國 立 交 通 大 學

應用數學系

碩 士 論 文

一個新密度泛函理論推導公式之

三維有限元素數值解

3D Finite Element Solution of a New

Formulation in Density Functional Theory

研 究 生：蔡維哲

指導老師：劉晉良　教授

中 華 民 國 九 十 四 年 六 月

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摘　　要

　　在這一篇論文中有二個部分。在第一個部分裡，我們主要探討電子限制在量子奈米結構中的情況。我們主要學習使用 self-consistence 迭代方式來處理一個非線性偏微分系統，這系統是由普瓦松方程式與薛丁格方程式共同組成。藉由這個非線性偏微分系統來描述電子在量子奈米結構中的變化。在第二個部分裡，我們嘗試使用許正餘教授在密度泛函理論所推導出來一個新的公式，從這新的公式出發，使用有限元素法希望能夠得到電子在原子與分子結構中很好的描述，我們在處理這問題同時，也嘗試學習使用更有效率的數值方法來處理有限元素法整理出來的大型矩陣。

3D Finite Element Solution of a New Fromulation in Density Functional Theory

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Abstract

There are two parts in the thesis. In the first part, we discuss that electrons confine in quantum nanostructures. We use self-consistence iteration method for solving the nonlinear PDE system. The system consists of Poisson equation and Schrodinger equation. It describes the electronic changes in quantum nanostructures by the nonlinear PDE system. In the second part, we try to compute a new formulation derived by Prof. Hsu. From the formulation, we hope to get good numerical results by using finite element method. The main goal of this thesis is to simulate electronic properties of well-known atomic models by using our still under development finite element codes for future research on density functional theory.

誌謝

陳之藩先生說：「凡事得之於人者太多，出之於己者太少。」我在碩士生涯中深刻體會到這句話的深意。兩年碩士生涯中，我最要感謝我的指導教授 劉晉良教授，劉教授引導我從徬徨到冷靜面對問題，指導我如何做學問，也教導我正確的研究方法與精神，雖然是短短兩年，卻讓我在求學過程中得到最大成長，也因為劉教授，讓我能夠接觸不同領域的學者，開拓我的視野，劉老師 謝謝您。我還要特別感謝博士班 陳人豪學長，學長用他豐富的研究經驗，帶領我在黑暗中前進，讓我能夠整理出精采的碩士論文，我要特別謝謝陳學長。

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Contents

Part I
Electron confinement in quantum nanostructures

1   Introduction

In the world of quantum, the interesting problems are the problems in three-dimension (3D). But the complicated problems are always constructed from the simple problems. Thus, we compute the self-consistent electron states and confining potential, $V(r; T)$, for laterally confined cylindrical quantum wires at a temperature T from a numerical solution of the coupled *Poisson* and *Schrödinger (PS) equations*.

Our purposes are two fold.

First, we compute the self-consistent electron density function $n(r; T)$ and confining potential $V(r; T)$ for laterally confined cylindrical quantum wires from a numerical solution of the coupled *Poisson* and *Schrödinger (PS) equations*.

The second purpose is to contrast the results of the relatively simple Thomas-Fermi approach with those of the coupled PS theory and thereby assess the validity of the Thomas-Fermi approximation in laterally confined nanostructures.

2   The Model Problem and Numerical Methods

We begin by obtaining the eigenstates of an electron that is bound in two dimensions by a cylindrically symmetric nanostructure. The wave function factors in the usual way,

$$\Psi_{l;m;k} \;=\; \frac{1}{\sqrt{L}}\Phi_{l;m}(r)e^{im\theta}e^{ikz} \tag{2.1}$$

where $m = 0; \pm1; \pm2; \ldots$ is the azimuthal quantum number, $l = 1; 2; 3; \ldots$ is the radial quantum number, and L is the length of the cylinder. The subband spectrum is then labeled by three quantum numbers, $E_{l;m;k} = (h^2{=}2m^*)k^2 + \lambda_{l;m}$, where $\lambda_{l;m}$ is the eigenvalue associated with the eigenstate $\Phi_{l;m}$ of the radial *Schrödinger equation*,

$$\frac{-h^2}{2m^*}\left[\frac{1}{r}\frac{d}{dr}\left(r\frac{d}{dr}\right) - \frac{m^2}{r^2}\right]\Phi_{l;m}(r) + V(r)\Phi_{l;m}(r) = \lambda_{l;m}\Phi_{l;m}(r) \tag{2.2}$$

and the boundary condition is :

$$\Phi_{l;m}(R) = 0, \text{ at the exterior surface} \tag{2.3}$$

We assume that the $\Phi_{l;m}$ have been normalized according to

$$2\pi \int_0^R dr\, r \Phi_{l;m}^2(r) = 1. \tag{2.4}$$

Using the one-electron wave function $\Psi_{l;m;k}$, the density function is given by

$$n(r) = N_1 \sum_{l;m} \Phi_{l;m}^2(r) F_{-\frac{1}{2}}[\beta(\mu - \lambda_{l;m})] \tag{2.5}$$

where

$$N_1 \equiv (2m^* = \pi\beta\hbar^2)^{1=2}$$

and

$$F_{-\frac{1}{2}}[\beta(\mu - \lambda_{l;m})] = \frac{1}{\mathsf{P}=\pi} \int_0^1 dx\, x^{-\frac{1}{2}}[1 + \exp(x - \beta(\mu - \lambda_{l;m}))]^{-1}$$

,where $F_{-\frac{1}{2}}$ is a Fermi-Dirac integral, β is $1=(K_B T)$, $K_B T \equiv \hbar^2(3\pi^2 N_d)^{2=3}=2m^*$, and μ is the chemical potential(Fermi-level).

Equation (2.5) gives the density of the electron gas at a distance r from the central axis.

We then obtain the electrostatic potential ϕ from *Poisson's equation* ,

$$-\frac{1}{r}\frac{d}{dr}[r\frac{d\phi(r)}{dr}] = \frac{e}{"}f N_d - n[\phi(r)]g , \tag{2.6}$$

where N_d is the number density of donors and where " is the dielectric constant. The potential energy V of the electron is given by $V = -e\phi$. The boundary condition of equation (2.6) is

$$V(R) - \mu = 0{:}7eV$$

2.1 Finite Element Method

2.1.1 Introduction

The basic idea in the finite element method is to find the solution in infinite dimensional space by approximating it in a finite dimensional subspace. Moreover, in the finite element method, it will often be possible to improve or refine the approximate solution by spending more computational effort.

2.1.2 Numerical procedure

In this approach, starting from an initial guess for ϕ, one repeats solving the *Schrödinger equation* , computing $n(r)$, and then updating $\phi(r)$, until the iterates converge to a the self-consistent solution.

Employing the standard 1D finite element method, the radial *Schrödinger equation* (2.2) is equivalent to the matrix eigenvalue problem $A\phi = \lambda B\phi$, where A and B are tridiagonal.

Algorithm）
(1)To get an initial guess Φ by solving Poisson's eqnation.
(2)According to $V(r) = -e * \Phi(r)$,we can know the potential energy V of the electron.
(3)To Get $\Phi_{l;m}(r)$ by sloving the Schrödinger equation.
(4)Eigenvectors normalized by $2\pi \int_0^R drr\, \Phi^2_{l;m}(r) = 1$.
(5)Compute $n(r)$. The density function is given by

$$n(r) = N_1 \sum_{l;m} \Phi^2_{l;m}(r) F_{-\frac{1}{2}}[\beta(\mu - \lambda_{l;m})]$$

(6)To obtain the electrostatic potential Φ from Poisson's equation.
(7)Repeating the procedures (1)~(6) until the iterates converge.

2.1.3   Discretization

Finite Element Method for 1D Poisson's Equation

$$-\frac{1}{r}\frac{d}{dr}[r\frac{d\Phi(r)}{dr}] \equiv \frac{e}{"} fN_d - n[\Phi(r)]g$$

Boundary Conditions:

$$V(R) - \mu = 0:7eV$$

.

