d^3\mathbf{r}' \left(\sum_{n=1}^{Z} \delta^3(\mathbf{r}-\mathbf{r}_n) - \rho(\mathbf{r}) \right) V(\mathbf{r}-\mathbf{r}') \left(\sum_{m=1}^{Z} \delta^3(\mathbf{r}'-\mathbf{r}_m) - \rho(\mathbf{r}') \right)$$

$$= \int d^3\mathbf{r} d^3\mathbf{r}' \Bigg[\sum_{n=1}^{Z} \delta^3(\mathbf{r}-\mathbf{r}_n) V(\mathbf{r}-\mathbf{r}') \sum_{m=1}^{Z} \delta^3(\mathbf{r}'-\mathbf{r}_m) - \sum_{n=1}^{Z} \delta^3(\mathbf{r}-\mathbf{r}_n) V(\mathbf{r}-\mathbf{r}') \rho(\mathbf{r}')$$
$$- \sum_{m=1}^{Z} \delta^3(\mathbf{r}'-\mathbf{r}_m) V(\mathbf{r}-\mathbf{r}') \rho(\mathbf{r}) + V(\mathbf{r}-\mathbf{r}') \rho(\mathbf{r}) \rho(\mathbf{r}') \Bigg]$$

or

$$0 \le \sum_{n,m=1}^{Z} V(\mathbf{r}_n - \mathbf{r}_m) - 2 \sum_{n=1}^{Z} \int d^3\mathbf{r} V(\mathbf{r}-\mathbf{r}_n) \rho(\mathbf{r}) + \int d^3\mathbf{r}\, d^3\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') V(\mathbf{r}-\mathbf{r}') \qquad (4.2)$$

since

$$V(\mathbf{r}_n - \mathbf{r}_m) = V(\mathbf{r}_m - \mathbf{r}_n) \qquad (4.3)$$

thus

$$\sum_{n,m=1}^{Z} V(\mathbf{r}_n - \mathbf{r}_m) = 2 \sum_{n>m}^{Z} V(\mathbf{r}_n - \mathbf{r}_m) + ZV(0) \qquad (4.4)$$

Accordingly (4.2) leads to

$$2 \sum_{n>m}^{Z} V(\mathbf{r}_n - \mathbf{r}_m) \ge 2 \sum_{n=1}^{Z} \int d^3\mathbf{r} V(\mathbf{r}-\mathbf{r}_n) \rho(\mathbf{r}) - ZV(0) - \int d^3\mathbf{r}\, d^3\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') V(\mathbf{r}-\mathbf{r}')$$

$$\sum_{n>m}^{Z} V(\mathbf{r}_n - \mathbf{r}_m) \ge \sum_{n=1}^{Z} \int d^3\mathbf{r} V(\mathbf{r}-\mathbf{r}_n) \rho(\mathbf{r}) - \frac{Z}{2} V(0) - \frac{1}{2} \int d^3\mathbf{r}\, d^3\mathbf{r} \rho(\mathbf{r}) \rho(\mathbf{r}') V(\mathbf{r}-\mathbf{r}')$$

$$\sum_{n>m}^{Z} V(\mathbf{r}_n - \mathbf{r}_m) \ge \sum_{n=1}^{Z} \Phi(\mathbf{r}_n) - \frac{Z}{2} V(0) - \frac{1}{2} \int d^3\mathbf{r}\, d^3\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') V(\mathbf{r}-\mathbf{r}') \qquad (4.5)$$

where we have used the definitions

$$V(\mathbf{r}-\mathbf{r}') = \int \frac{d^3\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')} \tilde{V}(\mathbf{k}) \tag{4.6}$$

$$\rho(\mathbf{r}) = \int \frac{d^3\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k}\cdot\mathbf{r}} \tilde{\rho}(\mathbf{k}) \tag{4.7}$$

$$\Phi(\mathbf{r}) = \int d^3\mathbf{r}\, \rho(\mathbf{r}') V(\mathbf{r}-\mathbf{r}') \tag{4.8}$$

Equation (4.5) finally leads to the inequality

$$\sum_{n>m}^{Z} V(\mathbf{r}_n - \mathbf{r}_m) \geq \sum_{n=1}^{Z} \Phi(\mathbf{r}_n) - \frac{Z}{2} \int \frac{d^3\mathbf{k}}{(2\pi)^3} \tilde{V}(\mathbf{k}) - \frac{1}{2} \int \frac{d^3\mathbf{k}}{(2\pi)^3} \tilde{\rho}^*(\mathbf{k}) \tilde{\rho}(\mathbf{k}) \tilde{V}(\mathbf{k})$$

$$= \sum_{n=1}^{Z} \Phi(\mathbf{r}_n) - \frac{1}{2} \int \frac{d^3\mathbf{k}}{(2\pi)^3} \left\{ |\tilde{\rho}(\mathbf{k})|^2 \tilde{V}(\mathbf{k}) + Z\tilde{V}(\mathbf{k}) \right.$$

$$= \sum_{n=1}^{Z} \Phi(\mathbf{r}_n) - \frac{1}{2} \int \frac{d^3\mathbf{k}}{(2\pi)^3} \left\{ \frac{\left|\tilde{\Phi}(\mathbf{k})\right|^2}{\tilde{V}(\mathbf{k})} + Z\tilde{V}(\mathbf{k}) \right\} \tag{4.9}$$

Where $\Phi(\mathbf{r})$ is arbitrary and real provided that the integrals on the right-hand side of the above inequality exist.

4.2 A Lower Bound to the Electron-Electron Interaction Potential

We have seen that for V of positive type, $\sum_{n>m}^{Z} V(\mathbf{r}_n - \mathbf{r}_m)$ can be bounded from below with arbitrary one-particle potentials. Since the Coulomb potential becomes infinite at 0, it is first necessary to find a smaller function finite at 0 and with a positive Fourier transformation, which is an idea due to Thirring(1981). We introduce the potential:

$$V(\mathbf{r}) = \frac{1-\exp(-\mu r)}{r} \leq \frac{1}{r} \tag{4.10}$$

For the subsequent analysis we use the following properties

$$\delta^3(\mathbf{r}) = \int \frac{d^3\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k}\cdot\mathbf{r}} \tag{4.11}$$

$$\nabla^2 \frac{1}{r} = -4\pi\delta^3(\mathbf{r}) \tag{4.12}$$

$$\nabla^2\left(\frac{1-e^{-\mu r}}{r}\right) = \nabla^2 \frac{1}{r} - \nabla^2 \frac{e^{-\mu r}}{r} \tag{4.13}$$

Consider

$$\nabla^2 \frac{1}{r} = -4\pi \int \frac{d^3\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k}\mathbf{r}}$$

$$\frac{1}{r} = \frac{-4\pi}{\nabla^2} \int \frac{d^3\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k}\cdot\mathbf{r}}$$

or

$$\frac{1}{r} = -4\pi \int \frac{d^3\mathbf{k}}{(2\pi)^3} \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{(-k^2)} \tag{4.14}$$

Thus the Fourier transform of $\frac{1}{r}$ is equal to $\frac{4\pi}{k^2}$. Next we consider the following expression

$$\nabla^2 \frac{e^{-\mu r}}{r} = \nabla \bullet \left[\frac{\nabla e^{-\mu r}}{r} + e^{-\mu r} \nabla \frac{1}{r} \right]$$

$$= \frac{\left(\nabla^2 e^{-\mu r}\right)}{r} + \left(\nabla \bullet e^{-\mu r}\right)\left(\nabla \frac{1}{r}\right) + \left(\nabla^2 \frac{1}{r}\right) e^{-\mu r} + \left(\nabla \bullet \frac{1}{r}\right)\left(\nabla e^{-\mu r}\right) \tag{4.15}$$

