Effective local potentials in quantum many body systems

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Chapter 1

Introduction

In quantum mechanics we solve Schrödinger equation to get wave functions for the system. Once we know wave function of the system all physical properties of the system can be studied by finding out expectation of the corresponding operators. But as the number of particles in the system increases it becomes very difficult to solve Schrödinger equation. If we have a noninteracting system, it is comparatively easier to solve (using variable separation of variables). But once we have interaction in the system, Schrödinger equation can’t be solved exactly just by variable separation. Even for a single particle system, we can’t solve Schrödinger equation for any weird form of potential. Therefore several approximate methods have been developed which are applicable not only for single particle system but also for a many particle systems. Before discussing several methods let us fix our regime of the theory:-

- We assume nucleus to be a point particle with infinite mass\(^1\)
- We are neglecting Spin-spin interactions, radiative corrections, relativistic effects\(^2\)

\(^1\)So that there won’t be any mass polarzation term in Hamiltonian once we go to centre of mass frame
\(^2\)these effects are very small
For an N particle system Schrödinger equation can be written as:

\[
\left(-\frac{1}{2}\nabla^2 + \sum_{i=1}^{N} v_{\text{ext}}(\vec{r}_i) + \sum_{i<j}^{N} \frac{1}{r_{ij}}\right)\psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) = E\psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N)
\]

Effects of Coulomb interactions should be included along with the final wave function being antisymmetric. These leads to Pauli-Coulomb correlation effects. These effects makes the Schrödinger equation difficult to solve. Therefore one of the first approximation that was done is know as Central field approximation which says that each electron moves in an effective potential which represents the average effect of attraction from nucleus and repulsion from other electrons.

### 1.1 Variational principle

All many particle theories are based on the variational principle. We can guess ground state wave function and then find out the parameters involved in it by minimizing the ground state energy. By variational principle it can be proved that ground state energy is less than any energy calculated by guessing the wave function. Let us say \(|\psi >\) is the initial guess of wave function for the ground state. Then we can write this in terms of linear combination of original wave functions (which are normalized) as:

\[
|\psi > = \sum_i c_i |\phi >
\]

Expectation value of energy for the guessed wave function:

\[
<\psi|\hat{H}|\psi > = \sum_{i,j} c_j^* c_i <\phi|\hat{H}|\phi >
\]

\[
<\psi|\hat{H}|\psi > = \sum_i |c_i|^2 E_i
\]

As \(E_{gs} < E_i\) for all \(i's\) except for ground state. We get

\footnote{All equations are written in atomic units}
1.2 Different approaches

There are basically two approaches for solving a many particle system:-

- **Wave function based approaches**: In this approach many particle nature of the system is retained. We directly solve Schroedinger equation using many particle wave function $\psi(r_1, r_2, ..., r_N)$ by using several parameters. Then calculate parameters by using variational principle. Example:- Hartree Fock theory

- **Density based approach**: Second class of approach is density based approach. In this approach N- particle Schroedinger equation is mapped to a equivalent single particle Schroedinger equation. Therefore an equation in 3N variables is reduced to a 3 variable equation. This approach is exact in principle. Example :- Density functional theory, Thomas Fermi theory

Density based approaches are very useful as they require less computation and they are exact in principle. But extension of this approach to excited state is very difficult.

---

4 Does not take into account self interaction energy, correlation energy

5 Does not take into account negative ions, good for properties related to average electron motion like for total energy not good for valence electron properties like ionization potential
Density Functional theory