Multiply (2:6) by an aribitrary test function $v(x)$, and integrate over $(0;R)$.Now choose $v(x)$ satisfying $v(R) = v(0) = 0$, and then we get the form

$$A(\Phi;v) = \int_0^R (\frac{d\Phi}{dr}\frac{dv}{dr} - \frac{V}{r}\frac{d\Phi}{dr}); F(v) = \int_0^R fvdr$$

.

$\Rightarrow$ $A(\Phi_h; v_h) = F(v_h)$, for all $v_h \in fv \in S^h; v(0) = v(R) = 0g$.Without considering B.C.s, we have the matrix formulation $AU = F$.

$$A = \begin{cases} a_{ii} = \ln(2h + r_{i-1})(\frac{r_{i-1}}{h^2}) + \ln(2r_{i-1})(-\frac{1}{h} - \frac{r_{i-1}}{h^2}) + \ln(2h + 2r_i)(\frac{1}{h} + \frac{r_i}{h^2}) \\ \qquad\qquad + \ln(2r_i)(\frac{r_i}{h^2}); i = 1:::N \\ a_{i(i-1)} = \ln(2h + 2r_{i-1})(-\frac{r_{i-1}}{h^2}) + \ln(2r_{i-1})(\frac{r_{i-1}}{h^2}); i = 2:::N \\ a_{(i-1)i} = \ln(2h + 2r_{i-1})(-\frac{1}{h} - \frac{r_{i-1}}{h^2}) + \ln(2r_{i-1})(\frac{1}{h} + \frac{r_{i-1}}{h^2}); i = 2:::N \end{cases}$$

$$U = \begin{bmatrix} U_1 \\ U_2 \\ \vdots \\ \vdots \\ \vdots \\ U_N \end{bmatrix}$$

$$F = \begin{cases} (F_i = \int_{r_{i-1}}^{r_{R+1}} f\Phi_i \approx f(r_i)h; i = 2:::N-1) \\ F_1 = \dfrac{h}{2}f(r_1); F_N = \dfrac{h}{2}f(r_N) \end{cases}$$

Impose B.C.,

Solve AU = F by the *Preconditional Conjugate Gradient Method*.

2.1.4 Finite Element Method for 1D Schrödinger's Equation

$$-\frac{\hbar}{2m^*}[\frac{1}{r}\frac{d}{dr}[r\frac{d}{dr}] - \frac{m^2}{r^2}]\Phi_{l;m}(r) + V(r)\Phi_{l;m}(r) = \lambda_{l;m}\Phi_{l;m}(r) \qquad (1)$$

Boundary condition: $\Phi(R) = 0$.

The process of Finite Element Method:

1. (1) Choosing an arbitrary test function $v(r)$ and integrate over $(0;R)$.

=)

$$-\frac{\hbar^2}{2m^*}(\int_0^R \frac{1}{r}\frac{d}{dr}(r\frac{d\Phi(r)}{dr})v(r) - \int_0^R \frac{m^2}{r^2}\Phi(r)v(r)) + \int_0^R V\Phi v = \lambda\int_0^R \Phi v$$

=)

$$-\frac{\hbar^2}{2m^*}(\frac{v(r)}{r}(r\frac{d\Phi(r)}{dr})|_0^R - \int_0^R (r\frac{d\Phi(r)}{dr})d(\frac{v(r)}{r})) + \frac{\hbar^2}{2m^*}m^2\int_0^R \frac{\Phi(r)v(r)}{r^2}$$

$$+\int_0^R V\Phi v$$

$$= \lambda\int_0^R \Phi v$$

Set the test function $v(0) = v(R) = 0$

=)

$$\frac{\hbar^2}{2m^*}\int_0^R (r\frac{d\Phi(r)}{dr})(\frac{r\frac{dv(r)}{dr} - v(r)}{r^2}) + \frac{\hbar^2}{2m^*}m^2\int_0^R \frac{\Phi(r)v(r)}{r^2} + \int_0^R V\Phi v = \lambda\int_0^R \Phi v$$

=)

$$\frac{\hbar^2}{2m^*}\int_0^R (\frac{d\Phi(r)}{dr}\frac{dv(r)}{dr} - \frac{d\Phi(r)}{dr}\frac{v(r)}{r}) + \frac{\hbar^2}{2m^*}m^2\int_0^R \frac{\Phi(r)v(r)}{r^2} + \int_0^R V\Phi v = \lambda\int_0^R \Phi v$$

)

$$A(\sum_{j=1}^{N} U_j\Phi_j; v_h) = \lambda B(\sum_{j=1}^{N} U_j\Phi_j; v_h)$$

=)

$$A(\Phi;v) = \frac{\hbar^2}{2m^*}(\int \frac{d\Phi}{dr}\frac{dv}{dr} - \int \frac{d\Phi}{dr}\frac{v}{r}) + \frac{m^2\hbar^2}{2m^*}\int \frac{v}{r^2}\Phi + \int V\Phi v \quad , \quad B(\Phi;v) = \int \Phi v$$

4

$$a_{ij} = A(\Phi_j; \Phi_i); \quad b_{ij} = B((\Phi_j; \Phi_i)$$

We have to only compute $a_{i(i-1)}; a_{ii}; a_{i(i+1)}; b_{i(i-1)}; b_{ii}; b_{i(i+1)}$, other elements are zero.

Example for $a_{i(i+1)}$:

$$a_{i(i+1)} = A(\Phi_{i+1}; \Phi_i) = \frac{h^2}{2m^*} \int_0^R \left(\frac{d\Phi_{i+1}(r)}{dr} \frac{d\Phi_i(r)}{dr} - \frac{d\Phi_{i+1}(r)}{dr} \frac{\Phi_i(r)}{r} \right)$$
$$+ \frac{h^2}{2m^*} m^2 \int_0^R \frac{\Phi_{i+1}(r)\Phi_i(r)}{r^2} + V \int_0^R \Phi_{i+1}\Phi_i$$

Linear Transformation:
$$\frac{r - r_i}{r_{i+1} - r_i} = \frac{\xi + 1}{2}$$

$$\Rightarrow \quad r = \frac{(\xi + 1)h}{2} + r_i$$

Linear shape function: $\psi_1(\xi) = \frac{1-\xi}{2}; \psi_2(\xi) = \frac{1+\xi}{2}$

$$a_{i(i+1)} = \frac{h^2}{2m^*} \left(\int_{-1}^1 \left(\frac{d\psi_2(\xi)}{d\xi} \frac{d\psi_1(\xi)}{d\xi} \cdot \left(\frac{2}{h}\right)^2 \cdot \frac{h}{2} d\xi \right) - \int_{-1}^1 \frac{d\psi_2(\xi)}{d\xi} \frac{\psi_1(\xi)}{\frac{(\xi+1)h}{2} + r_i} \cdot \frac{2}{h} \cdot \frac{h}{2} d\xi \right)$$
$$+ \frac{h^2}{2m^*} m^2 \int_{-1}^1 \frac{\psi_2(\xi)\psi_1(\xi)}{(\frac{(\xi+1)h}{2} + r_i)^2} \cdot \frac{h}{2} d\xi + V \int_{-1}^1 \psi_2(\xi)\psi_1(\xi) \cdot \frac{h}{2} d\xi$$

$$a_{i(i+1)} = \frac{h^2}{2m^*} \int_{-1}^1 \left(-\frac{1}{4} \cdot \frac{2}{h} d\xi \right) - \frac{h^2}{2m^*} \int_{-1}^1 \left(\frac{1}{2} \frac{1-\xi}{(\xi+1)h + 2r_i} d\xi \right)$$
$$+ \frac{h^2}{2m^*} m^2 \int_{-1}^1 \frac{1-\xi^2}{((\xi+1)h + 2r_i)^2} \cdot \frac{h}{2} d\xi + V \int_{-1}^1 \frac{1-\xi}{2} \cdot \frac{1+\xi}{2} \cdot \frac{h}{2} d\xi$$

$$a_{i(i+1)} = \frac{h^2}{2m^*}\left(-\frac{1}{h}\right) - \frac{h^2}{2m^*}\frac{1}{2} \int_{-1}^1 \left(\frac{1-\xi}{(\xi+1)h + 2r_i} d\xi \right) + \frac{h^2}{2m^*} m^2 \cdot \frac{h}{2} \int_{-1}^1 \frac{1-\xi^2}{((\xi+1)h + 2r_i)^2}$$
$$+ V \cdot \frac{h}{8} \cdot \left(\frac{4}{3}\right)$$

5

Using Gaussian Quadrature(Zienkiewicz and Taylor, The FEM,#4th ed,McGraw-Hill,1989)

compute $\int_{-1}^{1}(\frac{1-\xi}{(\xi+1)h+2r_i}d\xi)$, $\int_{-1}^{1}\frac{1-\xi^2}{((\xi+1)h+2r_i)^2}d\xi$.