Upon using

$$\nabla^2 \Rightarrow \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}$$

because of the spherical symmetry of the problem at hand, we obtain

$$\nabla^2 \frac{e^{-\mu r}}{r} = \mu^2 \frac{e^{-\mu r}}{r} - \frac{2\mu}{r^2} e^{-\mu r} - 4\pi\delta^3(\mathbf{r}) e^{-\mu r} + 2\mu \frac{e^{-\mu r}}{r^2}$$

Since $\delta^3(\mathbf{r}) e^{-\mu r} = \delta^3(\mathbf{r})$, this gives

$$\nabla^2 \frac{e^{-\mu r}}{r} = \mu^2 \frac{e^{-\mu r}}{r} - 4\pi\delta^3(\mathbf{r})$$

or

$$\left(\nabla^2 - \mu^2\right)\frac{e^{-\mu r}}{r} = -4\pi\delta^3(\mathbf{r})$$

thus

$$\frac{e^{-\mu r}}{r} = -\frac{4\pi}{\left(\nabla^2 - \mu^2\right)}\int\frac{d^3k}{(2\pi)^3}e^{i\mathbf{k}\cdot\mathbf{r}}$$

$$= -4\pi\int\frac{d^3k}{(2\pi)^3}\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\left(-k^2 - \mu^2\right)} \tag{4.16}$$

So the Fourier transform of $\frac{e^{-\mu r}}{r}$ is $\frac{4\pi}{k^2 + \mu^2}$. Therefore the Fourier transform of

$$\frac{\left(1 - e^{-\mu r}\right)}{r} \text{ is } \frac{4\pi}{k^2} - \frac{4\pi}{\left(k^2 + \mu^2\right)}$$

That is

$$\tilde{V}(\mathbf{k}) = \frac{4\pi\mu^2}{k^2\left(k^2 + \mu^2\right)} \tag{4.17}$$

Next, we set

$$\Phi(\mathbf{r}) = \int d^3\mathbf{r}\frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{4.18}$$

From (4.9), upon transforming back to **r**–space we obtain:

$$\sum_{n>m}^{Z} V(\mathbf{r}_n - \mathbf{r}_m) \geq \sum_{n=1}^{Z}\Phi(\mathbf{r}_n) - \frac{1}{2}\left\{\int d^3\mathbf{r}\,\Phi(\mathbf{r})\rho(\mathbf{r}) + 4\pi\mu^{-2}\int d^3\mathbf{r}\,\rho^2(\mathbf{r}) + Z\mu\right. \tag{4.19}$$

Optimizing this equation with respect to μ we obtain

$$0 = \frac{-8\pi}{\mu^3} \int d^3\mathbf{r}\, \rho^2(\mathbf{r}) + Z \tag{4.20}$$

or

$$\mu = \left[\frac{8\pi}{Z} \int d^3\mathbf{r}\, \rho^2(\mathbf{r}) \right]^{1/3} \tag{4.21}$$

Upon substituting μ in (4.9) and using the bound (4.10):

$$\sum_{n>m}^{Z} V(\mathbf{r}_n - \mathbf{r}_m) \leq \sum_{\alpha<\beta}^{Z} \frac{1}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|} \tag{4.22}$$

we get

$$\sum_{\alpha<\beta}^{Z} \frac{1}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|} \geq \sum_{\alpha=1}^{Z} \int d^3\mathbf{r}\, \frac{\rho(\mathbf{r})}{|\mathbf{r}_\alpha - \mathbf{r}|} - \frac{1}{2} \int \frac{d^3\mathbf{r} d^3\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \rho(\mathbf{r}) \rho(\mathbf{r}')$$

$$- 2\pi \frac{\int d^3\mathbf{r} \rho^2(\mathbf{r})}{\left[\frac{8\pi}{Z} \int d^3\mathbf{r} \rho^2(\mathbf{r}) \right]^{2/3}} - \frac{1}{2} Z \left[\frac{8\pi}{Z} \int d^3\mathbf{r} \rho^2(\mathbf{r}) \right]^{1/3}$$

$$= \sum_{\alpha=1}^{Z} \int d^3\mathbf{r}\, \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{r}_\alpha|} - \frac{1}{2} \int \frac{d^3\mathbf{r} d^3\mathbf{r}}{|\mathbf{r} - \mathbf{r}'|} \rho(\mathbf{r}) \rho(\mathbf{r}')$$

$$-\frac{2\pi\int d^3\mathbf{r}\rho^2(\mathbf{r})+\frac{1}{2}Z\left[\frac{8\pi}{Z}\int d^3\mathbf{r}\rho^2(\mathbf{r})\right]}{\left[\frac{8\pi}{Z}\int d^3\mathbf{r}\rho^2(\mathbf{r})\right]^{2/3}}$$

$$=\sum_{\alpha=1}^{Z}\int d^3\mathbf{r}\frac{\rho(\mathbf{r})}{|\mathbf{r}_\alpha-\mathbf{r}|}-\frac{1}{2}\int\frac{d^3\mathbf{r}d^3\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\rho(\mathbf{r})\rho(\mathbf{r}')-\frac{6\pi\int d^3\mathbf{r}\rho^2(\mathbf{r})}{\left(\frac{8\pi}{Z}\right)^{2/3}\left(\int d^3\mathbf{r}\rho^2(\mathbf{r})\right)^{2/3}}$$

or

$$\sum_{\alpha<\beta}^{Z}\frac{1}{|\mathbf{r}_\alpha-\mathbf{r}_\beta|}\geq\sum_{\alpha=1}^{Z}\int d^3\mathbf{r}\frac{\rho(\mathbf{r})}{|\mathbf{r}_\alpha-\mathbf{r}|}-\frac{1}{2}\int\frac{d^3\mathbf{r}d^3\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\rho(\mathbf{r})\rho(\mathbf{r}')-\frac{3}{2}\pi^{1/3}Z^{2/3}\left(\int d^3\mathbf{r}\rho^2(\mathbf{r})\right)^{1/3} \tag{4.23}$$

Here $\rho(\mathbf{r})$ is an arbitrary real function provided that the integrals on the right-hand side of the above inequality exist.

Chapter V

Upper Bound for the Exact Ground-State Energy of Atoms for Large Z $(Z \to \infty)$

In this chapter we will develop an upper bound for the exact ground-state energy of atoms for large Z.

We consider first the seemingly unrelated problem of a one–body potential with Hamiltonian

$$h = \frac{\mathbf{p}^2}{2m} + V(r) \tag{5.1}$$

where $V(r)$ is the Thomas–Fermi potential

$$V(r) = -\frac{Ze^2}{r} + e^2 \int d^3\mathbf{r}' \frac{n(r')}{|\mathbf{r} - \mathbf{r}'|}$$

$$= Z^{4/3} v(R)$$

$$= -\frac{\hbar^2}{2m}\left(3\pi^2\right)^{2/3} Z^{4/3} \left(\rho_{TF}(R)\right)^{2/3}, \ \mathbf{r} = \mathbf{R}/Z^{1/3} \tag{5.2}$$

and $n(r) = Z^2 \rho_{TF}(R)$ is the Thomas–Fermi density normalized as

$$\int d^3\mathbf{r}\; n(r) = Z$$

The Green function corresponding to (5.1) satisfies the equation

$$\left[-i\hbar\frac{\partial}{\partial t} - \frac{\hbar^2}{2m}\nabla^2 + V(r)\right] G_{\pm}(\mathbf{r}t, \mathbf{r}'0) = \delta^3(\mathbf{r}-\mathbf{r}')\delta(t) \tag{5.3}$$

where with appropriate boundary conditions:

$$G_{\pm}(\mathbf{r}t, \mathbf{r}'0) = \mp\left(\frac{i}{\hbar}\right)\Theta(\mp t) G_0(\mathbf{r}\tau, \mathbf{r}'0; V), \qquad \tau = t/\hbar \tag{5.4}$$

where $\Theta(t)$ is the step function. We write quite generally

$$G_0(\mathbf{r}\tau, \mathbf{r}'0; V) = \int \frac{d^3\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')} e^{-i\left[\frac{\hbar^2 k^2}{2m}\tau + U(\mathbf{r},\tau,\mathbf{k})\right]} \tag{5.5}$$