Density functional theory is generally used for ground state calculations. In general ground state energy can be a functional of both number density and external potential. But by using variational theorem it can be proved that there exists one to one correspondence between external potential and non degenerate ground state density. This theorem is known as Hohenberg Kohn theorem. For proof let us assume there exists two potentials $v(\vec{r})$ and $v(\vec{r})'$ differing by more than a constant having corresponding wave functions as $\psi$ and $\psi'$ and having same ground state density as $\rho(\vec{r})$. Ground state energy $E$ for $v(\vec{r})$ can be written as:

$$E = \langle \psi | \hat{H} | \psi \rangle$$

$$E < \langle \psi' | \hat{H} | \psi' \rangle$$

$$E < E' + \int (v(\vec{r}) - v(\vec{r})') \rho(\vec{r}) d^3r$$

Similarly if we use variation principle for the potential $v'$ we get

$$E' < E + \int (-v(\vec{r}) + v(\vec{r})') \rho(\vec{r}) d^3r$$

\(^1\)Potentials can differ only by a constant
On adding both the equations we get \( E + E' < E + E' \). This is a contradiction therefore potentials must differ only by constant to give rise to same ground state density.

This theorem just proves the existence of one to one correspondence but to get the ground state density a second theorem needs to be taken into account. According to second theorem the total ground state density functions \( E_0[\rho] \) has its minimum value at the density equal to the ground state density of system. Here

\[
E_0[\rho] = F[\rho] + \int v(\vec{r})\rho \tilde{d}^3r
\]

subject to constraint \( \int \rho \tilde{d}^3r = N \).

Here \( F[\rho] = \langle \psi | \hat{T} + \hat{V}_{ee} | \psi \rangle \)

\[
\rho(\vec{r}) = \int dr_2 dr_2 ... dr_N |\psi_0(\vec{r}, r_2, r_3 ... r_N)|^2
\]

Minimization of \( F[\rho] \) with respect to \( \rho \) subject to the given constraint on \( \rho(\vec{r}) \) gives

\[
\frac{\delta F}{\delta \rho} + v_{ext} = \mu
\]

This is known as HK equations. Here \( \mu \) is lagrange multiplier.

In order to find out the functional form of these HK functional i. e. \( F[\rho] \) we go for Kohn-Sham Formulation which is based on an assertion i. e. if we consider a system of \( N \) non interacting electrons subject potential \( V_{KS} \). Then it is possible to choose this potential such that ground state density of this system is same as ground state density of an interacting system subject to some external potential \( V_{ext} \). As non interacting system is separable we have a set of single particle orbitals \( \psi_i(\vec{r}, s), i = 1, 2 ... N \) \(^2\) So we can write density as

\[
\rho(\vec{r}) = \sum_{i=1}^{N} \sum_s |\psi_i(\vec{r})|^2
\]

\(^2\)Total wave function will be the slater determinant formed by these orbitals.
Expectation value of kinetic energy

\[ T_s[\rho] = \sum_{i=1}^{N} \sum_s \int dr \frac{1}{2} \frac{\psi_i^*(\vec{r})}{\rho} \nabla^2 \psi_i(\vec{r}) \]

By minimization of energy subject to constraint of density \( \int \rho(r) dr = N \) using variational method leads to–

\[
\frac{\delta}{\delta \psi} \left[ T_s + V_{KS} \left[ \int \rho(r) dr - N \right] + \sum_{j,k} \epsilon_{j,k} \left( \int \psi_j^* \psi_k - \delta_{ij} \right) \right] = 0
\]

After diagonalizing we get KS equations of the form:-

\[ ((-1/2)\nabla^2 + V_{KS})\psi_i(\vec{r}) = E_i \psi_i(\vec{r}) \ldots \ldots 1 \]

where

\[ V_{KS} = U(\vec{r}) + \int dr \frac{\rho(\vec{r})}{|\vec{r} - \vec{r}'|} + \frac{\delta E_{xc}}{\delta \rho} \]

and ground state energy can be written as

\[ E_0[\rho] = T_s[\rho] + \frac{1}{2} \int dr dr' \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + U[\rho] + E_{xc}[\rho] \]