Hence we can get all values of $a_{i(i+1)}$,$i = 1; 2; ::::; N-1$

By the same way, the values of $a_{i(i-1)}; a_{ii}; b_{i(i-1)}; b_{ii}; b_{i(i+1)}$ will be obtained easily.

Discretization completed, and the next topic is how to find out the efficient solver of $AU = \lambda BU$.

For large scale matrix,we use *Jacobi-Davidson method* to compute the eigenpairs.

2.2   Linear system solvers

2.2.1   Jacobi-Davidson Method

Algorithm , Jacobi-Davidson method for linear eigenvalue problem:

Choose an initial unit vector v_1 ; $V_1 \equiv [v_1]$;

Inner Loop : For $k = 1,...,m$ do:

- compute $H_k = V_k^T A V_k$;

- compute the desired eigenpair (λ_k, y_k) of H_k;

- compute the corresponding Ritz vector $u_k = V_k^T y_k$;

- compute the residual $r_k = A u_k - \lambda_k u_k$;

- if convergence then exit;

- compute the new direction $t_k = \varepsilon M^{-1}u_k - M^{-1}r_k$, $\varepsilon = \dfrac{u_k^T M^{-1} r_k}{u_k^T M^{-1} u_k}$

- orthonormalize $[V_k; t_k]$ into V_{k+1};

Restart : use a few of the last Ritz vectors as initial vector;

Algorithm , JD method for Linear Eigenvalue Problem

2.2.2   Conjugate Gradient Method

The pseudocode for the Preconditioned Conjugate Gradient Method is given below.

1. Compute $r^{(0)} = b - Ax^{(0)}$ for some initial guess $x^{(0)}$.

Begin Loops for $i = 1, 2, \ldots$

2. Solve $Mz^{(i-1)} = r^{(i-1)}$

3. $\rho_{i-1} = r^{(i-1)^\mathsf{T}} z^{(i-1)}$

4. **If $i = 1$**

   $p^{(1)} = z^{(0)}$

   Else

   $\beta_{i-1} = \rho_{i-1}/\rho_{i-2}$
   $p^{(i)} = z^{(i-1)} + \beta_{i-1}p^{(i-1)}$

   End If

5. $q^{(i)} = Ap^{(i)}$

6. $\alpha_i = \rho_{i-1}/p^{(i)^\mathsf{T}} q^{(i)}$

7. $x^{(i)} = x^{(i-1)} + \alpha_i p^{(i)}$

8. $r^{(i)} = r^{(i-1)} - \alpha_i q^{(i)}$

9. **Check convergence continue if necessary**
   End Loops.

2.3   Numerical Results

FIG. 1. Self-consistent confining potentials (dashed curves, right ordinate) and electron density functions (solid curves, left ordinate) for (a) Poisson-Schrödinger theory and (b) finite-temperature Thomas-Fermi approximation, for $T = 10$ and 300 K and indicated doping densities (units of 10^{18} cm^{-3}).

FIG. 3. Partial electron density functions at $T = 10$ K associated with various values of the angular momentum quantum number, along with the total density function that results from summing the individual contributions for all values of $|m|$.

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APPENDIX

FERMI-DIRAC FUNCTIONS

Fermi-Dirac Function

Part II
3D Finite Element Method of Self-consistent Density Functional Theory

3   Introduction

Density functional theory is an extremely successful approach for the description of metals, semiconductors, and insulators. The last decade has witnessed a proliferation in methodologies for numerically solving large-scale self-consistent eigenvalue problems. The result of Kohn-Sham equation in density functional theory will be reviewed. We mainly foucs on a new formulation in density functional theory by HSU [HSU,2003] using the 3D finite element method. The new formulation that drops the exchange-correlation term makes the computation potentially much traceable in physics without any *ad hoc* assumption. Single atoms (e.g., H,He,Li,Be,B,...) will be included in our test programs. Besides, we will discuss some computations of excited state of single atomic system with considering Singlet and Triplet state. Summary of the above description, some objectives of the thesis are

1. To Implement Kohn-Sham equation in order to review the results of single atomic system.

2. To run programs for new Hsu's DFT formulation.

3. To show the results of new Hsu's DFT formulation imposing electrons of Singlet and Triplet state.

4   Literature Survey

4.1   Theoretical Development

The key problem in the structure of matter is to solve the Schrödinger equation for a system of N interacting electrons in the external coulombic field created by a collection of atomic nuclei. It is a very difficult problem in many-body theory and, in fact, the exact solution is known only in the case of the uniform electron gas, for atoms with a small number of electrons and for a few small molecules. It usually gets these solutions by numerical skill. At the analytic level, one always has to resort to approximations.

4.1.1   Hartree approximation

The first approximation may be considered the one proposed by Hartree. It consists of postulating that the many-electron wave function can be written as a

simple product of one-electron wave functions. The Hartree approximation treats the electrons as distinguishable particles.

4.1.2 Hartree-Fock (HF) or self-consistent field (SCF) approximation

It is to introduce Pauli exclusion principle (Fermi statistics for electrons) by proposing an antisymmetrized many-electron wave function in the form of a Slater determinant. It has been for a long time the way of choice of chemists for calculating the electronic structure of molecules. In fact, it provides a very reasonable picture for atomic systems and also provides a reasonably good description of inter-atomic bonding.

4.1.3 Thomas-Fermi (TF) approximation

Parallel to the development of this line in electronic structure theory, Thomas and Fermi proposed, at about the same time as Hartree (1927-1928), that the full electronic density was the fundamental variable of the many-body problem and derived a differential equation for the density without resorting to one-electron orbitals. The Thomas-Fermi (TF) approximation was actually too crude because it did not include exchange and correlation effects and was also unable to sustain bound states because of the approximation used for the kinetic energy of the electrons. However, it set up the basis for the later development of density functional theory (DFT), which has been the way of choice in electronic structure calculations in condensed matter physics and it also became accepted by the quantum chemistry community because of its computational advantages compared to HF-based methods.

4.1.4 Hohenberg-Kohn theorem

In 1964, Hohenberg and Kohn formulated and proved a theorem that put on solid mathematical grounds the former ideas, which were first proposed by Thomas and Fermi. In Hohenberg-Kohn theorem the electronic density determines the external potential, but it is also needed that the density corresponds to some ground state antisymmetric wave function, and this is not always the case. Up till now, both the exact ground state density as well as the Hohenberg-Kohn functional is still unknown, so one cannot make use of the Hohenberg-Kohn theorems to calculate the molecular properties.

4.1.5 Kohn-Sham equations

In 1965, Kohn and Sham proposed the idea of replacing the kinetic energy of the interacting electrons with that of an equivalent non-interacting system, because this latter can be easily calculated. Kohn and Sham introduced a fictitious system of N non-interacting electrons to be described by a single determinant wave function in N "orbits." We have seen that a reasonably good description can be obtained by separating the electrostatic (classical Coulomb energy), exchange and correlation contributions. The biggest difficulty is to deal with correlation.This

is, in fact, an active field of research that has produced significant improvements in the past decade. This correlation term has to tread on an approximate manner. Although there are many different functions available, almost all of them are derived from the electron density of a uniform electron gas, which can be calculated by means of statistical thermodynamics.

