10.675 LECTURE 3

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1. Today

→ Hartree Theory and Self Consistent Solutions
→ Slater Determinant
→ Hartree-Fock Theory
Reminder, Tuesday's Evening Class 7-8:30 rm 1-115

2. Concepts

→ Mean Field Theory → Self Consistent Solutions

3. Quick Review

$H\Psi_0 = E_i\Psi_0$ for the ground state system. The full hamiltonian is below.

$$H = \frac{-1}{2}\sum_i^N \nabla_i^2 - \sum_i^N \sum_j^M \frac{Z_k}{v} ecr_i - \vec{R_k} + \sum_i^N \sum_{i<j}^N \frac{1}{\vec{r_i} - \vec{r_j}}$$

The difficulty arises in the last term, because it's not separable.

4. Hartree Theory 1928

Trial Wave Function $\chi_1(\vec{x_1})\chi_2(\vec{x_2})$
Go from a many bodied problem to a single electron problem.
$\rho_j \rightarrow$ electron density of j.
$\rho_j(\vec{r}) = \Psi_j^*(\vec{r})\Psi_j(\vec{r})$
Sooo...

$$\sum_i^N \sum_{i<j}^N \frac{1}{\vec{r_i} - \vec{r_j}} \rightarrow \sum_{j=2}^N \frac{\chi_1(\vec{x_1})\chi_2(\vec{x_2})}{|\vec{r_i} - \vec{r_j}|}$$

and that is the "Mean Field Term."

$$H_1^{Hartree} = \frac{-1}{2}\sum_i^N \nabla_i^2 - \sum_i^N \sum_j^M \frac{Z_k}{\vec{r_i} - \vec{R_k}} + \sum_{j=2}^N \frac{\rho(\vec{r_i})}{|\vec{r_i} - \vec{r_j}|} dr_i$$

Summed up from $H_1^{Hartree} + H_2^{Hartree} ... + H_N^{Hartree}$ for each electron.
Thus, we solve $H_1^{Har}\chi_1^{Har}(1) = \epsilon_1\chi_1^{Har}(1)$
Example

Date: Fall 2004.

$$
\begin{array}{l}
Initially \\
\chi_1(1)\chi_2(2)\chi_3(3) \\
\downarrow \\
\chi_1^{'}(1)\chi_2(2)\chi_3(3) \\
\downarrow \\
\chi_1^{'}(1)\chi_2^{'}(2)\chi_3(3) \\
\downarrow \\
\chi_1^{'}(1)\chi_2^{'}(2)\chi_3^{'}(3) \\
\downarrow \\
\chi_1^{''}(1)\chi_2^{'}(2)\chi_3^{'}(3) \\
\downarrow \\
\chi_1^{''}(1)\chi_2^{''}(2)\chi_3^{'}(3) \\
\downarrow \\
Convergence!
\end{array}
$$

The major problem left to deal with is the fact that $\chi_1(\vec{x_1})\chi_2(\vec{x_2})$ is symmetric in regards to exchange of electron positions. Thus, we need to make it anti-symmetric by converting via a slater determinant.

5. Slater Determinant

$$
\begin{aligned}
\Psi(\vec{x_1},\vec{x_2}) &= \frac{1}{\sqrt{2}}[\chi_i(\vec{x_1})\chi_i(\vec{x_2}) - \chi_i(\vec{x_2})\chi_i(\vec{x_1})] \\
&= \frac{1}{\sqrt{2}}\begin{vmatrix} \chi_i(\vec{x_1}) & \chi_i(\vec{x_2}) \\ \chi_j(\vec{x_1}) & \chi_j(\vec{x_2}) \end{vmatrix}
\end{aligned}
$$

The above is known as a "Slater" determinant.
Now, we want to expand this relationship for an N-electron system.

$$
\Psi(\vec{x_1}\vec{x_2}\vec{x_3}...\vec{x_N}) = \frac{1}{\sqrt{N}}\begin{vmatrix} \chi_i(1) & \chi_j(1) & \chi_k(1) \\ \chi_i(2) & \chi_j(2) & \chi_k(2) \\ . & . & . \\ . & . & . \\ . & . & . \\ \chi_i(N) & \chi_j(N) & \chi_k(N) \end{vmatrix}
$$

with each spin being orthonormal!
$\int \chi_i^*(\vec{x})\chi_i\vec{x}dx = \delta_{ij}$