We want to solve this equation for U in the limit $Z \to \infty$. To this end (5.3) leads to

$$\int \frac{d^3\mathbf{k}}{(2\pi)^3}\left\{-\frac{\hbar^2}{2m}\left[\nabla\bullet\left(\left(\nabla e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')}\right)e^{-iU} + \left(\nabla e^{-iU}\right)e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')}\right)\right] + Ve^{-i\mathbf{k}(\mathbf{r}-\mathbf{r}')-iU}\right\} e^{-i\frac{\hbar^2\mathbf{k}\tau}{2m}}$$

$$= i\hbar\int \frac{d^3\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')} e^{-i\left[\frac{\hbar^2 k^2\tau}{2m}+U\right]}\left(-i\frac{\hbar k^2}{2m} - i\frac{\partial U}{\partial t}\right)$$

$$\int \frac{d^3\mathbf{k}}{(2\pi)^3}\left\{-\frac{\hbar^2}{2m}\left[\left(\nabla^2 e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')}\right)\left(e^{-iU}\right)+\left(\nabla e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')}\right)\bullet\left(\nabla e^{-iU}\right)+\left(\nabla^2 e^{-iU}\right)\left(e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')}\right)\right.\right.$$

$$\left.\left.+\left(\nabla e^{-iU}\right)\bullet\left(\nabla e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')}\right)\right]+Ve^{-i\mathbf{k}(\mathbf{r}-\mathbf{r}')-iU}\right\}$$

$$=\int\frac{d^3\boldsymbol{k}}{(2\pi)^3}e^{i\boldsymbol{k}(\boldsymbol{r}-\boldsymbol{r}')}e^{-i\left[\frac{\hbar^2 k\tau}{2m}+U\right]}\left(\frac{\hbar^2k^2}{2m}+\frac{\partial U}{\partial\tau}\right) \tag{5.6}$$

We readily see that U satisfies the equation

$$-\frac{\partial U}{\partial\tau}+V-\frac{\hbar^2}{m}\mathbf{k}\bullet\nabla U+\frac{\hbar^2}{2m}(\nabla U)^2+\frac{i\hbar^2}{2m}\nabla^2U=0 \tag{5.7}$$

with the boundary condition $U\big|_{\tau=0}=0$. We are particularly interested in the integral

$$\int d^3\mathbf{r}\,G_0(\mathbf{r}\tau,\mathbf{r}0;V) \tag{5.8}$$

where the $\exp[i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')]$ in (5.5) becomes simply replaced by one. Since $\mathbf{r}$ and $\mathbf{k}$ in (5.8) are merely integration variables, we have the liberty of making convenient changes of these variables

To solve this equation we carry out the following changes of variables and substitutions:

$$\mathbf{r}=\frac{\mathbf{R}}{Z^{1/3}},\qquad \mathbf{k}=Z^{2/3}\mathbf{K} \tag{5.9}$$

$$V(r)=Z^{4/3}v(R),\qquad \tau=\frac{T}{Z^{4/3}} \tag{5.10}$$

$$\nabla_r = Z^{1/3}\nabla_R \qquad\qquad \nabla_r^2 = Z^{2/3}\nabla_R^2 \tag{5.11}$$

Equation (5.7) then simply becomes

$$-Z^{4/3}\frac{\partial U}{\partial T} + Z^{4/3}v(R) - Z\mathbf{K}\bullet\frac{\hbar^2}{m}\nabla_R U + Z^{2/3}\frac{\hbar^2}{2m}(\nabla_R U)^2 + \frac{i\hbar}{2m}Z^{2/3}\nabla_R^2 U = 0 \tag{5.12}$$

or

$$-\frac{\partial U}{\partial T} + v(R) - \frac{\hbar^2}{m}\frac{\mathbf{K}}{Z^{1/3}}\bullet\nabla_R U + \frac{\hbar^2}{2m}\frac{1}{Z^{2/3}}(\nabla_R U)^2 + \frac{i\hbar}{2m}\frac{\nabla_R^2 U}{Z^{2/3}} = 0 \tag{5.13}$$

When we take limit $Z \to \infty$ the latter equation collapses to the simple equation:

$$-\frac{\partial U}{\partial T} + v(R) = 0 \tag{5.14}$$

Or

$$U = v(R)T \tag{5.15}$$

where $v(R)$ is independent of Z.

To find a bound on the sum of the negative eigenvalues of (5.1) for $Z \to \infty$, we start with

$$G_0(\mathbf{r}\tau, \mathbf{r}0; V) = \int\frac{d^3\mathbf{k}}{(2\pi)^3}e^{-i\left[\frac{\hbar^2k^2}{2m} + v(R)Z^{4/3}\right]\tau} \tag{5.16}$$

for $Z \to \infty$, and consider the following elementary limit:

$$\lim_{Z\to\infty} \int d^3\mathbf{r} \frac{2}{2\pi i} \int_{-\infty}^{\infty} \frac{d\tau}{\tau - i\varepsilon} G_0(\mathbf{r}\tau, \mathbf{r}0; V) \tag{5.17}$$

To integrate the latter we use the residue theorem. Let $\alpha = \left[\left(\hbar^2 k^2/2m\right) + v(R)Z^{4/3}\right]$.

For $\alpha > 0$, we close the contour of integration in the complex τ-plane from below to obtain (Figure 5.1)

$$\int_{-\infty}^{\infty} \frac{d\tau}{\tau - i\varepsilon} e^{-i|\alpha|\tau} = 0$$

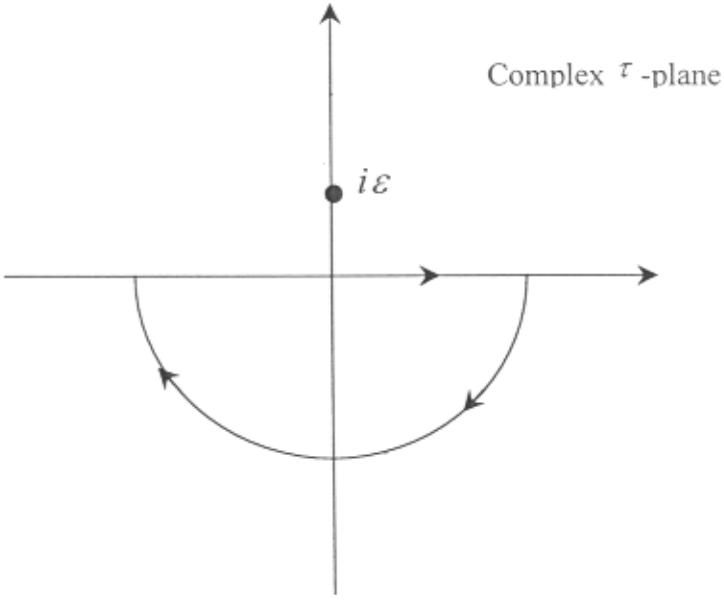

Figure 5.1. The contour of integration in the complex τ-plane is closed from below.