4.1.6 Hsu Formulation

A generic derivation from cluster expansion results in a new DFT formulation without the exchange-correlation term that makes the computation much traceable in physics without *ad hoc* (e.g., local density spin approximation (LDSA)) assumption.[J.Y.Hsu, PRL 2003]

4.2 Numerical Methods

The last decade has witnessed a proliferation in methodologies for numerically solving large-scale problems in physics. The rapid growth has been driven because a wide variety of computational methods and numerical algorithms have exploited that physical locality. This review examines one subset of these new computational methods, namely real-space techniques. Real space methods can be loosely categorized as one of three types: finite differences (FD), finite elements (FE), or wavelets. All three lead to structured, very sparse matrix representations of the underlying differential equations on meshes in real space. Applications of wavelets in electronic structure calculations have been thoroughly reviewed recently [Arias, 1999]. As implied in the title, the primary focus is on calculations in density functional theory (DFT); real-space methods are in no way limited to DFT, but since DFT calculations comprise a dominant theme in modern electrostatics and electronic structure, the discussion here will mainly be restricted to this particular theoretical approach. The early development of FD and FE methods for solving partial differential equations stemmed from engineering problems involving complex geometries, where analytical approaches were not possible [Strang and Fix, 1973]. Example applications include structural mechanics and fluid dynamics in complicated geometries. However, even in the early days of quantum mechanics, attention was paid to FD numerical solutions of the Schrodinger equation [Kimball and Shortley, 1934; Pauling and Wilson, 1935]. Real-space calculations are performed on meshes; these meshes can be as simple as Cartesian grids or can be constructed to conform to the more demanding geometries arising in many applications. Finite-difference representations are most commonly constructed on regular Cartesian grids. They result from a Taylor series expansion of the desired function about the grid points. The advantages of FD methods lie in the simplicity of the representation and resulting ease of implementation in efficient solvers. Disadvantages are that the theory is not variational, and it is difficult to construct meshes flexible enough to conform to the physical geometry of many problems. Finite-element methods, on the other hand, have the advantages of

significantly greater flexibility in the construction of the mesh and an underlying variational-type formulation. Other advantages include easier parallel implementation using domain decomposition and possible mesh refinement in regions where solution changes rapidly, as mentioned earlier. However, the cost of the flexibility is an increase in complexity and more difficulty in the implementation of multi-scale or related solution methods [Thomas, 2000].Nevertheless, we mainly discuss the fundamentals of FEM solutions of the self-consistent nonlinear coupled *Poisson* and *Schrödinger (PS) equations* in density-functional theory (DFT) in this thesis.

5 Density Functional Theory

The Hamiltonian in its original form is very complex:

$$H = -\frac{\hbar^2}{2m}\sum_i \nabla^2_{r_i} + \sum_{i,j}\frac{e^2}{|r_i - r_j|} - \sum_i\sum_k \frac{Z_k e^2}{|r_i - R_k|} - \frac{\hbar^2}{2M}\sum_k \nabla^2_{R_k} + \sum_{k,l}\frac{e^2}{|R_k - R_l|}$$

$$(2)$$

which involves sums over all electrons/nuclei and their pairs involving kinetic energy and columbic potentials.

5.1 Hartree Approximation

Hartree approximation consists of postulating that the many-electron wave function can be written as a simple product of one-electron wave functions. It seems plausible that it might be useful to start with a wavefunction of the general form

$$\Phi(r_1, r_2, r_3, \ldots, r_N) = \psi_1(r_1) * \psi_2(r_2) * \cdots * \psi_N(r_N)$$

which is known as a Hartree Product. While this functional form is fairly convenient, it has at least one major shortcoming: it fails to satisfy the antisymmetry principle, which states that a wavefunction describing fermions should be antisymmetric with respect to the interchange of any set of space-spin coordinates.

5.2 Hartree-Fock Approximation

Hartree-Fock theory is fundamental to much of electronic structure theory. It is the basis of molecular orbital theory, which positulates that each electron's motion can be described by a single-particle function (orbital) which does not depend explicitly on the instantaneous motions of the other electrons. Hartree-Fock theory was developed to solve the electronic Schrödinger equation that results from the time-independent Schrödinger equation after invoking the Born-Oppenheimer approximation (Neglects motion of nuclei [heavier than electrons]). In atomic units, and with r denoting electronic and R denoting nuclear degrees of freedom, the electronic Schrödinger equation is

$$\left[-\frac{1}{2}\sum_i \nabla^2_i - \sum_{A,i}\frac{Z_A}{r_{Ai}} + \sum_{A>B}\frac{Z_A Z_B}{R_{AB}} + \sum_{i>j}\frac{1}{r_{ij}}\right]\Psi(r;R) = E\Psi(r;R) \qquad (5.1)$$

The Hartree approximation treats the electrons as distinguishable particles. A step forward is to introduce Pauli exclusion principle (Fermi statistics for electrons) by proposing an antisymmetrized many-electron wave function in the form of a Slater determinant:

$$\Phi(r;R) = SD\{\psi_j(r_i;\sigma_i)\} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(r_1;\sigma_1) & \psi_1(r_2;\sigma_2) & \cdots & \psi_1(r_N;\sigma_N) \\ \psi_2(r_1;\sigma_1) & \psi_2(r_2;\sigma_2) & \cdots & \psi_2(r_N;\sigma_N) \\ \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots \\ \psi_N(r_1;\sigma_1) & \psi_N(r_2;\sigma_2) & \cdots & \psi_N(r_N;\sigma_N) \end{vmatrix}$$

Hartree-Fock approximation has been for a long time the way of choice of chemists for calculating the electronic structure. In fact, it provides a very reasonable picture for atomic systems and, although many-body correlations are completely absent, it also provides a reasonably good description of inter-atomic bonding.

5.3 The Kohn-Sham Equations

The Kohn-Sham self-consistent eigenvalue equations for electronic structure can be written as follows:

$$\left(-\frac{1}{2}\nabla^2 + V_{eff}\right)\Psi_i(r) = \varepsilon_i\Psi_i(r), \tag{3}$$

where the density-dependent effective potential is

$$V_{eff}(r) = V_{e-nuc}(r) + V_{e-e}([\rho(r)]) + V_{xc}([\rho(r)];r), \tag{4}$$

V_{e-nuc} = external potential, $V_{e-e} = \int \frac{\rho(r')}{|r-r'|}dr'$, $V_{xc} = \frac{\delta E_{xc}}{\delta\rho}$, E_{xc} =exchange-correlation enery.

Local Spin Density Approximation (LSDA) : exchange-correlation energy E_{xc} is a simple known funtion

$$E_{xc}[\rho(r)] = -\frac{3}{4}\left(\frac{6}{\pi}\right)^{1/3}\int(\rho_\uparrow^{4/3}(r) + \rho_\downarrow^{4/3}(r))dr. \tag{5}$$

The classical electrostatic potential $V_{e-nuc}(r) + V_{e-e}(r)$ is due to both the electrons and nuclei, and the (in principle) exact exchange-correlation potential $V_{xc}([\rho(r)];r)$ incorporates all nonclassical effects. The exchange-correlation potential includes a kinetic contribution, since the expectation value of the Kohn-Sham kinetic energy is that for a set of noninteracting electrons moving in the one electron effective potential. The electron density $\rho(r)$ is obtained from the occupied orbitals :

$$\rho(r) = \sum_i^{occup.} |\Psi_i(r)|^2. \tag{6}$$

Standard electrostatics tells us that doing V_{e-e} integral is equivalent to solving Poisson's equation. Hartree Potential V_{e-e} is solution of the Poisson equation:

$$\nabla^2 V_{e-e} = -4\pi\rho(r). \tag{7}$$

We slove it by Conjugate Gradient Method once a distribution ρ is known.

5.3.1 Self Consistency

1.

$$(-\frac{1}{2}\nabla^2 + V_{e-nuc}(r) + V_{e-e}([\rho(r)]) + V_{xc}([\rho(r)]; r))\Psi_i(r) = \epsilon_i\Psi_i(r); i = 1, \ldots, i^{occup}.$$

2.

$$\rho(r) = \sum_i^{occup.} |\Psi_i(r)|^2.$$

3.

$$\nabla^2 V_{e-e} = -4\pi\rho(r).$$

The Self Consistent System can be viewed as a nonlinear eigenvalue problem, because V_{xc} and V_{e-e} both depend on ρ.

Self-Consistent Iteration :

1.

Initial Guess for V ,set $V_{e-e} = 0$

2.

Slove $(-\frac{1}{2}\nabla^2 + V_{eff})\Psi_i(r) = \epsilon_i\Psi_i(r)$

3.

