Understanding The Zhao-Parr Procedure and The Kramers-Henneberger States of Helium

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Certificate of Examination

This is to certify that the dissertation titled **Understanding The Zhao-Parr Procedure and The Kramers-Henneberger States of Helium** submitted by **Mr. Saurabh H. Mhatre(Reg. No. MS13026)** for the partial fulfillment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

Dr. K.R. Shamasundar	Dr. Arijit Kumar De	Dr. P. Balanarayan (Supervisor)

Dated: April 20, 2018

Declaration

The work presented in this dissertation has been carried out by me with Dr. P. Balanarayan at the Indian Institute of Science Education and Research Mohali. This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

Saurabh H. Mhatre
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In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. P. Balanarayan
(Supervisor)

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Saurabh H. Mhatre

"The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, but difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved."

Paul Dirac

"Without error there can be no brilliancy."

Emanuel Lasker

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Abbreviations

a.u.	**a**tomic **u**nits
KH	**K**ramers **H**enneberger
DFT	**D**ensity **F**unctional **T**heory
SCF	**S**elf **C**nsistent **F**ield
TDSE	**T**ime **D**ependent **S**chrödinger **E**quation
KS	**K**ohn **S**ham
CI	**C**onfiguration **I**nteractions
HF	**H**artree **F**ock

Physical Constants

Speed of Light $c = 2.997\ 924\ 58 \times 10^{8}\ ms^{-1}$

Reduced Planck's constant $\hbar = 1.054\ 571\ 80 \times 10^{-34}\ Js$

Charge of an electron $e = 1.602\ 176\ 62 \times 10^{-19}\ C$

Mass of an electron $m = 9.109\ 383\ 56 \times 10^{-31} Kg$

Dedicated to my loving Grandparents.

Abstract

The first part of the work deals with the implementation of Zhao-Parr procedure to find Kohn-Sham orbitals(Ψ) from a given position space electron densities(ρ), which which a route to obtain momentum space densities(γ). An algorithm for the Zhao-Parr procedure is developed on the basis of Hartree-Fock algorithm. In the second part of the work, helium atom in an intense laser field is analyzed with help of the Kramers-Henneberger framework. The possibility of stabilizing KH state using low frequencies is proposed and being investigated.

Chapter 1

Introduction to Density Functional Theory

According to the quantum mechanical postulate, every physical system consisting of particles is defined by a wave function, which determines every property of the system. Most of the early electronic theory calculations were directed towards determining these wave functions. But these calculations tend to get very complex and tedious with exponential computational complexity for many particles systems. Density functional theory provides us with an alternate approach in which electron density distribution is the focal point rather than the electronic wave function.

1.1 Historical background

Since the inception of wave mechanics, when Schrödinger gave his wave equation in 1926[2], electronic structure calculations were all about approximating wave function of many particle system. Although the most primitive version of DFT-'Thomas Fermi Model' was published only few year after the wave equation, its failure for systems other than jellium model[3] reduced its appeal to the scientific community. About five decades ago, Hohenberg-Kohn(1964)[4] and Kohn-Sham(1965)[5] laid the foundation of Density functional theory, potentially bringing down the complexity of N-electron systems calculations and cost of computations. It's popularity had gone up exponentially, since 1990's due to the advancement of more accurate approximations of exchange-correlation energy functionals.

1.2 Thomas Fermi Model

Just a few years after Schrödinger gave his wave equation, Lewellyn Thomas and Enrico Fermi separately worked out one of the earliest schemes for solving the many electron problem based on electron density($\rho(\vec{r})$) as a basic variable. The electron density is defined as[6],

$$\rho(\vec{r}) = \int \Psi^*(\vec{r}, \vec{r_2}, \vec{r_3}, ..., \vec{r_N})\Psi(\vec{r}, \vec{r_2}, \vec{r_3}, ..., \vec{r_N})dr_2dr_3...dr_N \tag{1.1}$$

In this model, the energy equation is given in terms of a functional of electron density as,

$$E^{TF}[\rho(\vec{r})] = T^{TF}[\rho(\vec{r})] + \int \rho(\vec{r})v_{ext}(\vec{r})d^3r + \frac{1}{2}\int\int \frac{\rho(\vec{r})\rho(\vec{r'})}{|\vec{r} - \vec{r'}|}d^3rd^3r' \tag{1.2}$$

The last two terms are nuclear-electron Coulomb attraction($v_{ext} = -\int Z/|\vec{r} - \vec{R}|d^3R$) and electron-electron repulsion respectively. Assuming that electrons are uniformly distributed over the space(uniform electron gas), one can obtain using Fermi-Dirac Statistics the first term in which kinetic energy of electrons is given by[3]

$$T^{TF}[\rho(\vec{r})] = C_k \int \rho(\vec{r})^{5/3}d^3r \tag{1.3}$$

where $C_k = \frac{3}{10}(3\pi^2)^{2/3}$. THe Thomas-Fermi model has many shortcomings. Mainly due to the manner in which kinetic energy is approximated. Electron density distribution is assumed to be uniform but this is not true for real systems. It does not lead to any chemical binding. However, it does give a relation between $\rho(\vec{r})$ and external potential $v(\vec{r})$ experienced by an electron. In one way, this idea was the starting point for Walter Kohn's more practical Density Functional Theory(DFT).

1.3 1^{st} Hohenberg-Kohn Theorem

DFT starts with the question, whether the electron density distribution $\rho(\vec{r})$ characterizes the system exactly. The first founding theorem given by Hohenberg and Kohn takes care of this. It states that *the ground state density* $\rho(\vec{r})$ *of a bound system of interacting electrons in some external potential* $v(\vec{r})$ *determines this potential uniquely* There is a very simple proof for this theorem.

Suppose a system of N electrons in the potential $v_1(\vec{r})$ has a non-degenerate ground state density $\rho(\vec{r})$ with corresponding spatial groundstate wave function Ψ_1 and energy E_1, then

$$\begin{aligned} E_1 &= \langle\Psi_1|\hat{H}_1|\Psi_1\rangle && (1.4)\\ &= \int v_1(\vec{r})\rho(\vec{r})d^3r + \langle\Psi_1|(\hat{T}+\hat{U})|\Psi_1\rangle, && (1.5)\end{aligned}$$

where $\hat{H}_1$ is a total Hamiltonian of a system in the $v_1(\vec{r})$ potential. $\hat{T}$ and $\hat{U}$ are kinetic energy operator and Coulomb interaction operator respectively.

Now, let us assume that there exists another potential $v_2(\vec{r})$ for the same system which is not equal to $v_1 + constant$ with ground state wave function Ψ_2 which also gives rise to the same $\rho(\vec{r})$, such that,

$$E_2 = \int v_2(\vec{r})\rho(\vec{r})d^3r + \langle\Psi_2|(T+U)|\Psi_2\rangle. \tag{1.6}$$

By the variational principle,

$$E_1 < \langle\Psi_2|H_1|\Psi 2\rangle = \int v_1(\vec{r})\rho(\vec{1})d^3r + \langle\Psi_2|(T+U)|\Psi_2\rangle \tag{1.7}$$

using the relation given by Equation(1.6),

$$E_1 < E_2 + \int [v_1(\vec{r}) - v_2(\vec{r})]\rho(\vec{r})d^3r \tag{1.8}$$

Similarly, we have

$$E_2 < E_1 + \int [v_2(\vec{r}) - v_1(\vec{r})]\rho(\vec{r})d^3r \tag{1.9}$$

Adding Equations (1.8) and (1.9) gives,

$$E_1 + E_2 < E_2 + E_1 \tag{1.10}$$

which is a contradiction. Thus, by *reductio ad absurdum* the assumption that there exists another potential which gives the same $\rho(\vec{r})$, is invalid. It is worth noting that even though we have proved each potential($v(\vec{r})$) is unique to the corresponding density ($\rho(\vec{r})$), this doesn't assure that each density can represent some kind of potential. This known as v-representability of problem of DFT.

As the density determines the external potential $v(\vec{r})$ and also number of electrons, $N = \int \rho r dr$, it gives us the total Hamiltonian of the system, defining its all properties including the wave function.

1.4 2^{nd} Hohenberg Kohn Theorem

The second theorem given by Hohenberg and Kohn lays down a principle for obtaining solution variationally which is the common procedure in quantum mechanics. It basically states that *the exact ground state density minimizes the total energy of a system.* In other words, one can find ground state density variationally.

As mentioned earlier, the electron density $\rho(\vec{r})$ determines the external potential($v(\vec{r})$) of a system. This $v(\vec{r})$ and the number of electrons(N) determines the total Hamiltonian($\hat{H}$) of the system, thus the entire system, including the wave function(Ψ) of the system.
If for a certain ground state density(ρ_g) of a system, Ψ_g is the ground state wave function such that,

$$E_g[\rho] = \langle \Psi_g | \hat{H} | \Psi_g \rangle \tag{1.11}$$

then,

$$E_g[\rho] = \int v(\vec{r})\rho_g(\vec{r})d^3r + F[\rho_g] \tag{1.12}$$

where, $F[\rho] = \langle\Psi|\hat{T} + \hat{V}|\Psi\rangle$ is an *universal functional* as for the kinetic energy and interactions energy remain same for N number of electrons and are independent of external potential $v(\vec{r})$.