Here \( E_{xc} \) is exchange-correlation energy. \( U(r) \) is external potential due to nucleus, \( T_s[\rho] \) is Kinetic energy of non interacting system. \( E_{xc} \) has the self interaction energy missing in Hartree Fock method, it also accounts for correlation energy resulting from Coulomb repulsion and Pauli exclusion. In addition it also has kinetic energy of electrons in an interacting system. Therefore once we know \( E_{xc} \) we can solve equation (1) along with the constraint of number of particles self consistently to get final solution to the system. For a system where we have large number of electrons an approximation of this exchange-correlation energy is used which gives quite good results.

\[ E_{xc} = \int dr \rho(r) E^H_{xc} \]

Where \( E^H_{xc} \) is exchange correlation energy for an infinite inhomogeneous electron gas moving in uniformly positively charged background which can be calculated to a good approximation.
Figure 2.1: Self consistent method in density functional theory
Chapter 3

Non interacting fermions in one dimension

It has been shown in many systems that DFT gives very accurate result for ground state. To study the analogy of HK theorem\[\text{\footnotesize (1)}\] for excited states I am going to work on a model system of two noninteracting particles in 1D infinite square well\[\text{\footnotesize (2)}\]

Let us take two systems with potentials \(v(x)\) and \(v(x)'\) having two noninteracting particles with same number density\[\text{\footnotesize (3)}\] We can write\[\text{\footnotesize (4)}\]-

\[
\begin{align*}
\left[-\frac{1}{2}\frac{d^2}{dx^2} + v(x)\right] \phi_i(x) &= \epsilon_i \phi_i(x) \\
\left[-\frac{1}{2}\frac{d^2}{dx^2} + v(x)\right] \phi_i'(x) &= \epsilon_i' \phi_i'(x)
\end{align*}
\]

where

\[
\rho(x) = \phi_i^2(x) + \phi_i'^2(x) = \phi_1^2(x) + \phi_1'^2(x) \tag{3.3}
\]

---

2. Length of the box is 1 and for all Schrödinger equations I am taking atomic units \(e = \hbar = m = 1\)
3. \(\rho(x) = \int dx_1 |\psi(x, x_1)|^2 + |\psi(x_1, x)|^2\)
4. \(i=1,2\)
Both the wave functions should be related through some unitary transformation. Taking rotation by an angle $\theta(x)$ as the transformation We get

$$\phi = R(\theta(x))\phi'$$

where $R$ is given by

$$
\begin{pmatrix}
\cos(\theta(x)) & \sin(\theta(x)) \\
-sin(\theta(x)) & \cos(\theta(x))
\end{pmatrix}
$$

For new modified potential we get:-

$$v'(x) = \epsilon'_1 + \frac{\ddot{\phi}_i(x)}{2\phi_i(x)}$$  \hspace{1cm} (3.4)

Energy difference between two electrons for same potentials can be calculated in terms of their respective wave functions and their derivatives. Defining

$$\Delta = \epsilon_1 - \epsilon_2$$

$$\Delta' = \epsilon'_1 - \epsilon'_2$$

Now in the expression of $\Delta'$ substituting $\phi_i'$ in terms of $\phi_i$ we get

$$\theta(x)\rho(x) + \dot{\theta}(x)\rho(x) + f(\phi_1, \phi_2, \Delta, \Delta', \theta) = 0$$  \hspace{1cm} (3.5)

where $f = 2\Delta\phi_1\phi_2 - \Delta'[2\phi_1\phi_2\cos(2\theta(x)) + (\phi_2^2 - \phi_1^2)\sin(2\theta)]$  \hspace{1cm} (3.6)

On solving differential equation (3.5) we can get the value of $\theta(x)$. Once we know $\theta(x)$ we can calculate new wave functions and hence the potential $v'(x)$ having same density. Now the aim is to look for multiple potentials for different parameter values.