For $\alpha < 0$, we close the contour of integration in the complex τ-plane from above

$$\int_{-\infty}^{\infty} \frac{d\tau}{\tau - i\varepsilon} e^{i|\alpha|\tau} = 2\pi i$$

or

$$\int_{-\infty}^{\infty} \frac{d\tau}{\tau - i\varepsilon} e^{-i\left[\frac{\hbar^2 k^2}{2m} + v(R)Z^{4/3}\right]\tau} = 2\pi i \qquad (5.18)$$

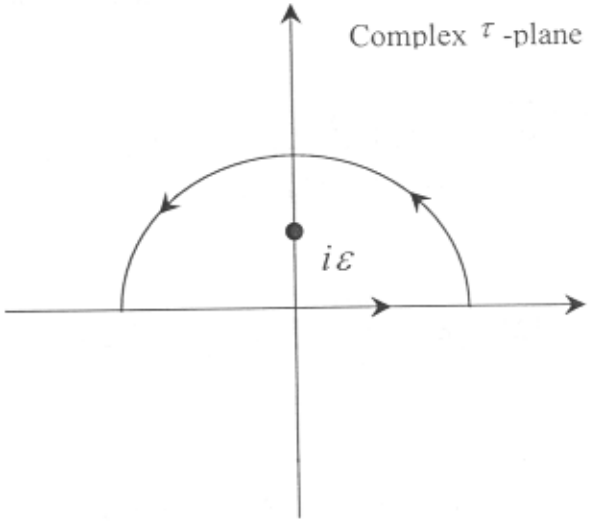

Figure 5.2. The contour of integration in the complex τ-plane is closed from above.

That is (5.17) is non-zero for $\alpha < 0$:

$$\frac{\hbar^2 k^2}{2m\hbar} + v(R)\frac{Z^{4/3}}{\hbar} < 0$$

$$k^2 < -\frac{2mv(R)}{\hbar^2} Z^{4/3}$$

$$k < \sqrt{-\frac{2mv(R)}{\hbar^2}}Z^{2/3}$$

which from (5.10) yields the following bound on $|\boldsymbol{K}|$, with $\mathbf{K}$ denoted in (5.9)

$$|\boldsymbol{K}| < \sqrt{-\frac{2mv(R)}{\hbar^2}} \tag{5.19}$$

Thus equation (5.17) reduces for $Z \to \infty$ to

$$\int d^3\boldsymbol{r}\,\frac{2}{2\pi i}\int_{-\infty}^{\infty}\frac{d\tau}{\tau - i\varepsilon}G_0(\boldsymbol{r}\tau,\boldsymbol{r}0;V) \to \int d^3r\,\frac{2}{2\pi i}\int\frac{d^3\boldsymbol{k}}{(2\pi)^3}\int_{-\infty}^{\infty}\frac{d\tau}{\tau - i\varepsilon}e^{-i\left[\frac{\hbar^2k^2}{2m}+v(R)\right]\tau}$$

$$\to 2\frac{(4\pi)}{(2\pi)^3}\int d^3\boldsymbol{r}Z^2\int_0^{\sqrt{-2mv(R)/\hbar^2}}|\boldsymbol{K}|^2\,d|\boldsymbol{K}|$$

$$= \frac{2}{3}\frac{(4\pi)}{(2\pi)^3}\int\frac{d^3\boldsymbol{R}}{Z}Z^2\left(-\frac{2mv(R)}{\hbar^2}\right)^{3/2}$$

$$= \frac{Z}{3\pi^2}\int d^3\boldsymbol{R}\left(-\frac{2mv(R)}{\hbar^2}\right)^{3/2}$$

$$= Z\int d^3\mathbf{R}\;\rho_{\mathrm{TF}}(R) = Z \tag{5.20}$$

where the factor 2 multiplying τ-integrals is to account for spin. The τ–integral projects out the negative spectrum of h, for $Z \to \infty$.

Equation (5.20), in particular, is of fundamental importance. It states that for large Z, the Hamiltonian h, allowing for spin, has Z (orthonormal) eigenvectors corresponding to its negative spectrum. Let $g_1(\mathbf{r},\sigma),...,g_Z(\mathbf{r},\sigma)$ denote these eigenvectors for large Z. Define the determinantal (anti–symmetric) function

$$\Phi_Z(\mathbf{r}_1\sigma_1,...,\mathbf{r}_Z\sigma_Z) = (Z!)^{-1/2}\det\left[g_\alpha(\mathbf{r}_\beta,\sigma_\beta)\right] \tag{5.21}$$

Since such an anti–symmetric function does not necessarily coincide with the exact ground–state function of the Hamiltonian H for neutral atom, the expectation value $\langle\Phi_Z|H|\Phi_Z\rangle$, with respect to Φ_Z in (5.21) can only over estimate the exact ground–state energy E_Z of H or at best be equal to it.

We rewrite the exact Hamiltonian equivalently as

$$H = \sum_{\alpha=1}^{Z} h_\alpha + \sum_{\alpha<\beta}^{Z}\frac{e^2}{|\boldsymbol{r}_\alpha - \boldsymbol{r}_\beta|} - e^2\sum_{\alpha=1}^{Z}\int\frac{d^3\boldsymbol{r}'}{|\boldsymbol{r}_\alpha - \boldsymbol{r}'|}n(r') \tag{5.22}$$

where h_α is defined in (5.1) with variables $\mathbf{r}_\alpha,\mathbf{p}_\alpha$ referring to the α^{th} electron, and where we recall that the exact Hamiltonian is

$$H = \sum_{\alpha=1}^{Z}\left(\frac{\mathbf{p}_\alpha^2}{2m} - \frac{Ze^2}{r_\alpha}\right) + \sum_{\alpha<\beta}^{Z}\frac{e^2}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|} \tag{5.23}$$

That is,

$$\langle\psi_{exact}|H|\psi_{exact}\rangle = E_Z \le \langle\phi(\mathbf{r}_1\sigma_1,...,\mathbf{r}_Z\sigma_Z)|H|\phi(\mathbf{r}_1\sigma_1,...,\mathbf{r}_Z\sigma_Z)\rangle \tag{5.24}$$

where $\Phi(\mathbf{r}_1\sigma_1,...,\mathbf{r}_Z\sigma_Z)$ is defined in (5.21), and ψ_{exact} denotes the exact ground-state wave function whose knowledge is not necessary.

Accordingly,

$$\lim_{Z\to\infty} Z^{-7/3}E_Z \le \lim_{Z\to\infty} Z^{-7/3}\langle\Phi_Z|H|\Phi_Z\rangle$$

$$= \lim_{Z\to\infty} Z^{-7/3}\sum_{\alpha=1}^{Z}\langle g_\alpha|h_\alpha|g_\alpha\rangle + \lim_{Z\to\infty} Z^{-7/3}F_Z \tag{5.25}$$

where

$$F_Z = -e^2\sum_\sigma \int\frac{d^3\mathbf{r}d^3\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}n_Z(\mathbf{r}\sigma,\mathbf{r}\sigma)n(r')$$

$$+\frac{e^2}{2}\sum_{\sigma,\sigma'}\int\frac{d^3\mathbf{r}\,d^3\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\Big[n_Z(\mathbf{r}\sigma,\mathbf{r}\sigma)n_Z(\mathbf{r}'\sigma',\mathbf{r}'\sigma') - |n_Z(\mathbf{r}\sigma,\mathbf{r}'\sigma')|^2 \tag{5.26}$$

$$n_Z(\mathbf{r}\sigma,\mathbf{r}'\sigma') = \sum_{\alpha=1}^{Z} g_\alpha(\mathbf{r},\sigma)g_\alpha^*(\mathbf{r}',\sigma') \tag{5.27}$$

or

$$F_Z \le -e^2\int\frac{d^3\mathbf{r}\,d^3\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\left[n(r')\left(\sum_\sigma n_Z(\mathbf{r}\sigma,\mathbf{r}\sigma)\right) - \frac{1}{2}\left(\sum_\sigma n_Z(\mathbf{r}\sigma,\mathbf{r}\sigma)\right)\left(\sum_{\sigma'} n_Z(\mathbf{r}'\sigma',\mathbf{r}'\sigma')\right)\right]$$

(5.28)

where in writing the equality in (5.26) we have used the machinery developed in Chapter III on expectation values with respect to determinantal functions.