Now, if we have some Ψ(not necessarily Ψ_g) which gives some density(again not necessarily ρ_g), then according to the variational principle, energy obtained from this wave functions will be greater than or equal to ground state energy,

$$\begin{aligned} E_g[\rho] \leq E[\rho] &= \langle\Psi|\hat{H}|\Psi\rangle \\ &= \int \rho(\vec{r})v(\vec{r})d^3r + F[\rho] \end{aligned} \tag{1.13}$$

such that, minimizing the energy with respect to both Ψ and ρ one gets,

$$\begin{aligned} E_g[\rho] &= \int \rho_g(\vec{r})v(\vec{r})d^3r + \langle\Psi_g|\hat{T} + \hat{V}|\Psi_g\rangle \\ &\leq \int \rho^{min}(\vec{r})v(\vec{r})d^3r + \langle\Psi^{min}|\hat{T} + \hat{V}|\Psi^{min}\rangle = E[\rho] \end{aligned} \tag{1.14}$$

This is known as second Hohenberg Kohn Theorem or Hohenberg Kohn variational principle. The above proof was given in independent works by Levy[8] and Lieb[9] which is famously known as Levy-Lieb constrained search method.

1.5 Levy-Lieb Constrained Search Method

Following the HK variational principle, Levy[8] and Lieb[9] proposed a method for obtaining ground state energy in two steps. Each step consists of minimizing energy by fixing one of the wave function Ψ or density ρ.

In first step, trial density $\rho^\star(\vec{r})$ is fixed and trial wave functions Ψ^i which give trial density $\rho^\star(\vec{r})$ are varied to find constrained minimum energy.

$$E_v[\rho^\star] = min_{\Psi\rightarrow\rho^\star}\langle\Psi^i|\hat{H}|\Psi^i\rangle \tag{1.15}$$
$$= \int \rho^\star(\vec{r})v(\vec{r})d^3r + F[\rho^\star] \tag{1.16}$$

where,

$$F[\rho^\star] = min_{\Psi\rightarrow\rho^\star}\langle\Psi^i|\hat{T}+\hat{V}|\Psi^i\rangle \tag{1.17}$$

In this step, one needs to somehow get or approximate the universal functional and obtain the minimum energy($E_v[\rho^\star]$) for the particular density (or potential). Then in the second step, energy is minimized over all trial densities $\rho^\star(\vec{r})$,

$$E_g \leq E[\rho^\star] = min_{\rho^\star}E_v[\rho^\star] \tag{1.18}$$

In this way, the problem is reduced from finding minimum energy with respect to trial wave functions with 3N degrees of freedom to a simpler problem of finding minimum energy with respect to density in 3 dimensional space. Here, one must note that trying to solve $F[\rho]$ explicitly, makes the problem 3N-dimensional. So, the better formulation and approximation of $F[\rho]$ has been the foremost concern among DFT developers, such that problem of ground state energies can be strictly formulated in terms of densities.

1.6 Kohn Sham Equations

In 1928, Hartree proposed an approximate description of the electronic structure of an atom with self-consistent single particle Schrödinger equations, treating every electron moving in an effective single particle potential. So, i^{th} particle equation is given as,

$$\Big\{-\frac{1}{2}\nabla_i^2 + v_{eff}(\vec{r})\Big\}\psi_i = \epsilon_i\psi_i \tag{1.19}$$

where,

$$v_{eff} = -\frac{Z}{r} + \int \frac{\rho(\vec{r'})}{|\vec{r} - \vec{r'}|} d^3r' \tag{1.20}$$

Here the first term is an electrostatic attraction between the nucleus and electron with Z as the atomic number. The second term is the potential experienced by an electron due to the continuous electronic density distribution $\rho(\vec{r})$ in the space. The above equations are called as self-consistent Hartree equations.

So, in light of self-consistent Hartree equations, Walter Kohn and Lu Sham laid out self consistent scheme for DFT with the use of HK theorems in 1965. At the start, let's assume a system of noninteracting electrons moving in an external potential $v(\vec{r})$, say nuclear-electron attraction, such that electrons will only possess pure kinetic energy(T_s). Then from the HK variational principle,

$$E_v[\rho] = T_s[\rho(\vec{r})] + \int \rho(\vec{r}) v(\vec{r}) d^3r \geq E_g \tag{1.21}$$

where,

$$T_s[\rho] \;=\; \sum_{i=1}^{N} \langle \psi_i | -\frac{1}{2}\nabla^2 | \psi_i \rangle \tag{1.22}$$

and $\rho(\vec{r})$ is defined in terms of single particle orbitals as,

$$\rho(\vec{r}) = \sum_{i=1}^{N} |\psi_i(\vec{r})|^2 \tag{1.23}$$

A constraint is applied on the number of electrons, N, such that, $N = \int \rho(\vec{r}) d^3r$. Using Euler-Lagrange equations and minimizing energy with respect to $\rho(\vec{r})$,

$$\delta E_v[\rho(\vec{r})] = \delta T_s[\rho(\vec{r})] + \int \{v(\vec{r}) - \epsilon\} \delta\rho d^3r = 0 \tag{1.24}$$

where ϵ is an unknown Lagrange multiplier. After functional differentiation with respect to ψ_i^* to find single particle orbital equations, one gets,

$$\Big\{-\frac{1}{2}\nabla^2 + v(\vec{r}) - \epsilon_i\Big\}\psi_i = 0 \tag{1.25}$$

The ground state energy, which is in principle exact, for a noninteracting electrons system is given by

$$E_g = \sum_{i=1}^{N} \epsilon_i \tag{1.26}$$

Above orbital equations resemble the Hartree equations, and hence can be solved self-consistently. Following a similar procedure, it is easy to find similar Kohn Sham equations for more complex, interacting systems.

Here the derivation of KS equations for an interacting system of electrons is presented as this result will be useful in the work given in the next chapter. Now, the energy equation for an interacting electrons system is given by

$$E_v[\rho(\vec{r})] = T_s[\rho(\vec{r})] + \int \rho(\vec{r})v_{ext}(\vec{r})d^3r + \frac{1}{2}\int \frac{\rho(\vec{r})\rho(\vec{r'})}{|\vec{r}-\vec{r'}|}d^3rd^3r' + E_{xc}[\rho(\vec{r})] \geq E_g \tag{1.27}$$

First two terms are familiar noninteracting kinetic energy and external potential interactions respectively. The third term indicates a coulomb interaction between two electrons or in this case average electrostatic potential seen by the particle at the particular point in the space. The last term, E_{xc} is the exchange-correlation energy of which exact form is unknown. Euler-Lagrange equation for N number of electrons is,

$$\delta E_v[\rho(\vec{r})] = \delta T_s[\rho(\vec{r})] + \int \{v_{eff}(\vec{r}) - \epsilon\}\delta\rho d^3r = 0 \tag{1.28}$$

where,

$$v_{eff}(\vec{r}) = v_{ext}(\vec{r}) + \int \frac{\rho(\vec{r'})}{|\vec{r}-\vec{r'}|}d^3r' + \frac{\delta E_{xc}[\rho(\vec{r})]}{\delta\rho(\vec{r})} \tag{1.29}$$

Similar to noninteracting system case, here particle is moving in a effective potential $v_{eff}(\vec{r})$ instead of $v(\vec{r})$. Using earlier treatment, we get similar KS eqations,

$$\Big\{ -\frac{1}{2}\nabla^2 + v_{eff}(\vec{r}) - \epsilon_i \Big\}\psi_i = 0 \tag{1.30}$$

We will be using this result in next chapter and derive Kohn Sham equations, when the exact physical electron density, experimental or from accurate wave function based calculations, is known. The quality of approximation for $E_{xc}[\rho(\vec{r})]$ dictates the reliability of DFT ground state, and there has lot of effort been made to approximate form of $E_{xc}[\rho(\vec{r})]$ which simple as well as reasonably accurate.

1.7 Momentum Space Densities from Position Space Electron Densities

Electron densities, both momentum space $\gamma(\vec{p})$ and position space $\rho(\vec{r})$, are experimentally measurable quantities complementing to each other in respective space. The wave functions in momentum space $\Phi(\vec{p})$ and position space $\Psi(\vec{r})$ are complementary quantities and related to each other by Fourier transform[3],

$$\begin{aligned}\Phi(\vec{p_1}, \vec{p_2}, ...\vec{p_N}) = \frac{1}{(2\pi)^{3N/2}} \int & \Psi(\vec{r_1}, \vec{r_2}, ...\vec{r_N}) \\ & \times e^{i\sum_{j=1}^{N} \vec{p_j}.\vec{r_j}} d^3r_1 d^3r_2 ......d^3r_N\end{aligned} \tag{1.31}$$

The respective densities are given by[3],

$$\rho(\vec{r}) = N \int |\Psi(\vec{r}, \vec{r_2}, ...\vec{r_N})|^2 d^3r_2.....d^3r_N \tag{1.32}$$

$$\gamma(\vec{p}) = N \int |\Phi(\vec{p}, \vec{p_2}, ...\vec{p_N})|^2 d^3p_2.....d^3p_N \tag{1.33}$$

But there is no direct relation between $\rho(\vec{r})$ and $\gamma(\vec{r})$. So the question arises whether one can calculate momentum space density given only the electron density? One can employ Zhao-Parr procedure, which is discussed in detail in next chapter, to obtain Ψ from ρ and then from this Ψ, γ can be easily calculated.

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Chapter 2

Zhao-Parr Formalism

In 1992, Q. Zhao and R. Parr[1] gave a method to calculate Kohn-Sham orbitals from a given(experimental or calculated) electron density. This scheme uses the fact that, density dectates the unique potential for the system(in other words, density defines the system), as stated in first Hohenberg-Kohn theorem.