Let us take infinite square well (of length 1) potential as $v(x)$. We get states an energies corresponding to this potential as

$$\phi_n = \sqrt{2}\sin(n \pi x)$$  \hspace{1cm} (3.7)

$$E_n = \frac{n^2 \pi^2}{2}$$  \hspace{1cm} (3.8)
3.1 Lowest excited state

We have one electron in ground state and another in first excites state. Corresponding density can be written as:

\[ \rho(x) = 2[\sin^2(\pi x) + \sin^2(2\pi x)] \]

Putting that in equation 3.6 we get

\[ f = 6\pi^2\sin(\pi x)\sin(2\pi x) - \Delta'[4\sin(\pi x)\sin(2\pi x)\cos(2\theta(x)) + 2\sin^2(2\pi x) - \sin^2\pi x\sin(2\theta(x))] \]  

(3.9)

By symmetry of \( \phi_1 \), antisymmetry of \( \phi_2 \) and symmetry of \( \rho(x) \) about \( x = 1/2 \) we find \( \theta \) to be antisymmetric about \( x = 1/2 \) so \( \theta(1/2) = 0 \). As \( x \to 0 \) we take large theta limit and assuming sin and cos to be rapidly oscillating in that limit we drop those terms from the diff equation 3.5. Finally we get

\[ \ddot{\theta}(x)\rho(x) + \dot{\theta}(x)\dot{\rho}(x) + 2\Delta\phi_1(x)\phi_2(x) = 0 \]  

(3.10)

Solution of this equation in the limit \( x \to 0 \) takes the form

\[ \theta(x) = C2 + \frac{1}{50}[\tan^{-1}(2 - \sqrt{5}\tan(\pi x/2))(50\pi - 8\sqrt{5}C1) + \tan^{-1}(2 + \sqrt{5}\tan(\pi x/2))(50\pi + 8\sqrt{5}C1)] + g(x) \]

\[ g(x) = 5C1(\cot(\pi x/2) - \tan(\pi x/2)) \]

This reduces to:

\[ \theta(x) \sim \frac{a}{x} + b + cx + O(x^2) \]  

(3.11)

So for a physical solution we need new wave functions to be not only normalized but also to have \( a \to 0 \) as \( x \) goes to zero. For normalization of \( \phi_1' \) we get

\[ \int_0^1 \phi_1'(x)^2dx - 1 = R = 0 \]  

(3.12)

\(^5\)if \( \phi_1' \) is normalized \( \phi_2' \) will also be normalized
Table 3.1: Table for the value of a for Normalized wave functions only for positive values of 
$\frac{d\theta}{dx}$ at $x = 1/2$

<table>
<thead>
<tr>
<th>$\Delta'$</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>-0.005834</td>
<td>-0.06096</td>
<td>-0.07959</td>
</tr>
<tr>
<td>15</td>
<td>-0.000074</td>
<td>-0.06442</td>
<td>-0.07755</td>
</tr>
<tr>
<td>20</td>
<td>0.004940</td>
<td>-0.06812</td>
<td>-0.07660</td>
</tr>
<tr>
<td>25</td>
<td>0.009001</td>
<td>-0.07168</td>
<td>-0.07615</td>
</tr>
<tr>
<td>30</td>
<td>0.012501</td>
<td>-0.07444</td>
<td>-0.07594</td>
</tr>
</tbody>
</table>

Therefore for a fixed value of parameter $\Delta'$ we have taken different-different boundary
conditions i.e. $\theta(1/2)$ to get wave functions for each initial value by solving equation (3.5) with
given $\rho(x)$. After that we plot $R$ from eqn 3.12 as a function of different initial values. So the
points intersecting x axis correspond to normalized wave functions. After that condition from
eqn 3.11 is checked to get the physical solution. If no physical solution is observed parameter
(fig 2, fig 3, fig 4) $\Delta'$ is varied over a range to get physical solution. Values of a of eqn 3.12
are plotted (fig 4) as a function of different values of parameter $\Delta'$ only for normalized wave
function. For lowest excited state we observe that only for $\Delta = \Delta' = 15$ we get a physically
acceptable solution. And solutions are same as original one (fig 5). Therefore we can conclude
that there exists one to one correspondence between lowest excited state density and external
potential (fig 6). This demonstrates of the G [6] theorem of DFT.