6. Hartree + Slater Determinant

$H^{Hf}\Psi_o = E_o\Psi$
Reorganizing via multiplying each side by Ψ_*
$E_o = \int \Psi_o^* H^{Hf}\Psi_o d\vec{x_1}d\vec{x_2}$

$$H^{Hf} = \frac{-1}{2}\nabla_i^2 - \sum_k \frac{Z_k}{\vec{r_i} - \vec{R_k}} + \frac{1}{\vec{r_1} - \vec{r_2}}$$

where $\frac{1}{r_1 - r_2}$ is often written $\frac{1}{r_{12}}$

$$E_o = \sum_a^N \int d\vec{x_1} \chi_a^*(\vec{x_1})[\frac{-1}{2}\nabla_i^2 - \sum_k \frac{Z_k}{\vec{r_i} - \vec{R_k}}]\chi_a(\vec{x_1})$$
$$+\frac{1}{2}\sum^N\sum^N \int\int d\vec{x_1} d\vec{x_2} \chi_a^*(1)\chi_b^*(2)\frac{1}{r_{12}}\chi_a(1)\chi_b(2)$$
$$+\frac{1}{2}\sum^N\sum^N \int\int d\vec{x_1} d\vec{x_2} \chi_a^*(1)\chi_b^*(2)\frac{1}{r_{12}}\chi_a(2)\chi_b(1)$$

Term 1 is the energy of a single electron. Term 2 is the coulomb interaction between electron 1 and 2. Term 3 is the "exchange" energy term.
→ The exchange energy term is a result of using the slater determinant, which deals with the exchange of electrons. This is a correction to the "mean field" term.
→ To note, when a=b, the last terms cancel out.

7. Symbolic Notation

The above was a complete mess, to simplify we'll use the following notation.
The single electron term $h(1) = \frac{-1}{2}\vec{\nabla_1^2} - \frac{Z_k}{r_{1k}}$
The coloumb term: $J_b(1)\chi_a(1) = [\int d\vec{x_2}\chi_b^*(2)r_{12}^{-1}\chi_b(2)]\chi_a(1)$
The exchange term: $K_b(1)\chi_a(1) = [\int d\vec{x_2}\chi_b^*(2)r_{12}^{-1}\chi_a(2)]\chi_b(1)$
Condense further to symbolic notation.
$E_o = \sum_a < a|h|a > + \frac{1}{2}\sum_{ab} < ab||ab >$
And this is equivalent to the entire mess is the previous section.
Let's expand the last term just to be clear.
$\frac{1}{2}\sum_{ab} < ab||ab >= \frac{1}{2}\sum_{ab}[aa|bb] - [ab|ba]$
In usage, this would appear as $[h(1) + \sum_{b\neq a} J_b(1) - K_b(1)]\chi_a(1) = \epsilon_a\chi_a(1)$
and the term in brackets is called the "fock" operator.

8. Basis Sets

$|\Psi_1(\vec{r})|^2 dr_i^2 = \rho_1(\vec{r_1})dr_1$ which is probability of finding electrons.
$\int \rho_1(\vec{r_1})d\vec{r_1} = 1$ over all space.
A "basis set" is a set of functions introduced to fit Ψ's, but it's not a rigorous basis set as solved analytically.
$\Psi(\vec{r}) = \sum_a c_a u_a(r)$
where c_a is a complex number and $u_a(r)$ is the basis. Together, they form vectors.
$\int d\vec{r} u_a^*(\vec{r})u_b(\vec{r}) = \delta_{ab}$ when orthnormal
$c_a = \int dr U_a^*(\vec{r})\Psi(\vec{r})$

9. Dirac Notation

$\int \Psi_a^*(\vec{r})\Psi_a(\vec{r}) =< \Psi_a|\Psi_b >=< a|b >$ where : $< a|$ is called the "bra" and $|b >$ is called the "ket"
H is a linear operator.
$H(C_a|a > + C_b|b >) = C_a H|a > + C_b H|b >$

$\int \Psi_a^* H \Psi_b^* dr =< a|H|b >$
H is hermitian meaning $H = H^\dagger$
$< a|H^\dagger|b >=< b|Ha >^*$
$< a|Hb >=< Ha|b >$
$< a|b >$ a is the complex conjugate.
The bras, kets define a matrix $H_{ab} =< a|H|b >= \begin{pmatrix} H_{11} & H_{12} & ... \\ H_{21} & H_{22} & ... \\ ... & ... & ... \end{pmatrix}$

10. Hermitian Details

Important properties
$\rightarrow$ Eigenfunctions are orthonormal
$\rightarrow$ Eigenvalues are real
$\rightarrow$ All observables are eigenvalues of hermitian operators
$\rightarrow dp(\alpha) = | < U_\alpha|\Psi > |^2 d\alpha =$ probability of getting α.
$\rightarrow dp(\vec{r}) = | < \vec{r}|\Psi > |^2$