But

$$\lim_{Z\to\infty} Z^{-2}\sum_{\sigma} n_Z(\boldsymbol{r}\sigma,\boldsymbol{r}\sigma) = \lim_{Z\to\infty} Z^{-2}\,\frac{2}{2\pi i}\int_{-\infty}^{\infty}\frac{d\tau}{\tau - i\varepsilon} G_0(\boldsymbol{r}\tau,\boldsymbol{r}0;V) \equiv \rho_{TF}(R) \tag{5.29}$$

$$\lim_{Z\to\infty} Z^{-7/3}\sum_{\alpha=1}^{Z}\langle g_\alpha | h_\alpha | g_\alpha\rangle = \lim_{Z\to\infty}\left(Z^{-7/3} 2\sum_{\lambda<0}\lambda\right)$$

$$= \lim_{Z\to\infty} Z^{-7/3}\int d^3\mathbf{r}\,\frac{2}{2\pi i}\int_{-\infty}^{\infty}\frac{d\tau}{\tau - i\varepsilon} i\frac{\partial G_0(\mathbf{r}\tau,\mathbf{r}0;V)}{\partial\tau} \tag{5.30}$$

Where $\sum_{\lambda<0}\lambda$ in $2\sum_{\lambda<0}\lambda$ is a sum over all the negative eigenvalues of h in (5.1) allowing for multiplicity but not spin degeneracy.

We can evaluate equation (5.30) explicitly upon using (5.16)

$$\lim_{Z\to\infty} Z^{-7/3}\int d^3\mathbf{r}\,\frac{2}{2\pi i}\int_{-\infty}^{\infty}\frac{d\tau}{\tau - i\varepsilon} i\frac{\partial G_0(\mathbf{r}\tau,\mathbf{r}0;V)}{\partial\tau} = \lim_{Z\to\infty} Z^{-7/3}\int d^3\mathbf{r}\, 2\int\frac{d^3\mathbf{k}}{(2\pi)^3}\left(\frac{\hbar^2k^2}{2m} + v(R)Z^{4/3}\right)$$

$$\times\Theta\left(\frac{-\hbar^2k^2}{2m\hbar} - v(R)Z^{4/3}\right)$$

$$= \lim_{Z\to\infty} Z^{-7/3}\int\frac{d^3\mathbf{R}}{Z} 2\frac{(4\pi)}{(2\pi)^3}\int Z^2\mathbf{K}^2 d\mathbf{K}$$

$$\times\left(\frac{\hbar^2}{2m} Z^{4/3}\mathbf{K}^2 + v(R)Z^{4/3}\right)\Theta\left(-|\mathbf{K}| + \sqrt{\frac{-2mv(R)}{\hbar^2}}\right)$$

$$= \frac{1}{\pi^2}\int d^3\mathbf{R}\left\{\frac{\hbar^2}{2m}\int_0^{\sqrt{-2mv(R)/\hbar^2}}\mathbf{K}^4 d\mathbf{K} + v(R)\int_0^{\sqrt{-2mv(R)/\hbar^2}}\mathbf{K}^2 d\mathbf{K}\right\}$$

$$= \frac{1}{\pi^2} \int d^3\mathbf{R} \left\{ \frac{\hbar^2}{10\mathrm{m}} \left(-\frac{2mv(R)}{\hbar^2} \right)^{5/2} + \frac{v(R)}{3} \left(-\frac{2mv(R)}{\hbar^2} \right)^{3/2} \right\}$$

(5.31)

From

$$\rho_{TF}(R) = \frac{1}{3\pi^2} \left(-\frac{2mv(R)}{\hbar^2} \right)^{3/2} \tag{5.32}$$

the expression on the right-hand side of equation (5.31) is equal to

$$= \frac{\left(3\pi^2\right)^{5/3} \hbar^2}{10m\pi^2} \int d^3\mathbf{R}\ \rho_{TF}^{5/3}(R) - e^2 \int \frac{d^3\mathbf{R}}{\mathbf{R}} \rho_{TF}(R)$$

$$+ e^2 \int \frac{d^3\mathbf{R}\, d^3\mathbf{R}'}{|\mathbf{R} - \mathbf{R}'|} \rho_{TF}(R) \rho_{TF}(R') \tag{5.33}$$

where

$$v(R) = Z^{-4/3} V(r) \qquad = Z^{-4/3} \left(\frac{Ze^2}{r} + e^2 \int \frac{d^3\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}') \right) \tag{5.34}$$

and

$$n(\mathbf{r}') = Z^2 \rho_{TF}(R')$$

$$\mathbf{r} = \frac{\mathbf{R}}{Z^{1/3}}$$

That is,

$$v(R) = -\frac{e^2}{R} + e^2 \int Z^2 \frac{\rho_{TF}(R')}{|\mathbf{R}-\mathbf{R}'|} d^3\mathbf{R} \frac{Z^{1/3}}{Z^{7/3}}$$

$$= -\frac{e^2}{R} + e^2 \int \frac{\rho_{TF}(R')}{|\mathbf{R}-\mathbf{R}'|} d^3\mathbf{R}' \tag{5.35}$$

From (5.25)–(5.30), (5.33), we obtain

$$\lim_{Z\to\infty} Z^{-7/3} E_Z \le \lim_{Z\to\infty} Z^{-7/3} 2\sum_{\lambda<0} \lambda - \lim_{Z\to\infty} Z^{-7/3} e^2 \sum_{\sigma} \int \frac{d^3\mathbf{r} d^3\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} n_Z(\mathbf{r}\sigma, \mathbf{r}\sigma) n(r')$$

$$+ \frac{e^2}{2} \lim_{Z\to\infty} Z^{-7/3} \sum_{\sigma,\sigma'} \int \frac{d^3\mathbf{r} d^3\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} \left[n_Z(\mathbf{r}\sigma, \mathbf{r}\sigma) n_Z(\mathbf{r}'\sigma', \mathbf{r}'\sigma') - |n_Z(\mathbf{r}\sigma, \mathbf{r}'\sigma')|^2 \right]$$

(5.36)

$$= \frac{(3\pi^2)^{5/3}}{10m\pi^2} \hbar^2 \int d^3\mathbf{R}\, \rho_{TF}^{5/3}(R) - e^2 \int \frac{d^3\mathbf{R}}{R} \rho_{TF}(R) + e^2 \int \frac{d^3\mathbf{R} d^3\mathbf{R}'}{|\mathbf{R}-\mathbf{R}'|} \rho_{TF}(R) \rho_{TF}(R')$$

$$- \frac{e^2}{2} \int \frac{d^3\mathbf{R}\, d^3\mathbf{R}'}{|\mathbf{R}-\mathbf{R}'|} \rho_{TF}(R) \rho_{TF}(R')$$

$$\lim_{Z\to\infty} Z^{-7/3} E_Z \le \frac{(3\pi^2)^{5/3}}{10m\pi^2} \hbar^2 \int d^3\mathbf{R}\, \rho_{TF}^{5/3}(R) - e^2 \int \frac{d^3\mathbf{R}}{R} \rho_{TF}(R)$$

$$+ \frac{e^2}{2} \int \frac{d^3\mathbf{R}\, d^3\mathbf{R}'}{|\mathbf{R}-\mathbf{R}'|} \rho_{TF}(R) \rho_{TF}(R') \tag{5.37}$$

The expression on the right-hand side of the above inequality is the coefficient of $Z^{7/3}$ of the exact ground-state energy of the Thomas-Fermi atom developed in

Chapter II (see equation (2.64)) and E_Z, here, denotes the exact ground-state energy of atoms.

Chapter VI

Lower Bound for the Exact Ground State Energy of Atoms of Large Z $(Z \to \infty)$

We will use the detailed derivation of the lower bound for the Coulomb potential given in Chapter IV to help us derive a lower bound of the exact ground-state energy of atoms for large Z

Given any arbitrary real and positive function $\rho(\mathbf{r})$, we have established in equation (4.23) of Chapter IV that

$$\sum_{\alpha<\beta}^{Z} \frac{1}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|} \geq \sum_{\alpha=1}^{Z} \int d^3\mathbf{r} \frac{\rho(\mathbf{r})}{|\mathbf{r}_\alpha - \mathbf{r}|} - \frac{1}{2}\int \frac{d^3\mathbf{r} d^3\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\rho(\mathbf{r})\rho(\mathbf{r}') - \frac{3}{2}\pi^{1/3} Z^{2/3}\left(\int d^3\mathbf{r}\rho^2(\mathbf{r})\right)^{1/3} \tag{6.1}$$

where $\rho(\boldsymbol{r})$ is real and arbitrary, i.e., may be chosen at will, to the extent that the integrals on the right – hand side of (6.1) exist. We will conveniently choose it in such a way that $\rho(\mathbf{r}) \to Z^2 \rho_{TF}(R)$ for $Z \to \infty$, where $\rho_{TF}(R)$ is the scaled Thomas-Fermi density given in (2.37).