Calculate new $\rho(r) = \sum_i^{occup.} |\Psi_i(r)|^2$

4.

Show $\nabla^2 V_{e-e} = -4\pi\rho(r)$ **for a new** V_{e-e}

5.

Compute $V_{xc} = f[\rho(r)]$ **,** $V_{new} = V_{e-nuc} + V_{e-e} + V_{xc}$

6.

If $|V_{new} - V| < TOL$, **STOP**

For example, we want to solve Li atom of configuration $1s^2 2s^1$ with 2 spin up and 1 spin down orbitals. First, we group all the orbitals into two types, spin up and down and then sum all the spin up orbitals to get $\rho_{\shortparallel}$ and $\rho_{\#}$ from spin down orbitals. Then put them into the exchange potential for different spin type. Finally, we solve the KS equations seperately with respect to different types of spin.We have $\rho_{\shortparallel} = |\Psi(1s; \shortparallel)|^2 + |\Psi(2s; \shortparallel)|^2$ and $\rho_{\#} = |\Psi(1s; \#)|^2$.

Therefore, the equation we solve is

$$(-\frac{1}{2}\nabla^2 + V_{eff;\shortparallel})\Psi_{i;\shortparallel} = \epsilon_{i;\shortparallel}\Psi_{i;\shortparallel} \tag{8}$$

for spin up orbitals and replace $\shortparallel$ by $\#$ for spin down orbitals.We can have the form of $V_{xc;\shortparallel} = \frac{\delta E[\rho^{\shortparallel};\rho^{\#}]}{\delta\rho^{\shortparallel}}$. The correlation functional is the same as exchange functional if we can find or have its functional form. If we can not have the correlation functional form for different spin types, just use the functional form without considering the spin type.

5.4 A New Density Functional Theory (J.Y.Hsu, PRL 2003)

The paper (J.Y.Hsu, PRL 2003) gives a new derivation of Density Functional Theory from a cluster expansion by truncating the higher-order correlations in one and only one term in the kinetic energy. The new formulation admits excited states and allows self-consistent calculation of the exchange correlation effect without any *ad hoc* assumptions.

The wave function Ψ is chosen as the product of a single-electron wave function Φ, and an N-body correlation function,

$$\Psi(\Gamma) = \Pi_{i=1}^{N}\Phi(r_i)U(\Gamma) \tag{9}$$

Γ is the N-particle phase space point equivalent to the expression $(r_1; r_2; ....; r_n)$. The exchange symmetry is imposed on U and on the indistinguishable particles so that each electron is described by the same Φ. This gives the density function as follows:

$$n(r) = \int \Pi_{i=2}^{N}d\tau_i |\Phi(r_i)|^2 |U(r_1; r_2; ....; r_N)\Phi(r)|^2 \equiv M(r)|\Phi(r)|^2 \equiv |\Psi_0(r)|^2; \tag{10}$$

where the index starting from $i = 2$ is chosen for convenience by imposing the exchange symmetry, and $d\tau_i$ is the volume element of ith particle. For the immobile ion I with charge Z_I and N representing the number of electrons, the last derived equation is

$$\epsilon\Psi_0(r) = -\frac{1}{2}\nabla^2\Psi_0(r) - \sum_{I}\frac{Z_I}{|r - R_I|}\Psi_0(r) + \frac{(N-1)}{2}\Psi_0(r)\left\langle\frac{1}{|r - r^0|}\right\rangle; \tag{11}$$

where

$$\frac{1}{|r-r^0|} = \frac{\int_R d\tau^0 \frac{|\Psi_0(r^0)|^2}{|r-r^0|}}{\int_R d\tau^0 |\Psi_0(r^0)|^2} : \tag{12}$$

The derivation of the density functional theory (DFT) from the cluster expansion corrects the spurious self-interaction energy in the classical DFT, admits the excited states, and has a self-consistent exchange correlation effect.

Excited States (Singlet and Triplet States)

Triplet States   Singlet States

For a particle j in an arbitrary orbital, the generalized equation is

$$"\Psi_j(r) = -\frac{1}{2}\nabla^2 \Psi_j(r) - \sum_I \frac{Z_I}{|r-R_I|}\Psi_j(r) + \frac{1}{2}\Psi_j(r)\sum_{j^0 \in j}^Z \int d\tau^0 \frac{|\Psi_{j^0}(r^0)|^2}{|r-r^0|}\Psi_j(r): \tag{13}$$

Varying a nonnegation trial function $\nu(r_1; r_2) \equiv \exp(\beta|r_1 - r_2|)$ and holding Ψ_0 constant to minimize the total energy, subject to particale conservation

$$N = \int d\tau_1 d\tau_2 |\nu(r_1; r_2)|^2 \rho(r_1)\rho(r_2) \equiv \int d\tau_1 d\tau_2 |\Psi(r_1; r_2)|^2 : \tag{14}$$

We reduce to the simplified $\beta = 0$ version

$$"\Psi_s(r_1) = -\frac{1}{2}\nabla^2 \Psi_s(r_1) - \sum_I \frac{Z_I}{|r_1-R_I|}\Psi_s(r_1) \tag{15}$$

$$+\frac{1}{2}\sum_{\sigma \in S}^Z \int d\tau_2 \frac{|\Psi_\sigma(r_2)|^2}{|r_1-r_2|}\Psi_s(r_1) \mp \frac{1}{2}\sum_{\sigma \in S}^Z \int d\tau_2 \frac{\Psi_\sigma^*(r_2)\Psi_s(r_2)}{|r_1-r_2|}\Psi_\sigma(r_1):$$

Example for excited Be(2 1S,1 2S,1 2P)

$$"\Psi_{2s}(r_1) = -\frac{1}{2}\nabla^2 \Psi_{2s}(r_1) - \sum_I \frac{Z_I}{|r_1-R_I|}\Psi_{2s}(r_1) \tag{16}$$

$$+ \int d\tau_2 \frac{|\Psi_{1s}(r_2)|^2}{|r_1-r_2|}\Psi_{2s}(r_1) + \frac{1}{2}\int d\tau_2 \frac{|\Psi_{2P}(r_2)|^2}{|r_1-r_2|}\Psi_{2s}(r_1)$$

$$\mp\frac{1}{2}\int d\tau_2 \frac{\Psi_{2P}^*(r_2)\Psi_{2s}(r_2)}{|r_1-r_2|}\Psi_{2P}(r_1):$$

6 NUMERICAL METHODS

6.1 Finite Element Method

6.1.1 Introduction

The Finite Element Method is a numerical method which can be used for the accurate solution of complex engineering problems. The method was first developed in 1956 for the analysis of aircraft structural problems. Thereafter, within a decade, the potentialities of the method for the solution of different types of applied science and engineering problems were recognized. Over the years, the finite element technique has been so well established that today it is considered to be one of the best methods for solving a wide variety of practical problems efficiently. In fact the method has become one of the active research areas for applied mathematicians. One of the main reasons for the popularity of the method in different fields of engineering is that once a general computer program is written, it can be used for the solution of any problem simply by changing the input data.

Many problems that find out its approximate numerical solution to predict the response of physical system subjected to the external influences arise in many areas of engineering, science, and applied mathematics. The Finite Element Method which is a computer-aid mathematical technique is just a powerful method for obtaining approximate numerical solution. Up to now,applications to date have occurred principally in the areas of solid mechanics, heat transfer, fluid mechanics, and electromagnetism. New areas of application are continually being discovered, recent ones include solid-state physics and quantum mechanics.

6.1.2 Procedure of Finite Element Method

Discretization The discretization of the domain into subregions is the first step in FEM. We choose the tetrahedral element as our basic element shape to partition the domain.

tetrahedral element

By the software (HyperMesh), we can partition the domain.