2.1 Kohn-Sham Equations from Zhao and Parr

In their novel approach Zhao and Parr used the following constraint[1], [2]:

$$C = \int \frac{[\rho(\vec{r}) - \rho_0(\vec{r})][\rho(\vec{r'}) - \rho_0(\vec{r'})]}{|\vec{r} - \vec{r'}|} d^3r d^3r' \tag{2.1}$$

such that $C = 0$, when calculated density is equal to target density. The constraint is physically follows from electrostatics[9]. If we apply this constraint, we get Kohn-Sham equation as follows[1], [2], [3],

$$\left\{\frac{1}{2}\nabla^2 + \lambda \int \frac{\rho(\vec{r'}) - \rho_0(\vec{r'})}{|\vec{r} - \vec{r'}|} d^3r'\right\}\psi_i = \epsilon_i \psi_i \tag{2.2}$$

here, $v_{eff}(\vec{r}) = \int \frac{\rho(\vec{r}) - \rho_0(\vec{r})}{|\vec{r} - \vec{r'}|} d^3r'$ is an external potential of the system and λ is an unknown Lagrange multiplier. So, to get useful Kohn-Sham orbitals out of these equations we need find the value of λ for which $\rho(\vec{r}) \approx \rho_0(\vec{r})$ where $\rho(\vec{r}) = \sum_i |\psi_i(\vec{r})|^2$.

2.2 Implementing the self consistent procedure

Solving Kohn-Sham equations is a self-consistent procedure, as one starts with some trial density $\rho(\vec{r})$, constructs $v_{eff}(\vec{r})$ from it, then solves the equation for wave functions $\psi_i(\vec{r})$; from these wave functions one recalculates the density. This recalculated density should be equal to the density, one started with. If that is not the case, then whole procedure should be repeated with a newly calculated density. It is very normal in electronic structure theory to solve the problems using this procedure. This was first introduced for solving self-consistent Hartree equations. The intricacies of the procedure are detailed in subsequent sections

2.3 Hartree-Fock algorithm

The Hartree-Fock method is a numerical way of solving many body Schrödinger equations for an atom or a molecule described in the Born-Oppenheimer approximation. In this frame work, a single Slater determinant is used to describe energy eigenfunction.

$$\widehat{H}|\Psi_0\rangle = E|\Psi_0\rangle \tag{2.3}$$

The Slater determinant represents the antisymmetric nature of one electron orbitals(wave functions) obeying Pauli exclusion principle. the wave function is given as[6],

$$|\Psi_0\rangle = |\chi_1\chi_2\chi_3 \cdots \chi_N\rangle \tag{2.4}$$

where, χ_i is a spin orbital[6],

$$\chi_i(x) = \begin{cases} \psi_j(r)\alpha(\omega) \\ \psi_j(r)\beta(\omega). \end{cases}$$

Hamiltonian is designed within a mean field approximation as,

$$\Big\{\hat{h}(1) + \sum_{b\neq a} \hat{J}_b(1) - \sum_{b\neq a} \hat{K}_b(1)\Big\}\chi_a(1) = \epsilon_a\chi_a(1) \tag{2.5}$$

$$\hat{f}(1)\chi_a(1) = \epsilon_a\chi_a(1) \tag{2.6}$$

where,

$$\hat{h}(1) = -\frac{1}{2}\nabla_1^2 - \sum_A \frac{Z_A}{|r_1 - R_A|} \tag{2.7}$$

is the kinetic energy and the potential energy due to nuclear attraction of electron one. And it is one electron operator. The other two terms are[6]

$$\hat{J}_b(1) = \int \chi_b^*(2) r_{12}^{-1} \chi_b(2) d^3r_2 \tag{2.8}$$

which is the Coulomb electron-electron repulsion operator and

$$\hat{K}_b(1) = \int \chi_b^*(2) r_{12}^{-1} \chi_a(2) d^3r_2 \tag{2.9}$$

is the exchange operator. Both of these operators are two electron operators. And the total Hamiltonian operator $\hat{f}(1)$ is called the Fock operator.

Here, for simplicity, we are only going to consider closed-shell restricted HF formalism. In this formalism, one conveniently integrates out spin part and eigenvalue equations is represented in terms of doubly occupied spatial orbitals $(\psi_a|a = 1, 2, ..., N/2)$.

$$\hat{f}(1)\psi_i(1) = \epsilon_i\psi_i(1) \tag{2.10}$$

$\hat{f}(1)$ is a closed-shell Fock operator,

$$\hat{f}(1) = \hat{h}(1) + \sum_{a}^{N/2} 2\hat{J}_a(1) - \hat{K}_a(1) \tag{2.11}$$

To solve these equations numerically, the unknown spatial wave function is expressed in terms of a set of M number of known spatial basis set, such that

$$\psi_i = \sum_{u=1}^{M} C_{ui}\phi_u \tag{2.12}$$

where $i = 1, 2, ..., M$. If the basis set$\{\phi_i\}$ is complete, then this will be an exact expansion, leading to a numerically exact solution of the problem. To make it complete one has to take very very large basis set($M \to \infty$). But this can not be achieved due to practical computational reasons.

Now, the problem of calculating molecular orbitals reduces to the problem of calculating coefficients C_{ui} of the known basis functions in the expansion.

$$f(1)\sum_{v} C_{vi}\phi_v(1) = \epsilon_i \sum_{v} C_{vi}\phi_v(1) \tag{2.13}$$

After multiplying by $\phi_u^*(1)$ to the left and then integrating, we get a matrix form of the Hartree-Fock equations,

$$\sum_{v} C_{vi} \int \phi_u^*(1) f(1)\phi_v(1) d^3r_1 = \epsilon_i \sum_{v} C_{vi} \int \phi_u^*(1)\phi_v(1) d^3r_1 \tag{2.14}$$

$$\sum_{v} F_{uv}C_{vi} = \epsilon_i \sum_{v} S_{uv}C_{vi} \tag{2.15}$$

where, S_{uv} and F_{uv} are overlap matrix and Fock matrix respectively.

$$S_{uv} = \int \phi_u^*(1)\phi_v(1) \tag{2.16}$$

$$F_{uv} = \int \phi_u^*(1) f(1)\phi_v(1) \tag{2.17}$$

These are known as Roothaan equations. For implementing the Hartree-Fock method, one needs explicit form of Fock matrix F which represents Fock operator$\hat{f}(1)$ [6]

$$\begin{aligned} F_{uv} &= \int \phi_u^*(1)\hat{f}(1)\phi_v(1)d^3r_1 \\ &= \int \phi_u^*(1)\hat{h}(1)\phi_v(1)d^3r_1 + \sum_a^{N/2} \int \phi_u^*(1)[2\hat{J}_a(1) - \hat{K}_a(1)]\phi_v(1)d^3r_1 \\ &= H_{uv}^{core} + \sum_a^{N/2} [2(uv|aa) - (ua|av)] \end{aligned} \tag{2.18}$$

where,

$$(uv|yz) = \int \phi_u^*(1)\phi_v(1)r_{12}^{-1}\phi_y^*(2)\phi_z(2)d^3r_1d^3r_2 \tag{2.19}$$

and H_{uv}^{core} is a core-Hamiltonian matrix[6],

$$H_{uv}^{core} = \int \phi_u^*(1)\hat{h}(1)\phi_v(1)d^3r_1 \tag{2.20}$$

By expanding $\hat{h}(1)$, one can see that H_{uv}^{core} matrix consist of two kinds of integrals - the kinetic energy integrals(T_{uv}) and nuclear attraction integrals(V_{uv}^{nucl})[6],

$$H_{uv}^{core} = T_{uv} + V_{uv}^{nucl} \tag{2.21}$$

where,

$$T_{uv} = \int \phi_u^*(1)\{-\frac{1}{2}\nabla_1^2\}\phi_v(1)d^3r_1 \tag{2.22}$$

$$V_{uv}^{nucl} = \int \phi_u^*(1)\Big\{ -\sum_A \frac{Z_A}{|r_1 - R_A|}\Big\}\phi_v(1)d^3r_1 \tag{2.23}$$

Now, returning to the solution of Fock matrix,

$$\begin{aligned} F_{uv} &= H_{uv}^{core} + \sum_a^{N/2}\sum_{zy} C_{za}C_{ya}^*[2(uv|yz) - (uz|yv)] \\ &= H_{uv}^{core} + \sum_{zy} P_{yz}[(uv|yz) - (uz|yv)/2] \end{aligned} \tag{2.24}$$

where, P is a charge density bond order matrix given as,

$$P_{uv} = 2\sum_{a}^{N/2} C_{ua}C_{va}^{*} \tag{2.25}$$

So, the final expression for Fock matrix becomes,

$$F_{uv} \quad = \quad H_{uv}^{core} + G_{uv} \tag{2.26}$$

where H_{uv}^{core} is the one electron integral part and G_{uv} is the two electron integral part. The large number of integral evaluations in calculation of G_{uv} matrix is the major difficulty in Hartree Fock calculations.