We rewrite the total Hamiltonian of the multi-electron atom

$$H = \sum_{\alpha}^{Z}\left[\frac{\mathbf{p}_\alpha^2}{2m} - \frac{Ze^2}{r_\alpha}\right] + e^2\sum_{\alpha<\beta}^{Z}\frac{1}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|} \tag{6.2}$$

as

$$H = \sum_{\alpha} h'_\alpha + e^2\sum_{\alpha<\beta}\frac{1}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|} - e^2\int d^3\mathbf{r}\frac{\rho(\mathbf{r})}{|\mathbf{r}_\alpha - \mathbf{r}|} \tag{6.3}$$

where

$$h'_\alpha = \sum_{\alpha}\left[\frac{\mathbf{p}_\alpha^2}{2m} - \frac{Ze^2}{r_\alpha} + e^2\int d^3\mathbf{r}\frac{\rho(\mathbf{r})}{|\mathbf{r}_\alpha - \mathbf{r}|}\right] \tag{6.4}$$

or

$$h'_\alpha = \frac{\mathbf{p}_\alpha^2}{2m} + V'(r_\alpha) \tag{6.5}$$

with

$$V'(r_\alpha) = -\frac{Ze^2}{r_\alpha} + e^2\int d^3\boldsymbol{r}\frac{\rho(r)}{|\boldsymbol{r}_\alpha - \boldsymbol{r}|}$$

The index α refers to the labeling of α^{th} electron in the atom. $V'(r_\alpha)$ is a Thomas-Fermi-like potential and will coincide with it only when we take $Z \to \infty$ with $\rho(\mathbf{r})$ conveniently chosen. $V'(r)$ may be chosen to be locally square integrable and such

that $V'(r)\to 0$ for $r\to\infty$. Let ψ be a normalized anti–symmetric function in $(\mathbf{r}_1\sigma_1,\ldots,\mathbf{r}_z\sigma_z)$. Then (6.1) implies that

$$\langle\psi|H|\psi\rangle \geq \langle\psi|\sum_\alpha h'_\alpha|\psi\rangle - \frac{1}{2}e^2\int\frac{d^3\mathbf{r}d^3\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\rho(\mathbf{r})\rho(\mathbf{r}') - \frac{3}{2}\pi^{1/3}Z^{2/3}e^2\left(\int d^3\mathbf{r}\rho^2(\mathbf{r})\right)^{1/3} \qquad (6.6)$$

since

$$H \geq \sum_\alpha\left(\frac{p_\alpha^2}{2m} - \frac{Ze^2}{r_\alpha} + e^2\int\frac{d^3\boldsymbol{r}\rho(\boldsymbol{r})}{|\boldsymbol{r}_\alpha-\boldsymbol{r}|}\right) - \frac{1}{2}e^2\int\frac{d^3\boldsymbol{r}\,d^3\boldsymbol{r}'}{|\boldsymbol{r}-\boldsymbol{r}'|}\rho(\boldsymbol{r})\rho(\boldsymbol{r}')$$

$$-\frac{3}{2}\pi^{1/3}Z^{2/3}e^2\left(\int d^3\boldsymbol{r}\rho^2(\boldsymbol{r})\right)^{1/3} \qquad (6.7)$$

$$= \sum_\alpha h'_\alpha - \frac{1}{2}e^2\int\frac{d^3\mathbf{r}\,d^3\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\rho(\mathbf{r})\rho(\mathbf{r}') - \frac{3}{2}\pi^{1/3}Z^{2/3}e^2\left(\int d^3\mathbf{r}\rho^2(\mathbf{r})\right)^{1/3} \qquad (6.8)$$

Consider the lowest energy E for the Hamiltonian $\sum_\alpha h'_\alpha$. Pauli's exclusion principle comes to the rescue here. Concerning the Hamiltonian $\sum_\alpha h'_\alpha$, the Z "non–interacting" electrons, but each interacting with an external potential V' can be put, according to Pauli's exclusion principle, in the lowest energy levels of $\sum_\alpha h'_\alpha$ (allowing for spin degeneracy) if Z is ≤ the number of such available levels. If Z is larger, then the remaining free electrons should have arbitrarily small kinetic energies to define the lowest energy of $\sum_\alpha h'_\alpha$. In either cases, $E \geq 2\sum_{\lambda<0}\lambda$, where $\sum_{\lambda<0}\lambda$ is defined as before, below equation (5.30), now applied to h'.

Accordingly,

$$\lim_{Z\to\infty} Z^{-7/3}\langle\psi|H|\psi\rangle \geq \lim_{Z\to\infty} K_Z \tag{6.9}$$

where

$$K_Z = Z^{-7/3}\int d^3\mathbf{r}\,\frac{2}{2\pi i}\int_{-\infty}^{\infty}\frac{d\tau}{\tau - i\varepsilon}\,i\frac{\partial G_0(\mathbf{r}\tau,\mathbf{r}0;V')}{\partial\tau} - Z^{-7/3}\frac{e^2}{2}\int\frac{d^3\mathbf{r}\,d^3\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\rho\,(\mathbf{r})\rho(\mathbf{r}')$$

$$-\frac{3}{2}\pi^{1/3}Z^{-5/3}e^2\left(\int d^3\mathbf{r}\left(\rho\,(\mathbf{r})\right)^2\right)^{1/3} \tag{6.10}$$

and $G_0(\mathbf{r}\tau,\mathbf{r}0;V')$ is defined as before, now corresponding to the potential V' in (6.5), and where we have used the equality on the extreme right-hand side of (5.30)

Since the right–hand side of the inequality (6.9) is independent of ψ, this inequality is true with ψ corresponding to the ground–state function of H as well, i.e., with $\langle\psi|H|\psi\rangle$ corresponding to

$$\min_{\psi}\langle\psi|H|\psi\rangle = E_Z \tag{6.11}$$

That is

$$\lim_{Z\to\infty} Z^{-7/3}E_Z \geq \lim_{Z\to\infty} K_Z \tag{6.12}$$

as well. To the extent that $\rho(\boldsymbol{r})$ is arbitrary we choose it conveniently to be given by

$$\rho(\mathbf{r}) \equiv Z^2\rho_{TF}(R)\left(1-e^{-Z\alpha R}\right)^{1/2} \tag{6.13}$$

where $\alpha > 0$ is an arbitrary scale parameter, and

$$\lim_{Z\to\infty} \rho(\mathbf{r}) \to Z^2 \rho_{TF}(R) \tag{6.14}$$

We recall from Section 2.3 that

$$\rho_{TF}(R) \underset{R\to 0}{\sim} \frac{1}{R^{3/2}} \tag{6.15}$$

$$\rho_{TF}(R) \underset{R\to\infty}{\sim} \frac{1}{R^{6}} \tag{6.16}$$

The factor $(1-\exp- Z\alpha R)^{1/2}$ will ensure the integrability of the last integral on the right–hand side of (6.10). We estimate the latter for $Z \to \infty$ as

$$\frac{3}{2}\pi^{1/3}\frac{e^2}{Z^{2/3}}\left[\int d^3\mathbf{R}\rho_{TF}^2(R)\left(1-e^{-Z\alpha R}\right)\right]^{1/3}$$

$$\leq \frac{3}{2}\pi^{1/3}e^2\left[\int_{\alpha R\leq 1/Z} d^3\mathbf{R}\frac{\alpha}{Z}R\rho_{TF}^2(R) + \frac{\left(1-e^{-Z}\right)}{Z^2}\int_{1>\alpha R>1/Z} d^3\mathbf{R}\rho_{TF}^2(R) + \frac{1}{Z^2}\int_{\alpha R\geq 1} d^3\mathbf{R}\rho_{TF}^2(R)\right]^{1/3} \tag{6.17}$$

where we have used the rigorous bound

$$1-e^{-Z\alpha R} \leq 1-e^{-Z\max(\alpha R)}$$

giving the coefficients

$$\frac{1-e^{-Z}}{Z^2}, \frac{1}{Z^2}$$

to the second and third integrals, respectively, in the square brackets in equation (6.17).