3.2 Second excited state

For second excited state one electron will be in ground state $n = 1$ and one in second excited
state ($n = 2$) of infinite square well potential. For this state we get density as :-

$$\rho(x) = 2[\sin^2(\pi x) + \sin^2(3\pi x)]$$

Energy difference will be $\epsilon_2 - \epsilon_1 = 4\pi^2 \approx 40$.

Putting that in equation 3.6 we get
\[ f = 16\pi^2 \sin(\pi x)\sin(3\pi x) - \Delta' \left[16\pi^2 \sin(\pi x)\sin(3\pi x)\cos(2\theta(x)) + 2\sin^2(3\pi x) - \sin^2\pi x\sin(2\theta(x))\right] \] (3.13)

An approach similar to lowest excited state is used for this state also. For various parameter values R of equation 3.12 is plotted versus initial conditions of \( \theta(1/2) \) (fig3.9, fig3.10, fig3.11, fig3.12). If we do not take the finiteness condition of \( \theta(x) \) as \( x \to 0 \), we do not get a physically acceptable solution even for \( \Delta = \Delta' = 40 \). So incorporating that limit we have as \( x \to 0 \) we take large theta limit and assuming \( \sin \) and \( \cos \) to be rapidly oscillating in that limit we drop those term from the diff equation 3.5. Finally we get
\[ \theta''(x)\rho(x) + \theta'(x)\rho'(x) + 2\Delta \phi_1(x)\phi_2(x) = 0 \] (3.14)

Solution of this equation in the limit \( x \to 0 \) takes the form.

\[ \theta(x) = C^2 + \frac{1}{100\pi} \left[-50\pi \tan^{1+\sec(2\pi x)} + 50\pi \tan^{-1}(1/2(1 - \tan(\pi x)^2)) + g(x)\right] \]

\(^7\)This time we get \( \theta(x) \) to be symmetric which leads to boundary condition \( \dot{\theta}(1/2) = 0 \)
\(^8\)Ignoring this condition has led to no physical solution in the paper [1]
Figure 3.2: 1-2 configuration $\Delta' = 15$

$$g(x) = (7+i)\sqrt{4 - 2iC_1 \tan^{-1} \left( \frac{(1 + i) \tan(\pi x)}{\sqrt{4 - 2i}} \right)} - (1+7i)\sqrt{4 + 2iC_1 \tanh^{-1} \left( \frac{(1 + i) \tan(\pi x)}{\sqrt{4 + 2i}} \right)} - 5C_1 \cot(\pi x)$$

where $C_1$ and $C_2$ are constants. This takes the form

$$\theta(x)_{x\rightarrow 0} \sim \frac{a}{x} + b + cx + O(x^2) \quad (3.15)$$

Therefore including the finiteness condition on $\theta(x)$ we get only one physical solution (fig 3.13, fig 3.14) corresponding to $\Delta = \Delta' = 40$ (from the table 3.2). Because only for that value we have finite value of rotation in the limit $x$ going to zero.

However exclusion of the finiteness condition on $\theta(x)$ leads to multiple wave functions as shown in fig-3.15-3.16. (leading to various symmetries), hence the multiple potentials (fig 3.17).

For different eigenvalue ($\Delta'$) having same density which is in appropriate in the given context. Hence from the results obtained we can conclude that even for excited states there may exist one to one correspondence between potential and density.

---

\[ A,B... \text{corresponds to the initial conditions for which wave functions are normalized} \]

\[ \text{Fit to the functions for other normalized wave function was bad. For only one value } a \approx 0 \]

\[ \text{As shown in the paper} \]
3.3 Comments and further works for the system

- Interaction due to spin of particles should be included if we are talking about electrons.