Once the Fock matrix is specified, one has to convert the Roothaan's equations($FC = SC\epsilon$) into usual eigenvalue equations($FC = C\epsilon$) which is the case with orthonormal basis set. So, now if we had a non-orthogonal basis, it should be orthogonalized using transformation matrix (X) such that[6],

$$X^{\dagger}SX = I \tag{2.27}$$

Using symmetric orthogonalization, we can get transformation matrix,

$$X \equiv S^{-1/2} = Us^{-1/2}U^{\dagger} \tag{2.28}$$

where, $s = U^{\dagger}SU$. Now, suppose a new coefficient matrix C' such that $C = XC'$ and substituting it into Roothaan's equations gives us transformed Roothan equations[6], [9],

$$\begin{aligned} FXC' &= SXC'\epsilon \\ (X^{\dagger}FX)C' &= (X^{\dagger}SX)C'\epsilon \\ F'C' &= C'\epsilon \end{aligned} \tag{2.29}$$

Solution of above eigen value equation can be found by diagonalizing transformed Fock matrix($F' = X^{\dagger}FX$). Ground state energy at each iteration in the HF method is given by,

$$E = \frac{1}{2}\sum_{u}\sum_{v} P_{vu}(H_{uv}^{core} + F_{uv}) \tag{2.30}$$

2.3.1 Implementing HF(SCF) method

1. First, specify the atom or molecule ie. nuclear charge(Z_A), coordinates(R_A) and number of electons(N) and choose a known basis set. Taking into consideration computational ease and reasonable reliability, we chose single centered s-type Gaussian basis set.

$$\phi_i(r) = Ne^{-\alpha|r|^2} \tag{2.31}$$

where α is an exponent and N is the normalization constant given by,

$$N = \Big(\frac{2\alpha}{\pi}\Big)^{3/4} \tag{2.32}$$

2. Calculate S,H^{core} and two electron integrals($ab|cd$). In our case these have forms as follows[7],

$$S(a,b) = N^2\Big(\frac{\pi}{(a+b)}\Big)^{3/2} \tag{2.33}$$

$$H^{core}(a,b) = \frac{3ab}{a+b} + \frac{2}{\pi^{1/2}}(a+b)^{1/2}S(a,b) \tag{2.34}$$

and,

$$(ab|cd) = 2\Big(\frac{(a+b)(c+d)}{\pi(a+b+c+d)}\Big)^{1/2}S(a,b)S(c,d) \tag{2.35}$$

3. Get transformation matrix X by diagonalizing S matrix. And get guess P matrix. Here we got P matrix using H^{core} diagonalization.

4. Calculate G matrix from P matrix and the two electron integrals $(ab|cd)$ and obtain Fock matrix $F = H^{core} + G$.

5. Calculate transformed Fock matrix F'.

6. Diagonalize F' to get C' and ϵ.

7. Get back coefficient matrix $C = XC'$.

8. Form a new P matrix from coefficient matrix C. If the new density matrix is equal to previous density matrix within some convergence threshold criterion, then we can say that our procedure is converged. And if this is not the case, then repeat the procedure from step 4 with the new density matrix P.

2.4 Density Fitting Algorithm

The Zhao-Parr formalism demands the actual spatial electron density to be provided in order to get the Kohn-Sham orbitals.But this density is often provided in position space grid rather than some analytical form. So, here we propose an fitting algorithm using basis set expansion of Gaussian functions.

Suppose we have been provided with $\rho_0(\vec{r})$-an grid based density. We can represent it as an expansion in terms of basis set$\{\varphi\}$.

$$\rho_0(\vec{r}) = \sum_i d_i \varphi_i(\vec{r}) \tag{2.36}$$

Setting up a least squares,

$$\Delta = \min_{d_i} |\rho_0(\vec{r}) - \sum_i d_i \varphi_i|^2 \tag{2.37}$$

After minimizing, we get,

$$\int \rho_0(\vec{r})\varphi_i(\vec{r}) d^3r = \sum_j d_j \int \varphi_i^*(\vec{r})\varphi_j(\vec{r}) d^3r \tag{2.38}$$

These are the matrix equations of the form,

$$\begin{aligned} P_r &= S_{ij} D \\ D &= S^{-1} P_r \end{aligned} \tag{2.39}$$

This is easy enough equation to solve, provided S is invertible. This algorithm is coded and tested for functions and different systems. Some of them are shown below.

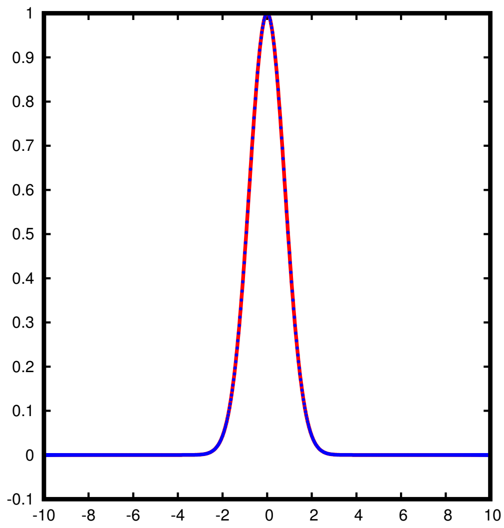

FIGURE 2.1: (a)$\rho(r) = e^{-\pi r^2/4}$ fitting with $\sigma = 2.45 \times 10^{-2}$.

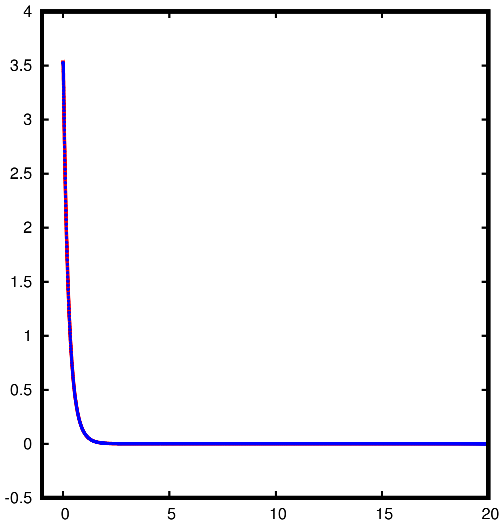

FIGURE 2.2: Fit of Helium atom ground state density with $\sigma = 2.629 \times 10^{-3}$.

2.5 Zhao-Parr KS orbitals Algorithm

Given the similarities between Kohn-Sham equations and Hartree-Fock equations, solving them is almost similar to where equations turn into non linear eigenvalue problem, $F^{KS}C = SC\epsilon$. Specifying the Hamiltonian matrix F^{KS} which is analogous to the Fock matrix, is the only difference in between HF method and KS SCF.

In the case of Zhao-Parr formalism, F^{KS} becomes,

$$F^{KS}_{uv} = H^{core}_{uv} + \lambda \int \phi^*_u(\vec{r}) \frac{(\rho(\vec{r'}) - \rho_0(\vec{r'}))}{|\vec{r} - \vec{r'}|} \phi_v(\vec{r}) d^3r d^3r' \tag{2.40}$$

where, H^{core} solely consist of the kinetic energy[1] and nuclear attraction potential energy part can be included for faster convergence[3]. So, for single centered s-type Gaussian basis functions, we have already seen H^{core}'s analytical form. The second term in F^{KS} equations, can be broken down into two terms

$$V_\rho = \left\langle \phi_u \right| \int \frac{\rho(\vec{r'})}{|\vec{r} - \vec{r'}|} d^3r' \left| \phi_v \right\rangle \tag{2.41}$$

which is nothing but the two electron integral as we solved in HF method and also has analytical form for Gaussian type basis functions as seen earlier. And the other term is,

$$V_{\rho_0} = \left\langle \phi_u \right| \int \frac{\rho_0(\vec{r'})}{|\vec{r} - \vec{r'}|} d^3r' \left| \phi_v \right\rangle \tag{2.42}$$

This term can be solved by numerical integration or by finding an analytical form depending upon the form in which ρ_0 is provided. Using the fitting procedure, discussed earlier, one can represent the grid based density in very convenient Gaussian basis. Then the above equation can be written as,

$$V_{\rho_0} = \left\langle \phi_u \right| \sum_i \int \frac{d_i \varphi_i(\vec{r'})}{|\vec{r} - \vec{r'}|} d^3r' \left| \phi_v \right\rangle \tag{2.43}$$

And for Gaussian basis($\{\varphi_i\} \equiv e^{-\delta_i r^2}$) this integral takes following form($\{\phi_u\}$-single centered s-type Gaussian basis set),

$$V_{\rho_0} = N_a N_b N_\delta \frac{2\pi^{5/2}}{(a+b)\delta(a+b+\delta)} \tag{2.44}$$

After specifying F^{KS}, it is fairly easy task to perform SCF method and obtain Kohn-Sham orbitals.

2.6 Numerical Results

The code is tested for two systems with reasonable results: (1) a test Gaussian density $e^{\pi r^2/4}$ and (2) the helium atom density(He density is obtained from GAMESS). It is observed that as Lagrange multiplier λ increases the density(ρ) tends to converge at given density(ρ_0) till certain critical λ. After that ρ decreases little more and then converges as λ goes to infinity.

Although we would have liked to extend our calculations to the systems with more than two electrons, the increasing complexity and restricted time frame prevented us from doing so. Yet, the ZP procedure remains a promising method and needs more research to be carried out.