From (6.15) the second integral on the right–hand side is at worst logarithmic in Z. Hence the last term on the right–hand side of (6.8) vanishes for $Z \to \infty$. Since $-\left(1-e^{-Z\alpha R}\right) \geq -1$, the second term (with the minus sign) on the right-hand side of (6.10) is bounded below by

$$-\frac{e^2}{2}\int d^3\mathbf{R}\, d^3\mathbf{R}'\,\frac{\rho_{TF}(R)\rho_{TF}(R')}{|\mathbf{R}-\mathbf{R}'|} \tag{6.18}$$

Now we can find a lower bound to the exact ground state energy E_Z for $Z \to \infty$.

From

$$2\sum_{\lambda<0}\lambda = \int d^3\mathbf{r}\,\frac{2}{2\pi i}\int_{-\infty}^{\infty}\frac{d\tau}{\tau - i\varepsilon}\,i\,\frac{\partial G_0(\mathbf{r}\tau,\mathbf{r}0;V')}{\partial\tau}$$

and from (6.10)-(6.18) we have

$$\lim_{Z\to\infty} Z^{-7/3}E_Z \geq \lim_{Z\to\infty} Z^{-7/3}\,2\sum_{\lambda<0}\lambda - \frac{1}{2}\lim_{Z\to\infty} Z^{-7/3}e^2\int\frac{d^3\mathbf{r}\,d^3\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\rho(\mathbf{r})\rho(\mathbf{r}')$$

$$\geq \frac{\left(3\pi^2\right)^{5/3}\hbar^2}{10m\pi^2}\int d^3\mathbf{R}\,\rho_{TF}^{5/3}(R) - e^2\int\frac{d^3\mathbf{R}}{R}\rho_{TF}(R) + e^2\int\frac{d^3\mathbf{R}\,d^3\mathbf{R}'}{|\mathbf{R}-\mathbf{R}'|}\rho_{TF}(R)\rho_{TF}(R')$$

$$-\frac{1}{2}e^2\int\frac{d^3\mathbf{R}\,d^3\mathbf{R}'}{|\mathbf{R}-\mathbf{R}'|}\rho_{TF}(R)\rho_{TF}(R') \tag{6.19}$$

where we have used (6.18) and (5.33).

That is

$$\lim_{Z\to\infty} Z^{-7/3} E_Z \geq \frac{\left(3\pi^2\right)^{5/3}\hbar^2}{10m\pi^2}\int d^3\mathbf{R}\,\rho_{TF}^{5/3}(R) - e^2\int\frac{d^3\mathbf{R}}{R}\rho_{TF}(R) + \frac{1}{2}e^2\int\frac{d^3\mathbf{R}\,d^3\mathbf{R}'}{|\mathbf{R}-\mathbf{R}'|}\rho_{TF}(R)\rho_{TF}(R') \tag{6.20}$$

Again the expression on the right-hand side of the above inequality is the coefficient of $Z^{7/3}$ of the exact ground-state energy of the Thomas-Fermi atom developed in Chapter II (see (2.64)), and E_Z, here, denotes the exact ground-state energy of atoms.

Chapter VII

Conclusion

The conclusion of our research investigation follows by tracing back our derivations of upper and lower bounds to the exact ground-state energy E_Z of neutral atoms for $Z \to \infty$. We first reconsider our derivation of the upper bound for E_Z. The exact Hamiltonian of neutral atoms

$$H = \sum_{\alpha=1}^{Z}\left(\frac{\mathbf{p}_\alpha^2}{2m} - \frac{Z}{r_\alpha}\right) + \sum_{\alpha<\beta}^{Z}\frac{e^2}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|} \tag{1.1}$$

was re-written as

$$H = \sum_{\alpha=1}^{Z} h_\alpha + \sum_{\alpha<\beta}^{Z}\frac{e^2}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|} - e^2\sum_{\alpha=1}^{Z}\int\frac{d^3\mathbf{r}}{|\mathbf{r}_\alpha - \mathbf{r}|}\,n(r) \tag{5.22}$$

where

$$h_\alpha = \frac{\mathbf{p}_\alpha^2}{2m} - \frac{Ze^2}{r_\alpha} + e^2\int\frac{d^3\mathbf{r}}{|\mathbf{r}_\alpha - \mathbf{r}|}n(r) \tag{7.1}$$

and α denotes the labeling of the electrons, and $n(r)$ is the Thomas-Fermi density normalized as

$$\int d^3\mathbf{r}\, n(r) = Z \tag{7.2}$$

For $Z \to \infty$, the " Hamiltonian" $\sum_{\alpha=1}^{Z} h_\alpha$ was shown to have Z eigenvectors corresponding to its negative spectrum. The expectation value of the exact

Hamiltonian H in (1.1) with respect to the determinantal function constructed out of these Z eigenvectors can only over estimate, or at best be equal to, the exact ground-state energy E_Z of H. By considering the expectation value of H, with respect to the determinanatal function just discussed, and by a systematic analysis, in the process, of scaling properties of integrals involving the one-body Green function corresponding to the " Hamiltonian" h_α defined in (7.1), we have derived the following upper bound in Chapter V:

$$\lim_{Z\to\infty} Z^{-7/3} E_Z \le \frac{\left(3\pi^2\right)^{5/3}}{10m\pi^2}\hbar^2 \int d^3\mathbf{R}\, \rho_{TF}^{5/3}(R) - e^2 \int \frac{d^3\mathbf{R}}{R}\rho_{TF}(R)$$

$$+\frac{e^2}{2}\int \frac{d^3\mathbf{R}\, d^3\mathbf{R}'}{|\mathbf{R}-\mathbf{R}'|}\rho_{TF}(R)\rho_{TF}(R') \tag{5.37}$$

where $\rho_{TF}(R)$ is the scaled Thomas-Fermi density in (2.37). The expression on the right-hand side of the above inequality is exactly the coefficient of $Z^{7/3}$ of the ground-state energy of the Thomas-Fermi atom (see (2.65)).