The meshes of 3D computation domain(r=20 Bohr)

Shape Functions   The typical 3-D linear tetrahedral element trial solution can be written

$$\vartheta(r; \alpha) = \sum_{j=1}^{x} \alpha_j N_j (x; y; z)$$

The special coordinates are introduced defined by

$$x = L_1 x_1 + L_2 x_2 + L_3 x_3 + L_4 x_4 \qquad (8.a)$$

$$y = L_1 y_1 + L_2 y_2 + L_3 y_3 + L_4 y_4 \qquad (8.b)$$

$$z = L_1 z_1 + L_2 z_2 + L_3 z_3 + L_4 z_4 \qquad (8.c)$$

$$1 = L_1 + L_2 + L_3 + L_4 \qquad (8.d)$$

The coordinates of point P [Zienkiewicz and Taylor,2000]

Sloving Eq(8) gives $L_i = \dfrac{a_i + b_i x + c_i y + d_i z}{6V_c}$ etc.

$$V_c = \begin{vmatrix} 1 & x_1 & y_1 & z_1 \\ 1 & x_2 & y_2 & z_2 \\ 1 & x_3 & y_3 & z_3 \\ 1 & x_4 & y_4 & z_4 \end{vmatrix}$$

$$a_i = \begin{vmatrix} x_j & y_j & z_j \\ x_k & y_k & z_k \\ x_l & y_l & z_l \end{vmatrix}$$

$$b_i = - \begin{vmatrix} 1 & y_j & z_j \\ 1 & y_k & z_k \\ 1 & y_l & z_l \end{vmatrix}$$

$$c_i = - \begin{vmatrix} x_j & 1 & z_j \\ x_k & 1 & z_k \\ x_l & 1 & z_l \end{vmatrix}$$

and

$$d_i = \begin{vmatrix} x_j & y_j & 1 \\ x_k & y_k & 1 \\ x_l & y_l & 1 \end{vmatrix}$$

The linear shape functions for the linear element are simply

$$N_i = L_i; N_j = L_j; N_k = L_k; N_l = L_l$$

where V_c represents the volume of the tetrahedron.

6.1.3   Weighted residual approach

Variational approach requires a knowledge of a variational problem(functional to be extremized or made stationary) for the given problem. Usually we encounter problems for which the variational principles are not known. Weighted residual approach in the finite element method can be applied even in these cases.We can derive directly from the governing differential equations of the problem without any need of knowing the 'functional' by weighted residual approach.

For a particle J of one nucleus system in an orbital, the governing equation is written as

$$-\frac{1}{2} \bigtriangledown^2 \Psi_J(r) - \frac{Z}{r}\Psi_J(r) + \Pi_J \Psi_J(r) = "\Psi_J(r) \tag{17}$$

$$\Pi_J = \frac{1}{2} \sum_{J^0 \& J}^{Z} d\tau \frac{j\Psi_{J^0}(r^0)j^2}{jr - r^0 j} \tag{18}$$

where Ψ_J is the density function of a a particle J in an orbital that is limited to two electrons with spin polarization to satisfy the Pauli exclusion principle, r and

R is the coordinate from the zero point of the computing space, **Z** is the number of positive charge of the nucleus, the subscript **I** means the kind of nucleus .

STEP 1.

Using a trial solution $\vartheta(r;\alpha)$ to approximate the density function $\Psi(r)$, we first write down the residual equation for each orbital **J** :

$$R_J(r;\alpha) = -\frac{1}{2}\nabla^2\vartheta(r;\alpha) - \frac{Z}{r}\vartheta(r;\alpha) + \Pi_J\vartheta(r;\alpha) - \varepsilon\vartheta(r;\alpha) \qquad (19)$$

The typical 3-D element trial solution is always written in the general form $\vartheta(r;\alpha) = \sum_{j=1}^{n}\alpha_j N_j(r)$, and one residual equation is

$$\int\int\int R_J(r;\alpha)N_i(r)dV = 0 \; ; \; i = 1,2,\ldots,n \qquad (20)$$

where it integrates over one element and n is the number of nodes in an element.

$$\Rightarrow \int\int\int \left\{ -\frac{1}{2}\nabla^2\vartheta(r;\alpha) - \frac{Z}{r}\vartheta(r;\alpha) + \Pi_J\vartheta(r;\alpha) - \varepsilon\vartheta(r;\alpha) \right\} N_i(r)dV = 0 \; ; \; i = 1,2,\ldots,n$$

$$(21)$$

STEP 2.

Divergence Theorem $\Rightarrow$

$$\frac{1}{2}\int\int\int \frac{\partial N_i(r)}{\partial x}\frac{\partial\vartheta(r;\alpha)}{\partial x} + \frac{\partial N_i(r)}{\partial y}\frac{\partial\vartheta(r;\alpha)}{\partial y} + \frac{\partial N_i(r)}{\partial z}\frac{\partial\vartheta(r;\alpha)}{\partial z}dV \qquad (22)$$

$$-Z\int\int\int \frac{N_i(r)\vartheta(r;\alpha)}{r}dV$$

$$+ \int\int\int \Pi_J N_i(r)\vartheta(r;\alpha)dV$$

$$-\varepsilon\int\int\int N_i(r)\vartheta(r;\alpha)dV$$

$$= \frac{1}{2}\left[\int \frac{\partial\vartheta(r;\alpha)}{\partial x}N_i(r)n_x dydz + \int \frac{\partial\vartheta(r;\alpha)}{\partial y}N_i(r)n_y dxdz + \int \frac{\partial\vartheta(r;\alpha)}{\partial z}N_i(r)n_z dxdy \right]$$

where n_x, n_y and n_z are the direction vectors of the outward unit normal to the element boundary. The R.H.S. of above Equation is the boundary term contains the flux must vanish from the system equations for the eigenproblems , so Equation (22) is rewritten as follows:

$$\frac{1}{2}\int\int\int \frac{\partial N_i(r)}{\partial x}\frac{\partial\vartheta(r;\alpha)}{\partial x} + \frac{\partial N_i(r)}{\partial y}\frac{\partial\vartheta(r;\alpha)}{\partial y} + \frac{\partial N_i(r)}{\partial z}\frac{\partial\vartheta(r;\alpha)}{\partial z}dV \qquad (23)$$

$$-Z\int\int\int \frac{N_i(r)\vartheta(r;\alpha)}{r}dV$$

$$+ \int\int\int \Pi_J N_i(r)\vartheta(r;\alpha)dV$$

$$-\varepsilon\int\int\int N_i(r)\vartheta(r;\alpha)dV$$

$$= 0$$

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STEP 3.
Equation (23) is rearranged to satisfy the matrix solver as follows :

$$f''[M] + [N]g f\alpha g = 0 \tag{24}$$

where

$$[M]_{ij} = \iiint N_i(r)N_j(r)dV \tag{25}$$

$$[N]_{ij} = -\frac{1}{2}\iiint \frac{\partial N_i(r)}{\partial x}\frac{\partial N_j(r)}{\partial x} + \frac{\partial N_i(r)}{\partial y}\frac{\partial N_j(r)}{\partial y} + \frac{\partial N_i(r)}{\partial z}\frac{\partial N_j(r)}{\partial z}dV$$
$$+\iiint \frac{N_i(r)N_j(r)}{r}dV - \iiint \Pi_J N_i(r)N_j(r)dV \tag{26}$$

STEP 4.
To transfer the integrals of Equation(24) into a form appropriate for numerical evaluation.

$$[M]_{ij} = \iiint N_i(r)N_j(r)dV \tag{27}$$
$$(\text{if } i = j) = \frac{V_c}{10}$$
$$(\text{if } i \neq j) = \frac{V_c}{20}$$

$$[N] = [A] + [B] + [C] \tag{28}$$

$$[A] = -\frac{1}{2}\iiint \frac{\partial N_i(r)}{\partial x}\frac{\partial N_j(r)}{\partial x} + \frac{\partial N_i(r)}{\partial y}\frac{\partial N_j(r)}{\partial y} + \frac{\partial N_i(r)}{\partial z}\frac{\partial N_j(r)}{\partial z}dV \tag{29}$$
$$= -\frac{b_ib_j + c_ic_j + d_id_j}{72V_c}$$

$$[B] = \iiint \frac{N_i(r)N_j(r)}{r}dV \quad \text{(Gauss Cubic integration)} \tag{30}$$
$$= \frac{V_c}{36}\sum_{k=1}^{N} \frac{(a_i + b_ix_k + c_iy_k + d_iz_k)(a_j + b_jx_k + c_jy_k + d_jz_k)}{x_k^2 + y_k^2 + z_k^2}w_k$$

where N is the total numbers of the Gauss points, w_k is the weighting factor and the subscript k means that the related values on the Gauss point .