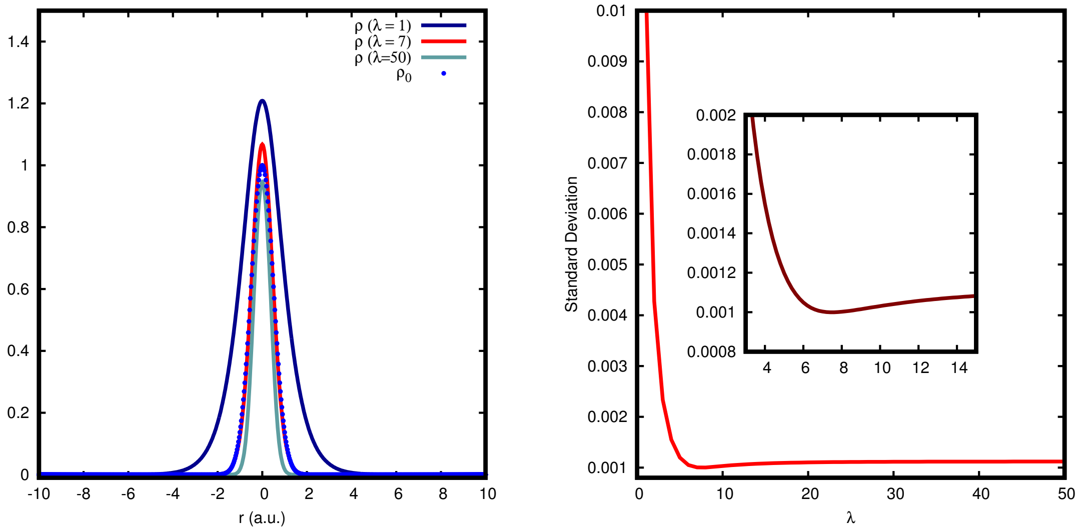

Figure 2.3: (a)Comparing known test density(ρ_0) and calculated density(ρ) (b)Plot of Standard Deviation with varying λ.

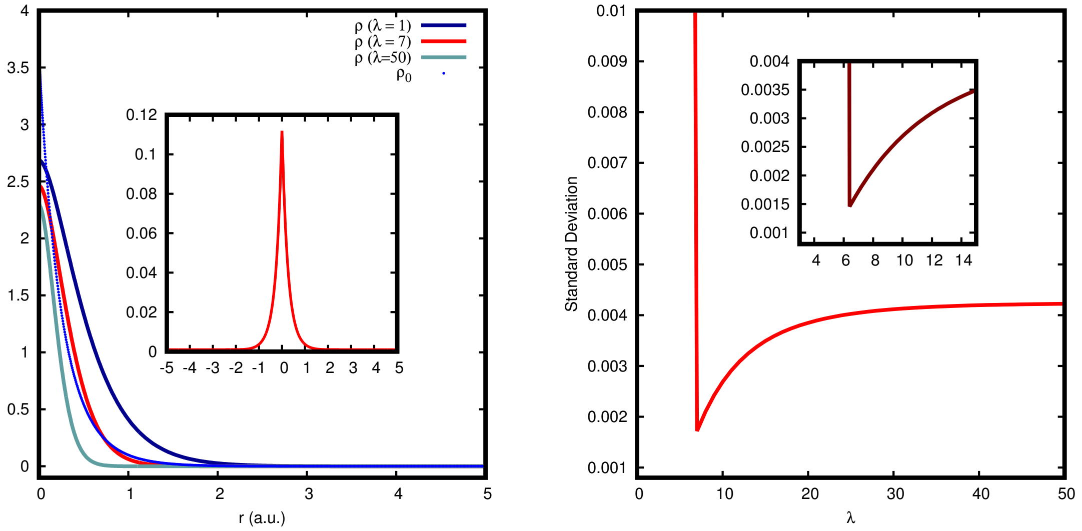

Figure 2.4: (a)Comparing known He density(ρ_0) and calculated density(ρ). (Embeddeed plot) calculated wavefunction of He. (b)Plot of Standard Deviation with varying λ.

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Chapter 3

Kramers-Henneberger State of He atom

3.1 Laser-atom interactions

Laser-atom interactions has been the 'hot topic' over past few decades. According to Einstein's photoelectric effect[1](1905), under electromagnetic radiations, atoms can emit electrons which gain energy from the light photons to get excited and eventually ionize. This causes ionization of the electron in an atom. So, it is very intuitive to say, more the number of photons in the radiation i.e. high intensity, more ionization should occur. And in many cases this is exactly true. But in 1976, Gersten and Mittleman[2] proposed that beyond certain laser conditions electron can get stabilized instead of ionizing due to its quiver motion in a high intensity and high frequency oscillating field.

In the presence of super-intense lasers, when the laser field is comparable or even stronger than normal electric field inside the atom, the system can no longer be treated by traditional perturbation theory. The electron experiences a binding potential due to the nuclear attraction force and the strong laser field instead of plain Coulomb forces which put together an atom. This new system which is stable against ionization is called as laser-dressed atom. As the field gets stronger, the electron, in some sense, becomes free by interacting with light wave and relatively ignoring the nuclear binding forces. But still this unbound electron which has gain massive kinetic energy could not simply break free, because of the oscillating electric force of light wave with electron exhibiting oscillating motion, moving back and forth in the direction of laser polarization. In this process, the 'unbound ' electron becomes stable with respect to ionization.

To fully understand this electron 'stabilization ', one should switch the frame of reference from laboratory frame to oscillating frame of electron where the electron remains stationary and sees a potential as averaged out over its oscillations. This switched frame is popularly known as Kramers-Henneberger frame and the mathematical procedure of switching is called as Kramers-Henneberger transformation.

3.2 Kramers-Henneberger transformation

When KH transformation was first introduce by Henneberger(1968)[3], it was not in the context of laser fields. It was Gavrila *et al.*[4] first used this frame work to explain Hydrogen atom under high frequency laser fields. In this transformation the time-dependent Hamiltonian expressed in terms a transformed Hamiltonian in which time dependent part of the Hamiltonian is included into the potential term.

Time-dependent Schrödinger equation in atomic units under dipole approximation for an atom in a oscillating vector field takes the form[5],

$$i\frac{\partial\psi(\vec{r},t)}{\partial t} = \Big\{ -\frac{[i\vec{p}+(q/c)\vec{A}(t)]^2}{2m} + V(\vec{r})\Big\}\psi(\vec{r},t) \tag{3.1}$$

where $\vec{A}(t)$ and $V(\vec{r})$ are the vector and scalar potentials. To achieve the aim of the transformation which is to remove time-dependent dipole term from the Hamiltonian, one can perform unitary transformation on wave function($\psi(\vec{r},t)$),

$$\psi^{KH}(\vec{r},t) = \hat{U}\psi(\vec{r},t) \tag{3.2}$$

where, unitary transform $\hat{U}$ is given as

$$\hat{U} = exp\Big\{\frac{i}{\hbar}\int^{t}\Big(\frac{i\hbar q}{mc}\vec{A}(t').\vec{\nabla} + \frac{q^2}{2mc^2}\vec{A}(t')^2\Big)dt'\Big\} \tag{3.3}$$

Applying this transformation to the Schrödinger equation gives,

$$i\hbar\frac{\partial}{\partial t}|\hat{U}^{\dagger}\psi^{KH}\rangle = \hat{H}|\hat{U}^{\dagger}\psi^{KH}\rangle \tag{3.4}$$

Simplifying this equation would give,

$$\begin{aligned} i\hbar\hat{U}^{\dagger}\frac{\partial}{\partial t}\psi^{KH}(\vec{r},t) &= \hat{H}\hat{U}^{\dagger}\psi^{KH}(\vec{r},t) \\ i\hbar\frac{\partial}{\partial t}\psi^{KH}(\vec{r},t) &= [\hat{U}\hat{H}\hat{U}^{\dagger}]\psi^{KH}(\vec{r},t) \\ i\hbar\frac{\partial}{\partial t}\psi^{KH}(\vec{r},t) &= H^{KH}\psi^{KH}(\vec{r},t) \end{aligned} \tag{3.5}$$

where Hamiltonian is transformed as $\hat{H}^{KH} = \hat{U}\hat{H}\hat{U}^{\dagger}$ which is known as Kramers-Henneberger Transformation.

This transformation expresses the time dependent laboratory frame Hamiltonian into accelerated frame commonly known as Kramers-Henneberger frame.

$$H^{KH} = \frac{\vec{P}^2}{2m} + V(r + \alpha(t)) \tag{3.6}$$

where, $\alpha(t)$ is the displacement of charged particle in its quiver motion.

In the case of electromagnetic field such as laser, where time-dependent electric field vector is given as, $\vec{E} = \alpha_0 cos(\omega t)$, the transformed Hamiltonian becomes,

$$H^{KH} = \frac{\vec{P}^2}{2m} + V(r + \alpha_0 cos(\omega t)) \tag{3.7}$$

where $\alpha_0 = \epsilon/\mu\omega^2$ is the amplitude of electric vector and the maximum distance to which electron oscillates.

3.3 Time Propagation

The time dependent Schrödinger equation for electron moving in the electric field is given as[11] ,

$$i\frac{\partial}{\partial t}\Psi(t) = \{\hat{H} - e\hat{\vec{\mu}}.\vec{E}(t) - i\lambda V_{absorb}\}\Psi(t) \tag{3.8}$$

where $\hat{\vec{\mu}}$ is dipole operator and V_{absorb} is the absorbing potential which is used to model the ionization. The time evolution of electronic wave function is to be seen. There are different methods which has been employed for solving TDSE. The time propagator method is one of such methods. The general solution of the Schrödinger equation is given in terms of separable form,

$$\Psi(\vec{r},t) = e^{-i\hat{H}t}.\Phi(\vec{r}) \tag{3.9}$$

The time dependent term $e^{-i\hat{H}t}$ is treated as the propagator operator. With the help of the Trotter factorization, the time-dependent wave function is propagated[11]

$$\begin{aligned}\Psi(t+\Delta t) &= e^{-i\hat{H}_{el}\Delta t/2}e^{-\lambda\hat{V}_{absorb}\Delta t/2}W^T \\ &\times\ e^{-iE(t+\Delta t/2)d\Delta t}W \\ &\times\ e^{-\lambda\hat{V}_{absorb}\Delta t/2}e^{-i\hat{H}_{el}\Delta t/2}\Psi(t)\end{aligned} \tag{3.10}$$

where, $W^TDW = d$ with D is the transition dipole matrix in the direction of laser field.

