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

\( H \Psi_0 = E_1 \Psi_0 \) for the ground state system. The full hamiltonian is below.

\[
H = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \sum_j \frac{Z_k}{r_{ij}} - R_k + \sum_i \sum_{i<j} \frac{1}{r_{ij}}
\]

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

4. HARTREE THEORY 1928

Trial Wave Function \( \chi_1(x_1)\chi_2(x_2) \)

Go from a many bodied problem to a single electron problem.

\( \rho_j \rightarrow \) electron density of \( j \).

\( \rho_j(r) = |\Psi_j(r)|^2 \)

Soooo...

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

and that is the “Mean Field Term.”

\[
H_1^{\text{Hartree}} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i Z_k \sum_j \frac{1}{r_{ij}^2} - R_k + \sum_i \frac{\rho(r_i)}{|r_i^2 - r_j^2|} dr_i
\]

Summed up from \( H_1^{\text{Hartree}} + H_2^{\text{Hartree}} + \ldots + H_N^{\text{Hartree}} \) for each electron.

Thus, we solve \( H_1^{\text{Hartree}} \chi_1^{\text{Hartree}}(1) = \epsilon_1 \chi_1^{\text{Hartree}}(1) \)

Example

Date: Fall 2004.
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!

The major problem left to deal with is the fact that \( \chi_1(x_1)\chi_2(x_2) \) 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

\[
\Psi(x_1, x_2) = \frac{1}{\sqrt{2}} [\chi_i(x_1)\chi_i(x_2) - \chi_i(x_2)\chi_i(x_1)]
\]

\[
= \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_i(x_1) & \chi_i(x_2) \\ \chi_j(x_1) & \chi_j(x_2) \end{vmatrix}
\]

The above is known as a "Slater" determinant.

Now, we want to expand this relationship for an N-electron system.

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

with each spin being orthonormal!

\[
\int \chi_i^*(\vec{x})\chi_i\,dx = \delta_{ij}
\]

6. Hartree + Slater Determinant

\[
H^{Hf}\Psi_o = E_o\Psi
\]

Reorganizing via multiplying each side by \( \Psi^* \)

\[
E_o = \int \Psi^* H^{Hf}\Psi_o\,dx_1\,dx_2
\]
\[ H^{Hf} = -\frac{1}{2} \nabla_i^2 - \sum_k \frac{Z_k}{r_i - R_k} + \frac{1}{r_1 - r_2} \]

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

\[ E_o = \sum_a \int dx_i \chi^*_a(x_i) \left[ -\frac{1}{2} \nabla_i^2 - \sum_k \frac{Z_k}{r_i - R_k} \right] \chi_a(x_i) \]

\[ + \frac{1}{2} \sum_a \sum_b \int \int dx_1 \chi^*_a(1) \chi^*_b(2) \frac{1}{r_{12}} \chi_a(1) \chi_b(2) \]

\[ + \frac{1}{2} \sum_a \sum_b \int \int dx_1 \chi^*_a(1) \chi^*_b(2) \frac{1}{r_{12}} \chi_a(2) \chi_b(1) \]

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 \( h(1) = -\frac{1}{2} \nabla_1^2 - \frac{2}{r_{1b}} \).

The coulomb term: \( J_1(a) \chi_a(1) = \left[ \int dx_1 \chi^*_a(2) r_{12}^{-1} \chi_b(2) \right] \chi_a(1) \)

The exchange term: \( K_1(b) \chi_b(1) = \left[ \int dx_1 \chi^*_a(2) r_{12}^{-1} \chi_a(2) \right] \chi_a(2) \)

Condense further to symbolic notation.

\[ E_o = \sum_a \langle a| h| a \rangle + \frac{1}{2} \sum_{ab} \langle ab| ab \rangle \]

And this is equivalent to the entire mess is the previous section.

Let’s expand the last term just to be clear.

\[ \frac{1}{2} \sum_{ab} \langle ab| ab \rangle = \frac{1}{2} \sum_{ab} \langle aa| bb \rangle - \langle ab| ba \rangle \]

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

\[ |\Psi_1(\vec{r})|^2 dr_1^2 = \rho_1(\vec{r}_1)dr_1 \] which is probability of finding electrons.

\[ \int \rho_1(\vec{r}_1)dr_1 = 1 \] over all space.

A “basis set” is a set of functions introduced to fit \( \Psi \)’s, but it’s not a rigorous basis set as solved analytically.

\[ \Psi(\vec{r}) = \sum_a c_a u_a(\vec{r}) \]

where \( c_a \) is a complex number and \( u_a(\vec{r}) \) is the basis. Together, they form vectors.

\[ \int d\vec{r} u^*_a(\vec{r})u_b(\vec{r}) = \delta_{ab} \] when orthonormal

\[ c_a = \int d\vec{r} U^*_a(\vec{r})\Psi(\vec{r}) \]

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.

\( H(C_1|a> + C_2|b>) = C_1H|a> + C_2H|b> \)
\[ \int \Psi_a^* H \Psi_b^* dr = \langle a | H | b \rangle \]

H is hermitian meaning \( H = H^\dagger \)

\[ \langle a | H^\dagger | b \rangle = \langle b | H a \rangle^* \]

\[ \langle a | H b \rangle = \langle H a | b \rangle \]

\[ \langle a | b \rangle \text{ is the complex conjugate.} \]

The bras, kets define a matrix \( H_{ab} = \langle a | H | b \rangle = \begin{pmatrix} H_{11} & H_{12} & \cdots \\ H_{21} & H_{22} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \)

10. Hermitian Details

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