To derive a lower bound for E_Z, we have first derived in Chapter VI, the following lower bound for the exact Hamiltonian H in (1.1):

$$H \ge \sum_\alpha h'_\alpha - \frac{1}{2}e^2 \int \frac{d^3\mathbf{r}\, d^3\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\rho(\mathbf{r})\rho(\mathbf{r}') - \frac{3}{2}\pi^{1/3}Z^{2/3}e^2\left(\int d^3\mathbf{r}\rho^2(\mathbf{r})\right)^{1/3} \tag{6.8}$$

where

$$h'_\alpha = \sum_\alpha \left[\frac{\mathbf{p}_\alpha^2}{2m} - \frac{Ze^2}{r_\alpha} + e^2\int d^3\mathbf{r}\frac{\rho(\mathbf{r})}{|\mathbf{r}_\alpha-\mathbf{r}|}\right] \tag{6.4}$$

and $\rho(\boldsymbol{r})$ is real and is otherwise an arbitrary function of $\boldsymbol{r}$. We have conveniently chosen

$$\rho(\mathbf{r}) \equiv Z^2 \rho_{TF}(R)\left(1-e^{-Z\alpha R}\right)^{1/2} \tag{6.13}$$

where $\alpha > 0$ is an arbitrary scale factor, and $\rho_{TF}(R)$ is the scaled Thomas-Fermi density. The factor $\left(1-e^{-Z\alpha R}\right)^{1/2}$ provides an important convergence factor (see (6.17)) and most conveniently approaches 1 for $Z \to \infty$. By using the lower bound on H in (6.8), using the definition of the function $\rho(\mathbf{r})$ in (6.13) and deriving, in the process, important scaling properties of integrals involving the one-body Green function corresponding to the "Hamiltonian" h'_α in (6.4), we have obtained, in Chapter VI, the following lower bound:

$$\lim_{Z\to\infty} Z^{-7/3} E_Z \geq \lim_{Z\to\infty} Z^{-7/3} 2\sum_{\lambda<0} \lambda - \frac{1}{2}\lim_{Z\to\infty} Z^{-7/3} e^2 \int \frac{d^3\mathbf{r}\, d^3\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\rho(\mathbf{r})\rho(\mathbf{r}')$$

$$\geq \frac{\left(3\pi^2\right)^{5/3}\hbar^2}{10m\pi^2}\int d^3\mathbf{R}\,\rho_{TF}^{5/3}(R) - e^2\int\frac{d^3\mathbf{R}}{R}\rho_{TF}(R) + e^2\int\frac{d^3\mathbf{R}\, d^3\mathbf{R}'}{|\mathbf{R}-\mathbf{R}'|}\rho_{TF}(R)\rho_{TF}(R')$$

$$-\frac{1}{2}e^2\int\frac{d^3\mathbf{R}\, d^3\mathbf{R}'}{|\mathbf{R}-\mathbf{R}'|}\rho_{TF}(R)\rho_{TF}(R')$$

$$= \frac{\left(3\pi^2\right)^{5/3}\hbar^2}{10m\pi^2}\int d^3\mathbf{R}\,\rho_{TF}^{5/3}(R) - e^2\int\frac{d^3\mathbf{R}}{R}\rho_{TF}(R) + \frac{e^2}{2}\int\frac{d^3\mathbf{R}\, d^3\mathbf{R}'}{|\mathbf{R}-\mathbf{R}'|}\rho_{TF}(R)\rho_{TF}(R')$$

(6.20)

Upon comparison of (5.37) and (6.20) above we have established without tears the basic result stated in our thesis. That is, $\lim_{Z\to\infty} Z^{-7/3} E_Z = E_{TF}$, where E_Z is the exact ground-state energy of atoms.

The method of investigation carried out in this work is expected to have applications in one of the most intriguing problems in theoretical physics: in the problem of "Stability of Matter." That is, why matter is stable and does not collapse with us and around us!

References

Arfken, G. B. and Weber, H. J. (1995). **Mathematical methods for physicists**. (4^{th}ed.). San Diego: Academic Press.

Baumgartner, B. (1976). The Thomas-Fermi theory as result of a strong-coupling limit. **Comm. Math. Phys.** 47: 215.

Bethe, H. A. and Jackiw, R. (1993). **Intermediate quantum mechanics** (3^{rd} ed.). Massachusetts: Addison-Wesley.

Bransden, B. H. and Joachain C. J. (1995). **Physics of atoms and molecules.** London, England: Longman.

Dreizler, R. M. and Gross, E. K. U. (1990). **Density functional theory**. Berlin, New York: Springer-Verlag.

Dyson, F. J.(1967). Ground-state energy of a finite system of charged particles. **Journ. Math. Phys.** 8: 1538.

Dyson, F. J. and Lenard A. (1967). Stability of matter I. **Journ. Math. Phys.** 8: 423.

Dyson, F. J. and Lenard A. (1968). Stability of matter II. **Journ. Math. Phys.** 9: 698.

Englert, B. G. and Schwinger, J. (1984a). Statistical atom: Handling the strongly bound electrons. **Phys. Rev. A** 29: 2331.

Englert, B. G. and Schwinger, J. (1984b). Statistical atom: Some quantum impovements. **Phys. Rev. A** 29: 2339.

Fermi, E. (1927). Un metodo statistico per la determinazione de alcune priorieta dell'atome. **Rend. Accad. Naz. Linzei.** 6: 602.

Fermi, E. (1928). A statistical method for the determination of some atomic properties and the application of this method to the theory of the periodic system of elecments. **Z. Phys.** 48: 73. [A translation into English may be found in March (1957)].

Fetter, A. L and Walecka, J. D. (1971). **Quantum of many-particle systems.** New York: McGraw-Hill.

Gombas, P. (1949). **Die statistischen theorie des atoms und ihre anwenodungen.** Berlin: Springer-Verlag.

Hohenbergè, P. and Kohn, W. (1964). Inhomogeneous electron gas. **Phys. Rev.** 136: B864.

Kohn, W. and Sham, L. J. (1965). Self-consistent equations including exchange and correlation effects. **Phys. Rev.** 140: A1133.

Lieb, E. (1976). The stability of matter. **Rev. Mod. Phys.** 48: 553.

Lieb, E. (1981). Thomas-Fermi and related theories of atoms and molecules. **Rev. Mod. Phys.** 53: 603.

Lieb, E. (1991). **The stability of matter from atoms to stars.** Berlin, New York: Springer-Verlag.

Lieb, E. H. and Simon, B. (1973). Thomas-Fermi theory revisited. **Phys. Rev. Lett.** 31: 681.

Lieb, E. H. and Simon, B. (1977). Thomas-Fermi theory of atoms, molecules and solids. **Adv. Math.** 23: 22.

Manoukian, E. B. and Bantitadawit, P. (1999). Direct derivation of the Schwinger quantum correction to the Thomas-Fermi atom. **Int. Journ. Theor. Phys.** 38: 897.

Manoukian, E. B. and Osaklung, J. (2000). Derivation of the $Z \to \infty$ limit for atoms. **Progr. Theor. Phys**. 103: (No. 4) (in press).

March, N. H. (1957). The Thomas-Fermi approximation in quantum mechanics. **Adv. Phys.** 6: 1. A Quarterly Supplement of the Philosophical Magazine.

Morgan, J. D. and Drake, G. W. (ed.). (1996). **Atomic and molecular handbook.** New York: American Institute of Physics.

Parr, R. G. and Yang, W. (1989). **Density-functional theory of atoms and molecules.** New York: Oxford University Press.

Rickayzen, G. (1980). **Green's functions and condensed matter**. London. Acadamic Press.

Schwinger, J. (1961). On the bound states of a given potential. **Proc. Natl. Acad. Sci.** (U.S.). 47: 122.

Schwinger, J. (1980). Thomas-Fermi model: The leading correction. **Phys. Rev.** A22: 1827.

Schwinger, J. (1981). Thomas-Fermi model: The second correction. **Phys. Rev.** A24: 2353.

Schwinger, J. (1993). The Greening of quantum field theory: George and I. Lecture given at Nottingham. July 14. (hep-ph/9310283).

Scott, J. (1952). The binding energy of the Thomas-Fermi atom. **Phil. Mag.** 43: 859.

Teller, E. (1962). On the stability of molecules in the Thomas-Fermi theory. **Rev. Mod. Phys.** 34: 627.

Thomas, L. H. (1927). The calculation of atomic fields. **Proc. Camb. Phil. Soc.** 23: 524.

Thirring, W. (1981). **A course in mathematical physics** (Vol.4). New York: Springer-Verlag.

Biography

Miss Jarin Osaklung was born on 7th February 1977 in Kalasin, Thailand. She graduated with a High School Diploma from Kanarat Bumroong Pathumtani in 1993. She later went to study in the Department of Physics, Faculty of science, at Kasetsart University, where she graduated with a B.Sc. Degree in Physics in 1997. After that she decided to study for a Master's degree in the School of Physics, Institute of Science, Suranaree University of Technology.