3.4 Time Propagation Calculation and Results

Before doing time propagation calculations, full CI calculations of helium atom were performed for Exponentially Tempered Gaussian(ExTG) basis set using GAMESS to generate Configuration Space Functions(CFS)

The ExTG basis set is generated using using following expression[12],

$$ln\xi_n = ln\xi_0 + \frac{exp(\beta n) - 1}{\beta} lna_0 \tag{3.11}$$

where ξ is the exponent of a Gaussian function. The basis set is generated using following basis parameters, By CI calculations using above basis set, 4753 CSFs were generated.

Table 3.1: Gaussian Basis set parameters

Gaussian Function	N	$ln\xi$	$\ln a_0$	β
s	28	4.939590	-0.506662	-0.03
p	15	1.741270	-0.301421	-0.03
d	11	1.844320	-0.291704	-0.03

In our calculations the time-dependent wave function is expanded in the basis of the configuration interactions singles(CIS): $\Psi(t) = \sum_{i=0} C_i(t)|\Psi_i\rangle$ And then using above mentioned time propagation, time-dependent coefficients are solved.

The time propagation calculations are performed for various laser pulse profiles. The stable KH state is found for the pulse with $\alpha_0 = 1.1a.u.$ and $\omega = 0.65a.u.$, at KH energy $1.7548a.u.$

The Helium atom KH orbitals are obtained and plotted. Looking at the orbital plots, one can say that under super-intense laser field, electrons of He atom experiences potential resembling to H_2 molecule potential.

3.5 Future Work

Stabilization of the KH state usually demands high frequency high intensity lasers. We would like to explore the possibility of KH stabilization using high intensity but relatively low frequency lasers. Our proposal is, rather than starting from the ground state, to populate a Rydberg state near the KH state, using this Rydberg state as an initial state and then try to find KH stabilization.

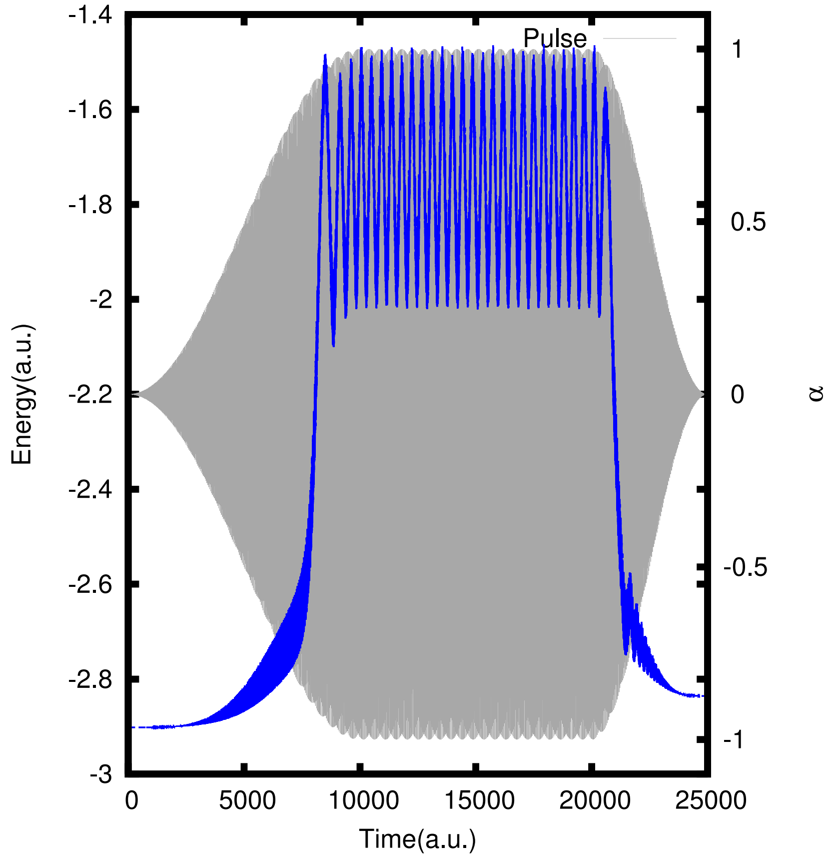

Figure 3.1: KH stabilization of helium atom

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Appendix A

Functional Derivatives

Functional is defined as the multivariable function, $F[f(x_1), f(x_2), ...]$. In other words functional is the function of a function such that $F[f(x)]$. Derivative of the function is nothing but the variation in function with respect to repective variable. Similar defination applies for for functional derivative. Variation in functional is given as,

$$\delta F[f(x)] = F[f(x + \delta x)] - F[f(x)] \tag{A.1}$$

Derivative for multivariable function is defined as,

$$df = \sum_i \frac{\partial f}{\partial x_i} dx_i \tag{A.2}$$

Similarly functional derivative is defined as,

$$\delta F = \int_a^b \frac{\delta F}{\delta f} \delta f dx \tag{A.3}$$

This defination only holds for finite range ie. for finite integral. One can also interprete the variation in $F[f(x)]$ in more accurate way as,

$$\int \frac{\delta F}{\delta f} \phi(x) dx = \lim_{\epsilon \to 0} \frac{F[f + \epsilon\phi] - F[f]}{\epsilon} \tag{A.4}$$

where $\phi(x)$ is an arbitrary function. This defination or reasoning is not mathematically rigorous, for furthur information please check *'Theoretical Numerical Analysis: A Functional Analysis Framework* by K. Atkinson and W. Han(Springer, Berlin, 2009).

Functional derivatives are at very heart of Lagrangian mechanics, and have been used for solving Euler-Lagrange equations, namely to reduce constraints to potentials. Let us see the simplification for Zhao-Parr constraint.

$$C = \int \frac{(\rho(\vec{r}) - \rho_0(\vec{r}))(\rho(\vec{r\prime}) - \rho_0(\vec{r\prime}))}{|\vec{r} - \vec{r\prime}|} d^3r d^3r\prime \tag{A.5}$$

By defination,

$$\int \frac{\delta C}{\delta \rho} \phi(\vec{r}) d^3r = \frac{d}{d\epsilon} \int C[\rho(\vec{r}) + \epsilon\phi(\vec{r})]_{\epsilon=0} d^3r \tag{A.6}$$

Simplifying the equation for C,

$$\begin{aligned}
\int \frac{\delta C}{\delta \rho} \phi(\vec{r}) d^3r &= \frac{d}{d\epsilon} \int \frac{(\rho(\vec{r}) - \rho_0(\vec{r}) + \epsilon\phi(\vec{r}))(\rho(\vec{r\prime}) - \rho_0(\vec{r\prime}) + \epsilon\phi(\vec{r\prime}))}{|\vec{r} - \vec{r\prime}|} d^3r d^3r\prime \\
&= \int \frac{[\rho(\vec{r}) - \rho_0(\vec{r})]\phi(\vec{r\prime}) + [\rho(\vec{r\prime}) - \rho_0(\vec{r\prime})]\phi(\vec{r})}{|\vec{r} - \vec{r\prime}|} d^3r d^3r\prime \\
&= 2\int \frac{[\rho(\vec{r\prime}) - \rho_0(\vec{r\prime})]\phi(\vec{r})}{|\vec{r} - \vec{r\prime}|} d^3r d^3r\prime
\end{aligned} \tag{A.7}$$

Thus, by comparing both sides, one gets the functional derivative of the C functional,

$$\frac{\delta C}{\delta \rho} = 2\int \frac{[\rho(\vec{r\prime}) - \rho_0(\vec{r\prime})]}{|\vec{r} - \vec{r\prime}|} d^3r\prime \tag{A.8}$$

so, v_{eff}'s form has been obtained as given in equation (2.2) with the integral factor is absorbed into the Lagrange multiplierλ