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No.	Order	Figure	Error	Points	Tetrahedral coordinates	Weig
1	Linear		$R = O(h^2)$	a	$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}, \frac{1}{4}$	1
2	Quadratic		$R = O(h^3)$	a b c d	$\alpha, \beta, \beta, \beta$ $\beta, \alpha, \beta, \beta$ $\beta, \beta, \alpha, \beta$ $\beta, \beta, \beta, \alpha$ $\alpha = 0.585\,410\,20$ $\beta = 0.138\,196\,60$	$\frac{1}{4}$
3	Cubic		$R = O(h^4)$	a b c d e	$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ $\frac{1}{2}, \frac{1}{6}, \frac{1}{6}, \frac{1}{6}$ $\frac{1}{6}, \frac{1}{2}, \frac{1}{6}, \frac{1}{6}$ $\frac{1}{6}, \frac{1}{6}, \frac{1}{2}, \frac{1}{6}$ $\frac{1}{6}, \frac{1}{6}, \frac{1}{6}, \frac{1}{2}$	$-\frac{4}{5}$ $\frac{9}{20}$

Numerical integration formula of Gauss for tetrahedral element [Zienkiewicz and Taylor, 20

$$[C] = - \int \Pi_j N_i(r) N_j(r) dV \qquad (31)$$

STEP 5.

We obtain the term Π_J from solving *Poisson's equation*

$$\nabla^2 \Pi_J(r) = -4\pi j \Psi_J(r) j^2 \qquad (32)$$

Boundary Condition :

$$\Pi_J(@\Omega) = \frac{1}{\text{the sphere radius of the domain}} \qquad (33)$$

Do all process of finite element method again as the same above. *Poisson's equation* is rearranged to satisfy the matrix solver as follows :

$$\overline{A}^{\,h\_i} [X] = \overline{B}^{\,h\_i}$$

=)

$$\left[\overline{A}\right]_i^h = - \int \int \int \left[\frac{\partial N_i(r)}{\partial x}\frac{\partial N_j(r)}{\partial x} + \frac{\partial N_i(r)}{\partial y}\frac{\partial N_j(r)}{\partial y} + \frac{\partial N_i(r)}{\partial z}\frac{\partial N_j(r)}{\partial z} \right] dV \quad (34)$$

$$= -\frac{b_i b_j + c_i c_j + d_i d_j}{36 V_c}$$

$$\left[\overline{B}\right]_i^h = -4\pi \int \int \int j \Psi_J(r) j^2 N_i(r) dV \quad \text{(Gauss Cubic integration)} \quad (35)$$

Deriving the element equations complete by above steps. The Conjugate Gradient Method can slove $\left[\overline{A}\right]^h [X] = \left[\overline{B}\right]^h$, and it means the Π_j term is known now. We get $[C]_{ij} = - \int \int \int \Pi_j N_i(r) N_j(r) dV$ to utilize Gauss Cubic integration. All elemental matrix equations are assembled to be algebra system that are then solved by Jacobi-Davidson matrix solver.

6.2 Numerical Linear Algebra

6.2.1 Jacobi-Davidson Method

The Jacobi-Davidson solver can efficiently deal with the large-scale sparse eigenvalue matrix equation, which is still a very challenging task even nowadays. One of the advantages in using Jacobi-Davidson algorithm to solve the DFT eigenvalue problem is the feasibility of parallelization in the future, considering the computational demanding of the problem itself.

The Jacobi-Davidson method [Voss and Betcke, 2002; Hwang, 2003] is based on a combination of two basic principles. The first one is to apply a Galerkin approach for the eigenproblem $Ax = \lambda x$, with respect to some given subspace spanned by an orthonormal basis $\{v_1, ..., v_m\}$. The Galerkin condition is

$$AV_m s - \theta V_m s \perp \{v_1, ..., v_m\}$$

where V_m denotes the matrix with columns v_1 to v_m. This equation has m solutions $(\theta_j^{(m)}, s_j^{(m)})$. This m pairs are called the Ritz values and Ritz vectors of A with respect to the subspace spanned by the columns of V_m. These Ritz pairs are approximations for eigenpairs of A, and our goal is to obtain better approximations by a well-chosen expansion of the subspace. Suppose that we have an eigenvector approximation u_j for an eigenvector x corresponding to a given eigenvalue λ. We suggest computing the orthogonal correction t for $u_j^{(m)}$.

$$A(u_j^{(m)} + t) = \lambda(u_j^{(m)} + t)$$

with $t \perp (u_j^{(m)})$, $t \in U^\perp \equiv \{v | v^* u_j = 0\}$.

The correction equation of Jacobi-Davidson is

$$(A^\perp - \theta_j I)t = -r_j \quad (36)$$

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where $r_j = (A - \theta_j I)u_j$, $A^? = (I - u_j u_j^*)A(I - u_j u_j^*)$.

The next is to solve the t from Eq:(34) and add t into subspace to expand the search subspace, then iterate again with expansive subspace until convergence. The Jacobi-Davidson method has similar convergence properties as inverse iteration if the correction equation is solved exactly.

The details of solving linear eigenvalue problem using Jacobi-Davidson method algorithm are summarized as follows [Wang et al., 2003]:

1. Given $A(\lambda) = \lambda A_1 + A_0$.

2. To choose a random vector $V i$ as the initial subspace.

3. To compute the Galerkin condition as $M_i = V^* A_i V$.

4. To compute the Ritz pairs $(\theta; s)$ of $(\theta M_1 + M_0)s = 0$ and select the desired Ritz pair to be eigenpair with $ksk_2 = 1$.

5. To compute $u = V s$, and the residual $r = A(\theta)u$.

6. If $krk_2 <$ ", $\lambda = \theta$, $x = u$, Quit.

7. To compute correction term t and orthogonalize t against V, $v = t=ktk_2$.

8. Expand $V = [V; v]$.

9. To back to process 3 (Restart : use a few of the last Ritz vectors as initial vectors) and iterate until $krk_2 <$ ".

6.2.2 Conjugate Gradient Method

The Conjugate Gradient method is an effective method for symmetric positive definite systems. It is the oldest and one of the best known nonstationary methods. (Nonstationary methods differ from stationary methods in that the computations involve information that changes at each iteration. Typically , constants are computed by taking inner products of residuals or other vectors arising from the iterative method.) The method proceeds by generating vector sequences of iterates i.e., successive approximations to the solution residuals corresponding to the iterates and search directions used in updating the iterates and residuals. Although the length of these sequences can become large only a small number of vectors needs to be kept in memory. In every iteration of the method two inner products are performed in order to compute update scalars that are defined to make the sequences satisfy certain orthogonality conditions. On a symmetric positive definite linear system these conditions imply that the distance to the true solution is minimized in some norm.

The iterates $x^{(i)}$ are updated in each iteration by a multiple $\alpha_{(i)}$ of the search direction vector $p^{(i)}$:

$$x^{(i)} = x^{(i-1)} + \alpha_{(i)} p^{(i)}:$$

Correspondingly the residuals $r^{(i)} = b - Ax^{(i)}$ are updated as

$$r^{(i)} = r^{(i-1)} - \alpha q^{(i)} \text{ where } q^{(i)} = Ap^{(i)}$$

The choice $\alpha = \alpha_i = r^{(i-1)^T} r^{(i-1)} = p^{(i)^T} Ap^{(i)}$ minimizes $r^{(i)^T} A^{-1} r^{(i)}$ over all possible choices for α. The search directions are updated using the residuals

$$p^{(i)} = r^{(i)} + \beta_{i-1} p^{(i-1)}$$

where the choice $\beta_i = r^{(i)^T} r^{(i)} = r^{(i-1)^T} r^{(i-1)}$ ensures that $p^{(i)}$ and $Ap^{(i-1)}$ or equivalently, $r^{(i)}$ and $r^{(i-1)}$ are orthogonal. In fact one can show that this choice of β_i makes $p^{(i)}$ and $r^{(i)}$ orthogonal to all previous $Ap^{(j)}$ and $r^{(j)}$ respectively.