- Even for same values of $\Delta'$ we can have different values of $\epsilon_i$ which will not be an eigen state of the Hamiltonian. In that case this approach is a bit questionable. Absolute value of energy should be taken for proper results.

- Another approach to solve the system can be used in which we can keep energy fix but take potential as a parameter.

- Inclusion of more number of particles will make this transformation complicated in turn making the evaluation of $\theta(x)$ not easily obtainable.

- If we include interaction, this approach completely fails as we cannot write independent particles orbitals.

- Trying similar approach but with some other unitary transformation.

- Checking the results for harmonic oscillator potential.
Figure 3.4: Values of $a$ from eqn 3.12 for small values of $x$ as function of parameter $\Delta'$

Figure 3.5: Physical solutions for $\Delta' = 15$
Figure 3.6: 1-2 configuration $\Delta' = 15$ Potential

Figure 3.7: Wave functions for $\Delta' = 25$
Figure 3.8: 1-2 configuration $\Delta' = 25$ Potential different from square well at boundary

Table 3.2: Table for the value of ‘a’ for Normalized wave functions various values of $d\theta(1/2)$ (for 1-3 configuration)

<table>
<thead>
<tr>
<th>$\Delta'$</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.00379147</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>-0.00379147</td>
<td></td>
<td>-0.00303702</td>
<td>-0.00683759</td>
<td>-0.00329403</td>
</tr>
<tr>
<td>40</td>
<td>-0.00002159</td>
<td>-0.0150336</td>
<td>-0.0136453</td>
<td>-0.00817969</td>
<td>-0.00580624</td>
</tr>
<tr>
<td>80</td>
<td>0.0131049</td>
<td>-0.015926</td>
<td>-0.0122711</td>
<td>-0.0158277</td>
<td>-0.00410315</td>
</tr>
<tr>
<td>120</td>
<td>-0.00434915</td>
<td>-0.0174066</td>
<td>-0.0145585</td>
<td>-0.00435088</td>
<td>-0.00237201</td>
</tr>
</tbody>
</table>
Figure 3.9: 1-3 configuration $\Delta' = 1$

Figure 3.10: 1-3 configuration $\Delta' = 40$
Figure 3.11: 1-3 configuration $\Delta'=80$

Figure 3.12: 1-3 configuration $\Delta'=160$
Figure 3.13: 1-3 configuration $\Delta'=40$ physical solution

Figure 3.14: 1-3 configuration $\Delta'=40$ potential
Figure 3.15: Normalized wave functions for $\Delta' = 160$ with $a \neq 0$

![Normalized wave functions for $\Delta' = 160$ with $a \neq 0$](image)

Figure 3.16: Normalized wave functions $\Delta' = 160$ with $a \neq 0$

![Normalized wave functions for $\Delta' = 160$ with $a \neq 0$](image)
Figure 3.17: Alternate potential for $\Delta' = 160$ in 1-3 configuration with $a \neq 0$
Chapter 4

Two interacting particles
and effective potential

After we have got the KS equations only problem left is to find out the exchange correlation functional. In this section I am going to present a model interacting system under periodic boundary condition and give a demonstration of strictly correlated electrons. Considering a 1D system (of length 2) having two interacting electrons with uniform density $\rho(x) = 1$. We impose periodic boundary conditions on the system. In general for free particles Coulomb repulsion between electrons can be written $1/|x_1 - x_2|$. But here as we have periodic boundary conditions potential is forced to modify to an effective potential as we want wave function to remain same w.r.t. translation of 2 unit and also we want it to be confined to length 2. This system can be considered equivalent to having two repulsive Coulomb force springs on a ring of length 2. As springs are compressed to $|x_1 - x_2|$ and $2 - |x_1 - x_2|$. So we have

$$V_{ee} = \frac{1}{2} \left[ \frac{1}{|x_1 - x_2|} + \frac{1}{2 - |x_1 - x_2|} \right]$$

$$V_{ee} = 1 + \epsilon^2 + O(\epsilon^4)$$

where $\epsilon = |x_1 - x_2| - 1$. Choosing constant external potential to be zero and to giving a parameter $\alpha$ measure of correlation between electrons on total Hamiltonian. If $\alpha$ is small it
will give small correlation and $\alpha$ is large it will give stron correlation in system.