Appendix B

Zhao-Parr DFT code

```
!----------------------------------------------------------------------------!
 MODULE PAR
!----------------------------------------------------------------------------!
 IMPLICIT NONE
 integer(kind=4), parameter  :: nbas=17, nele=2
 END
!----------------------------------------------------------------------------!
!----------------------------------------------------------------------------!
 program ZP_He
!----------------------------------------------------------------------------!
 USE PAR
 implicit none
 integer(kind=4), parameter  :: npt=1001, nf=17
 integer(kind=4) :: i, j, k, l, m, n, o, ip
 real(kind=8)    :: F(nbas,nbas), X(nbas,nbas), TEI(nbas,nbas,nbas,nbas)
 real(kind=8)    :: a(nbas), c(nbas), S(nbas,nbas),H(nbas,nbas),F1(nbas,nbas)
 real(kind=8)    :: expnt(nbas),cof(nbas)
 real(kind=8)    :: V(nbas,nbas), Energy, P(nbas,nbas), su, rh0
 real(kind=8)    :: core, rep, Energy1, conv, den(npt), check(nbas,nbas)
```

```
real(kind=8)    :: coef(nbas,nbas), coef1(nbas,nbas), ft(nbas,nbas)
real(kind=8)    :: E(nbas), co(nbas),G(nbas,nbas),V0(nbas,nbas), p1(nbas,nbas)
real(kind=8)    :: xi(npt), y, z, r2, dr, psi(npt), fun, total_density
real(kind=8), parameter :: xmin=0.0000d0, xmax=20.0000d0
real(kind=8), parameter :: pi=3.14159265359d0
real(kind=8)    :: lambda, std
real(kind=8)    :: norsum, norsum1, nor1, nor, add, w(npt), trace, rho, del(npt)
real(kind=8)    :: ncoef(nbas), nbasis(nbas), amin,amax, dens,ni
call basis(a,c)
call X_matrix(a, c, X)
call Two_electron_integral(a, c, TEI)
call Hcore(a, c, H)
call rho0(a, c, ncoef, nbasis, V0)
call guess_Density_matrix(H, P)
call Hcore(a, c, H)
call overlap(a, c, S)
Energy=0.00d0
Energy1=1.00d0
conv=1.00d0
n=0
open(12, file='lambda_vs_energy')
open(13, file='std1.dat')
open(14, file='lambda_vs_energy.dat')
lambda=10
p1(1,1)=1.00d0
do 1001 m=1, 101
write(*,*) n
do 111 i=1,nbas
   do 112 j=1,nbas
      add=0.00d0
      do 113 k=1,nbas
```

```
          do 114 l=1,nbas
          add=add+P(k,l)*(TEI(i,j,l,k)-0.50d0*TEI(i,k,l,j))
          114 enddo
       113 enddo
       G(i,j)=add
!      F(i,j)=H(i,j)+G(i,j)   !Hartree fock calculations
       F(i,j)=H(i,j)+lambda*(G(i,j)-V0(i,j))
    112 enddo
       write(*,'(7f14.7)') (G(i,j)-V0(i,j), j=1,nbas)
  111 enddo
 ft=matmul(F,X)
 F1=matmul(transpose(X),ft)
 core=0.00d0
 do 221 i=1,nbas
    do 222 j=1,nbas
       core=core+P(j,i)*(H(i,j)+F(i,j))
    222 enddo
 221 enddo
 n=n+1
 Energy1 = Energy
 Energy=0.5*core
 total_density=0.000d0
 norsum=0.000d0
 norsum1=0.00d0
 do 551 i=1, nbas
    do 552 j=1,nbas
       norsum1=norsum1+P1(i,j)*P1(i,j)
       norsum=norsum+P(i,j)*P(i,j)
    552 enddo
 551 enddo
 nor=dsqrt(norsum)
```

```
 nor1=dsqrt(norsum1)
 conv=nor1-nor
 if (dabs(conv)<1.0e-6)then
    exit
 else
    call CALL_DSYEV_WT_EIGVECS(F1, nbas, E, coef1)
    coef=matmul(X,coef1)
    do i=1,nbas
       do j=1,nbas
          p1(i,j)=P(i,j)
          P(i,j)=0.0d0
          do k=1,nele/2
             P(i,j)=P(i,j)+2*coef(i,k)*coef(j,k)
          enddo
       enddo
    enddo
 endif
 1001 enddo
 write(*,*) n, Energy, Energy1, conv, E(1), E(2)

!-------------------------------------------------------------------------------!
! Electron Density
!-------------------------------------------------------------------------------!
 call check_constraint(a, p, npt, xmin, xmax, rh0, w, xi, rho)
 open(11, file='zphe07w.dat')
 dr=(xmax-xmin)/(npt-1)
 del=0.00d0
 do 331 i=1,npt
    xi=xmin+(i-1)*dr
    r2=(xi(i)*xi(i))
    dens=0.00d0
```

```
    do 221 k=1, nbas
       su=0.00d0
       do 441 l=1, nbas
          su=su+coef(l,1)*dexp(-a(l)*r2)
          dens=dens+P(k,l)*((2*a(l)/pi)**0.75)&
              *((2*a(k)/pi)**0.75) *dexp(-(a(l)+a(k))*r2)
       441 enddo
    221 enddo
    fun=0.00d0
    do 151 m=1, nf
       fun=fun+ncoef(m)*((2.0d0*nbasis(m)/pi)**0.750d0)&
           *dexp((-(r2))*(nbasis(m)))
    151 enddo
    psi(i)=su
    den(i)=dens
    del(i)=dsqrt((del(i-1)+(den(i)-fun)**2)/(npt))
    std=del(i)
    total_density=total_density+w(i)*4*pi*r2*den(i)
    write(11,*) xi(i), psi(i), den(i), fun, del(i)
 331 enddo
 write(14, *) lambda, std,total_density, Energy
 write(*,*) total_density
 end
!-----------------------------------------------------------------------------!
!-----------------------------------------------------------------------------!
 subroutine basis(expnt, coef)
!-----------------------------------------------------------------------------!
 use par
 implicit none
 real*8   :: expnt(nbas), coef(nbas)
 CHARACTER(LEN=4) :: var
```

```
 INTEGER*4:: II, N1, NUM, IX, IY
 N1 = 0
 OPEN(11,FILE="coemd-ref")
 DO
  READ(11,*) VAR, NUM
  IF ( VAR(1:4) .EQ. "STOP") GOTO 100
     DO IX = 1, NUM
        N1 = N1 + 1
        READ(11,'(I3,E28.16,F21.7)') II, EXPNT(N1), COEF(N1)
     ENDDO
 ENDDO
 CLOSE(11)
100   RETURN
end
!-------------------------------------------------------------------------------!
!-------------------------------------------------------------------------------!
 subroutine check_constraint(a, P, n, xmin, xmax, rho0, w, r, rho)
!-------------------------------------------------------------------------------!
 USE PAR
 implicit none
 integer(kind=4):: i, j, k, n
 real(kind=8)   :: r(n), add, rho, rho0, fy, check
 real(kind=8)   :: xmin, xmax, w(n), a(nbas), P(nbas,nbas)
 real(kind=8), parameter:: pi=3.14159265359d0, piby4=pi*0.2500d0
 call LEGENDRE(n,xmin, xmax, w, r)
 rho=0.00d0
 rho0=0.00d0
 do 111 i=1,n
    add=0.00d0
    do 221 j=1,nbas
       do 222 k=1, nbas
```

```
          add=add+P(j,k)*dexp(-(a(j)+a(k))*r(i)*r(i))
       222 enddo
    221 enddo
    fy=dexp(-(pi/(4.00d0))*r(i)*r(i))
    rho=rho+w(i)*add
    rho0=rho0+w(i)*fy
    check=check+w(i)*(fy-add)*(fy-add)
 111 enddo
 end
!------------------------------------------------------------------------------!
 subroutine guess_Density_matrix(H, P)
!------------------------------------------------------------------------------!
 USE PAR
 implicit none
 real(kind=8)   :: H(nbas,nbas), P(nbas,nbas), v(nbas,nbas), coef1(nbas,nbas)
 real(kind=8)   :: E(nbas), a(nbas), c(nbas), coef(nbas,nbas)
 integer(kind=4):: i, j, k
 real(kind=8)   :: ft(nbas,nbas), ft1(nbas,nbas), X(nbas,nbas)
 call X_matrix(a,c,X)
 ft=matmul(H,X)
 ft1=matmul(transpose(X),ft)
 call CALL_DSYEV_WT_EIGVECS(ft1,nbas,E,coef)
 do i=1,nbas
    do j=1,nbas
       P(i,j)=0.0d0
       do k=1, nele/2
          P(i,j)=P(i,j)+2.0d0*coef(i,k)*coef(j,k)
       enddo
    enddo
 enddo
 end
```

```
!-------------------------------------------------------------------------------!
 subroutine rho0(a, c, coef, basis, V0)
!-------------------------------------------------------------------------------!
 USE PAR
 integer(kind=4):: i, j, k, coef_read
 real(kind=8)   :: V0(nbas,nbas), a(nbas), c(nbas), S(nbas,nbas), mul
 real(kind=8), parameter:: pi=3.14159265359d0, piby4=pi*0.2500d0
 real(kind=8)   :: s1, s2, s4, alpha, coef(nbas), basis(nbas)
 integer(kind=8), parameter:: nf=17
 call overlap(a, c, S)
 open(15, file='he_density_basis.dat')
 do 100 coef_read=1, nf
 read(15,*) coef(coef_read), basis(coef_read)
 100 enddo
 do 111 i=1, nbas
    do 112 j=1, nbas
       s1=a(i)+a(j)
       mul=0.0d0
       do 113 k=1, nf
          s2=(basis(k))
          s4=(s1+s2)
          alpha=2.0d0*dsqrt((s1*s2)/(pi*s4))
          mul=mul+coef(k)*((2.0d0*a(i)/pi)**0.75)*((2*a(j)/pi)**0.75) &
       *((2.0d0*basis(k)/pi)**0.75)*2.00d0*((pi)**2.5)/(s1*s2*dsqrt(s4))
       113 enddo
       V0(i,j)=mul
       write(*,'(7F14.7)') V0(i,j)
    112 enddo
 111 enddo
 end
!-------------------------------------------------------------------------------!
```

```
 subroutine X_matrix(a, c, X)
!------------------------------------------------------------------------------!
 USE PAR
 implicit none
 integer(kind=4):: i, j, k,l
 real(kind=8)   :: S(nbas,nbas), a(nbas), c(nbas), s05(nbas,nbas)
 real(kind=8)   :: st(nbas), U(nbas,nbas)
 real(kind=8)   :: Ut(nbas,nbas), X(nbas,nbas), su
 call overlap(a, c, S)
 call CALL_DSYEV_WT_EIGVECS(S,nbas,st,U)
 s05=0.00000d0
 do 111 i=1, nbas
    s05(i,i)=st(i)**(-0.50d0)
 111 enddo
 Ut=matmul(s05, transpose(U))
 X= matmul(U,Ut)
 end
!------------------------------------------------------------------------------!
 subroutine Two_electron_integral(a, c, TEI)
!------------------------------------------------------------------------------!
 USE PAR
 implicit none
 integer(kind=4):: i, j, k, l
 real(kind=8)   :: a(nbas),S(nbas,nbas),c(nbas),
 real(kin=8)    :: alpha,TEI(nbas,nbas,nbas,nbas)
 real(kind=8), parameter:: pi=3.14159265359d0
 call overlap(a, c, S)
 do 111 i=1,nbas
    do 112 j=1,nbas
       do 113 k=1,nbas
          do 114 l=1,nbas
```

```
            alpha=2.0d0*((a(i)+a(j))*(a(k)+a(l))/(pi*(a(i)+a(j) &
                    +a(k)+a(l))))**0.50d0
            TEI(i,j,k,l)=S(i,j)*S(k,l)*alpha
         114 enddo
      113 enddo
   112 enddo
 111 enddo
 end
!------------------------------------------------------------------------------!
 subroutine Hcore(a, c, H)
!------------------------------------------------------------------------------!
 USE PAR
 implicit none
 real(kind=8)   :: V(nbas,nbas)
 integer(kind=4):: i, j
 real(kind=8)   :: omg, H(nbas,nbas)
 real(kind=8), parameter:: pi=3.14159265359d0
 real(kind=8)  :: S(nbas,nbas), a(nbas), c(nbas), T(nbas,nbas)
 call Kinetic_energy_matrix(a, c, T)
 call overlap(a, c, S)
 open(2000,file='test.dat')
 do 111 i=1,nbas
    do 112 j=1,nbas
       omg=2*(((a(i)+a(j))/pi)**0.50d0)
       V(i,j)=-nele*omg*S(i,j)
!      V(i,j)=0.0d0 !without (Z/r) term
       H(i,j)=V(i,j)+T(i,j)
    112 enddo
 111 enddo
 end
!------------------------------------------------------------------------------!
```

```
subroutine Kinetic_energy_matrix(a, c, T)
!-------------------------------------------------------------------------------!
USE PAR
implicit none
real(kind=8)   :: S(nbas,nbas), K(nbas,nbas), T(nbas,nbas)
real(kind=8)   :: a(nbas), c(nbas), su
integer(kind=4):: i, j, l
call overlap(a, c, S)
do 111 i=1, nbas
   do 112 j=1, nbas
      su=0.0000d0
      K(i,j)=(3.0d0*a(j)*a(i))/(a(j)+a(i))
      su=K(i,j)*S(i,j)
      T(i,j)=su
   112 enddo
111 enddo
end
!-------------------------------------------------------------------------------!
subroutine overlap(a, c, S)
!-------------------------------------------------------------------------------!
USE PAR
implicit none
real(kind=8), parameter:: xmin=-2.000d0, xmax=2.00d0, pi=3.1415926535
integer(kind=4):: i, j, k, l, p, q, r, k1, k2
integer(kind=4), parameter:: n=1001
real(kind=8)   :: x(n), y(n), z(n)
real(kind=8)   :: S(nbas,nbas), KE(nbas,nbas), T(nbas,nbas)
real(kind=8)   :: a(nbas), su, c(nbas), su1
do 1000 i=1, nbas
   do 1001 j=1, nbas
      S(i,j)=c(i)*c(j)*((4*a(i)*a(j))**0.75d0)/(a(i)+a(j))**1.50d0
```

```
   1001 enddo

 1000 enddo

 end
!----------------------------------------------------------------------------!
```