It uses a preconditioner M; for M = I one obtains the unpreconditioned version of the Conjugate Gradient Algorithm. In that case the algorithm may be further simplified by skipping the "solve" line and replacing $z^{(i-1)}$ by $r^{(i-1)}$.

7 Numerical Results and Conclusions

7.1 Hsu's Equation

7.1.1 A.(Basic Atoms):

$$"\Psi_0(r) = -\frac{1}{2} 5^2 \Psi_0(r) - \frac{Z_I}{jrj}\Psi_0(r) + \frac{1}{2}\Psi_0(r)^* \frac{1}{jr - r^0 j}^+ \tag{37}$$

Atom	Z	Energy	Exp	error
He	2	78.16	79	1.06%
Li$^+$	3	195.79	198	1.11%
Be^{+2}	4	368.80	371	0.59%
B^{+3}	5	595.95	600	0.68%
C^{+4}	6	877.05	882	0.56%

Atom	Z	Energy	Hsu	Error	Iteration	Time	Exp
He	2	78.16	78.63	0.60%	4	00:28	79
Li	3	197.87	201.12	1.62%	4	00:40	203.48
Be	4	386.31	394.24	2.01%	5	02:08	399.14
B	5	647.71	661.72	2.11%	7	03:47	670.96
C	6	984.38	1013.63	2.89%	7	03:50	1030.08
N	7	1406.58	1458.69	3.57%	8	07:48	1486.02
O	8	1929.05	2003.00	3.69%	8	07:51	2043.74

a. The standard Density Functional approach requires 20 or more self-consistency iterations to reach the ground state, but Hsu's formulation spends us only 4-8 self-consistency iterations.

b. For total energy point of view, Hsu's formulation provides good numerical results.

c. When Z=5~10 , the type of P orbit must separate into P_x, P_y, P_z orbits.

d. The contours of 3 orbitals for B are shown in Appendix.

7.1.2 B.(A Simple H_2^+ molecular model):

$$"\Psi_0(r) = -\frac{1}{2} 5^2 \Psi_0(r) - \frac{Z_1}{jr - R_1 j}\Psi_0(r) - \frac{Z_2}{jr - R_2 j}\Psi_0(r) \tag{38}$$

Z1	Z2	Distance	Nucleus energy	Total energy	Exp
(-1,0,0)	(1,0,0)	2	13.6eV	-16.32eV	-16.3eV
(-1,-1,0)	(1,1,0)	$2\sqrt{2}$	9.62eV	-15.79eV	x
(-1,-1,-1)	(1,1,1)	$2\sqrt{3}$	7.85eV	-15.21eV	x

a. During the molecular H_2^+ computation, the most important advantage is to use XYZ coordinates on locating the nucleus.

b. Because this case only has 1 electron, results are very close to experimental values.

c. When the distance of two nucleus is 2 , the energy of H_2^+ is in the most stable situation.

7.1.3   C.(Be with excited states):

$$"\Psi_{2S}(r_1) = -\frac{1}{2}\Gamma^2\Psi_{2S}(r_1) - \overset{\times}{\underset{Z}{}}\frac{Z_I}{jr_1 - R_Ij}\Psi_{2S}(r_1) \tag{39}$$

$$+ \overset{Z}{} d\tau_2\frac{j\Psi_{1S}(r_2)j^2}{jr_1 - r_2j}\Psi_{2S}(r_1) + \frac{1}{2}\overset{Z}{} d\tau_2\frac{j\Psi_{2P}(r_2)j^2}{jr_1 - r_2j}\Psi_{2S}(r_1)$$

$$\mp\frac{1}{2}\overset{Z}{} d\tau_2\frac{\Psi_{2P}^*(r_2)\Psi_{2S}(r_2)}{jr_1 - r_2j}\Psi_{2P}(r_1)$$

	Energy		Exp	Error	Time
Be	386.31		399.14eV	3.21%	02:06
Excited Be	381.98	4.33eV			04:32
Triplet State	384.47	1.84eV	2.72eV	32.35%	04:32
Singlet State	379.49	6.82eV	5.28eV	29.17%	04:32

a. Hsu's new approach Equation admits excited states, but traditional DFT doesn't.

b. We only present $\beta = 0$ version of Hsu's formulation, and the results are still room for improvement.

7.2   Hartree's Results:

$$"\Psi_0(r) = -\frac{1}{2}5^2\Psi_0(r) - \frac{Z_I}{jrj}\Psi_0(r) + (N-1)\Psi_0(r)^{\overset{*}{}}\frac{1}{jr - r^0j}^{\overset{+}{}} \tag{40}$$

Atom	Z	Energy	Exp	Error	Iteration	Time	Hsu
He	2	78.04	79	1.22%	6	00:45	78.63
Li	3	203.32	203.48	0.08%	6	01:11	201.12
Be	4	396.67	399.14	0.62%	8	03:14	394.24
B	5	664.83	670.96	0.91%	17	15:00	661.72

a. As Z is more and more large, and it takes more iterations and time.

b. Numerical results are very good on computing single atom.

7.3   Kohn Sham Equation:

$$(-\frac{1}{2}5^2 + V_{eff})\Psi_i(r) = "_i\Psi_i(r);$$

$$V_{eff} = V_{e-nuc} + V_{e-e} + \frac{\delta E_{xc}}{\delta \rho};$$

$$E_{xc}[\rho(r)] = -\frac{3}{4}(\frac{6}{\pi})^{1=3} \int^{Z} (\rho_{..}^{4=3}(r) + \rho_{\#}^{4=3}(r))dr \qquad (41)$$

Atom	Kin	Vie	Vee	Vxc	E	LSDA Exp	Error
He	77.49	-182.64	55.17	-23.87	-73.85	-74.09	0.32%

a. We review Kohn Sham Equation's results in order to compare with Hsu's results.

7.4 Virial theorem Check

He	Kin	V	Ratio
Hsu	84.97	-161.31	1.898
Hartree	77.39	-155.43	2.008
Kohn Sham	77.48	-151.34	1.953

a. Obviously, Hartree's result obeyes the virial theorem.

7.5 3D Finite Element Codes

a. During our DFT program, the Fortran program is composed of about 2000 lines.

b. $\frac{\text{volume of the largest element}}{\text{volume of the smallest element}} \approx 10000;$

c. For controlling memory efficiently, we use the method of random-pack-storage that only records the value of the nonzero entries of matrices.

d. Now, we mesh usually 117079 nodes(1740293 nonzero terms) or 282639 nodes(4204067 nonzero terms) on the domain in one single machine(CPU:2.4G ;Ram:1G).

e. The Gauss Cubic is a powerful numerical integration that can simplify a complicated integral and obtain a very good approximation.

f. Mesh Generation Tool

Atom He	Ansys	HyperMesh
Node	18974	14576
Energy	66.57	76.31

We observe that quality of grids in HyperMesh is better than in Ansys, but Ansys tool can extend linear element to quadratic element.

HyperMesh

Ansys

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APPENDIX

Atom B eigenvector1

Atom B eigenvector1

Atom B eigenvector1

Atom B eigenvector2

Atom B eigenvector2

Atom B eigenvector2

Atom B eigenvector3

Atom B eigenvector3

Atom B eigenvector3

The flow chart of the FEDFT.

Jacobi-Davidson algorithm

Compute $r^{(0)} = b - Ax^{(0)}$ for some initial guess $x^{(0)}$

for $i = 1, 2, \ldots$

    solve $Mz^{(i-1)} = r^{(i-1)}$

    $\rho_{i-1} = r^{(i-1)^T} z^{(i-1)}$

    if $i = 1$

      $p^{(1)} = z^{(0)}$

    else

      $\beta_{i-1} = \rho_{i-1}/\rho_{i-2}$

      $p^{(i)} = z^{(i-1)} + \beta_{i-1} p^{(i-1)}$

    endif

    $q^{(i)} = Ap^{(i)}$

    $\alpha_i = \rho_{i-1}/p^{(i)^T} q^{(i)}$

    $x^{(i)} = x^{(i-1)} + \alpha_i p^{(i)}$

    $r^{(i)} = r^{(i-1)} - \alpha_i q^{(i)}$

    check convergence; continue if necessary

end

the Preconditioned Conjugate Gradient Method