\[ H_\alpha = -\frac{1}{2} \frac{\partial^2}{\partial x_1^2} + -\frac{1}{2} \frac{\partial^2}{\partial x_2^2} + \alpha V_{ee}(x_1, x_2) \]

Schroedinger equation takes teh form

\[ H_\alpha \psi_\alpha = E_\alpha \psi_\alpha \]

If we neglect $O(\epsilon^2)$ term, we get a Harmonic term in the Hamiltonian and solution for which is easily obtainable as

\[ \psi_\alpha = \frac{1}{\sqrt{2}} (\alpha/\pi)^{1/8} \exp(-\sqrt{\alpha}(\epsilon)^2/2) X_{as}(\sigma_1, \sigma_2) \]

and energy of the form $E_\alpha = \alpha + \sqrt{\alpha}$. For exact wave function we must have wave function at $\epsilon = \pm 1$ to vanish because of singularity in potential. For large $\alpha$ wave function is takes large value at $\epsilon = 0$. Therefore whenever $|\epsilon|$ is very less that 1 we get where ever wave function is different from zero. So as $\alpha \to \infty$ we have probability distribution function of the form

\[ P_{SCE}(x_1, x_2) = \sum_{\sigma_1, \sigma_2} |\psi_\alpha(1, 2)|^2 = \delta(\epsilon) \]

. We can see from fig(4.1) the probability takes a peak at $|\epsilon| = 1$. A system of N electrons with a given smooth density function $\rho(x)$ is said to be strictly correlated if the positions of N discrete electrons represents continuous density as well as possible. i. e. $\int_{x_n}^{x_{n+1}} dx \rho(x) = 1$ for $n = 1, 2, ...N - 1$ Clustering of electrons is striclty suppressed. In this case in the limit $\alpha \to \infty$ we get correct density for $\epsilon = 1$. So these positions corresponds to striclty correlated electrons. There for any general system we can start backwards i. e. we assume certain relationship in the positions of electrons and then calculate correlation function and then calculate interaction energy functional $V_{ee}^{SCE}$ and hence solve for the wave functions of system. Finally solving the system completely (including correlation of electrons).
Figure 4.1: Strong correlated electrons probability density for $\alpha = 1000$

![Figure 4.1: Strong correlated electrons probability density for $\alpha = 1000$](image1)

Figure 4.2: Interaction Potential

![Figure 4.2: Interaction Potential](image2)
Chapter 5

Summary and conclusions

In order to study properties of many body systems, I studied the basic approach in Density Functional Theory. In order to look for the one to one correspondance between density and external potential I studied a system of two non interacting spinless electrons in infinite square well. By taking an alternate potential and keeping density same (using a unitary transformation of rotation) I studied the effect on the states corresponding to this alternate potential. From the results I concluded that for first and second excited state there exists a one to one correspondance between density and external potential. Due to that I figured out that this alternate potential gives rise to same state, in fact this alternate potential is nothing but the original square well potential. There may exist an analog of HK theorem for excited state as well. Furthermore I tried to include spin in the system by considering antisymmetric wave functions for space part (as spin part is symmetric) but I reached the same density. It did not give anything new.

After that I studied a system of two interacting particles subjected to periodic boundatry conditions which lead to a modified effective potential. I demonstrated the strong correlation limit of this system. This provides one way to calculate correlation energy in strictly correlated system.

In the project I could study only two body problems their effective potentials. Extension of the present work to many body problems requires some more analysis.
Chapter 6

Acknowledgement

This work was done under the guidance of Dr. Prasanjit Samal as a part of 6th semester project at NISER.
Chapter 7

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