Note: The LAPACK libraries are used for diagonalization.

Appendix C

Fitting Code

```
!--------------------------------------------------------------------------!
 Program fitting_3d_function
!--------------------------------------------------------------------------!
 implicit none
 integer(kind=4), parameter  :: npt=990, nbas=17
 integer(kind=4):: i, j, k, info, l
 real(kind=8)   :: f(npt), c(nbas), a(nbas)
 real(kind=8)   :: xmin, xmax
 real(kind=8)   :: x(npt), su, coef(nbas, nbas)
 integer(kind=4):: ipiv(nbas)
 real(kind=8)   :: a2(nbas,nbas), a2inv(nbas,nbas)
 real(kind=8)   :: b(nbas,1), work(nbas), w(npt)
 real(kind=8)   :: new_func(npt), fun, S(nbas,nbas)
 real(kind=8)   :: r(npt), d(nbas,1), integ
 real*8         :: norm(1,1),  check(1,nbas)
 real*8, parameter:: pi=3.141592653590d0
 real*8         :: rmin, rmax, sigma, wr(npt), f1(npt)
 real*8         :: amin,amax, var, var1
!-----Dummies
 real*8         :: dum1, dum2, dum4, fx
```

```
 open(31,file='he_density.dat') !data file or function file
 open(51, file='function.dat')
 open(1, file='he_density_basis.dat') !basis set+ coefficients to written
!-----reading function
 do 111 i=1, npt
    read(31,*) dum1, r(i), dum2, dum4, f(i)
    read(31,*) r(i), dum1, f(i)
    write(51,*) r(i), f(i)
 111 enddo
 xmin=r(1)
 xmax=r(npt)
 open(12, file='new_function2.dat')
 call basis(nbas, a, coef)
 call LEGENDRE(npt ,xmin, xmax, w, x)
!-----function/data direct feeding/testing
! do 111 i=1,npt
!      f(i)=((dexp(-x(i)/0.529)*(x(i)/(2.0d0*0.5290d0)))&
!           *(2.0d0/0.5290d0)**1.50d0)**2
!111 enddo
!-----overlap integrals
 call overlap(nbas, a, c, S)
 a2inv=S
 call DGETRF(nbas, nbas, a2inv, nbas, ipiv, info)
 if (info /= 0) then
     write(*,*)'matrix is sigular'
     stop
 endif
 call DGETRI(nbas, a2inv, nbas, ipiv,work, nbas, info)
 if (info /= 0) then
     stop
 endif
```

```
!-----numerical integrals
do 113 j=1, nbas
   integ=0.00d0
   fun=0.00d0
   do 112 i=1, npt
      fun=fun+w(i)*x(i)*x(i)*4*pi*f(i)*((2.00d0*a(j)/pi)**0.7500d0)&
               *dexp(-a(j)*x(i)*x(i))
   112 enddo
   b(j,1)=fun
113 enddo
do i=1, npt
   integ=integ+w(i)*f(i)*4*pi*x(i)*x(i) !(num)integration of given function
enddo
do i=1,nbas
   su=0.00d0
   do j=1,nbas
      su=su+S(i,j)
   enddo
enddo
d=matmul(a2inv,b)
check=matmul(transpose(d),S)
norm=matmul(check, d)
var=0.00d0
do 121 i=1,npt
    su=0.00d0
    do 131 j=1,nbas
       su=su+(d(j,1))*((2.00d0*a(j)/pi)**0.7500d0)*dexp(-a(j)*x(i)*x(i))
    131 enddo
    new_func(i)=su
    var=var+(new_func(i)-f(i))**2
121 enddo
```

```
 fx=0.00d0
 do i=1, npt
    write(12,*) x(i), new_func(i), f(i)
    fx=fx+w(i)*4*pi*x(i)*x(i)*new_func(i)
 enddo
 close(12)
 write(*,*) integ, fx, var**0.500d0
!-----writing new function in file as summation of basis
 do 1 i=1,nbas
    write(1,*) d(i,1), a(i)
 1 enddo
 end
!------------------------------------------------------------------------------!
 subroutine basis(nbas, expnt, coef)
!------------------------------------------------------------------------------!
 implicit none
 CHARACTER(LEN=4):: var
 INTEGER*4       :: II, N1, NUM, IX, IY, nbas
 real*8          :: expnt(nbas), coef(nbas)
 N1 = 0
 OPEN(11,FILE="coemd-ref")
 DO
  READ(11,*) VAR, NUM
 IF ( VAR(1:4) .EQ. "STOP") GOTO 100
    DO IX = 1, NUM
       N1 = N1 + 1
       READ(11,'(I3,E28.16,F21.7)') II, EXPNT(N1), COEF(N1)
    ENDDO
 ENDDO
 CLOSE(11)
100   RETURN
```

```
 end
!-----------------------------------------------------------------------------!
 subroutine overlap(nbas, a, c, S)
!-----------------------------------------------------------------------------!
 implicit none
 real(kind=8), parameter:: xmin=-2.000d0, xmax=2.00d0, pi=3.1415926535
 integer(kind=4):: i, j, k, l, p, q, r, k1, k2
 integer(kind=4):: nbas
 real(kind=8)   :: S(nbas,nbas)
 real(kind=8)   :: a(nbas), su, c(nbas), su1
 do 1000 i=1, nbas
    do 1001 j=1, nbas
       S(i,j)=((4.00d0*a(i)*a(j))**0.750d0)/(a(i)+a(j))**1.50d0
    1001 enddo
 1000 enddo
 end
!-----------------------------------------------------------------------------!
```

Note: The LAPACK libraries are used for calculating inverse