10.675 LECTURE 2

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1. LAST LECTURE REVIEW

→ Many Body PE surface.
→ Schrödinger's Equation (SE)
→ # Dimensions

2. IMPORTANT CONCEPTS

→ Many Body PE surface.
→ Schrodinger's Equation.
→ # Dimensions

3. MANY BODY SE

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

3N - 6 Degrees of Freedom (DOF) in Non-Linear Case
3N - 5 DOF for linear.
Each Molecule moves in the directions, hence 3N. In non-linear, substract 3 rotation and 3 translation (-6). In linear, substract 3 translation and 2 rotation (-5).

4. TODAY

→ QM and Atomic Orbitals
→ Permutation $\hat{P}_i j$ and Pauli Principle
→ Spin Orbitals
→ Valence band theory and molecular

5. BORN OPPENHEIMER APPROXIMATION

Theory that the electrons relax far faster than the protons. Thus, we can decouple nuclear-nuclear interaction terms from the electron terms.

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Date: Fall 2004.

6. Hydrogen Atom

$$H\phi_i(r) = E_i\phi_i(r)$$

H $\rightarrow$ Hamiltonian
$\phi_i \rightarrow$ "Atomic" orbital
r $\rightarrow$ position vector
We can solve for the hydrogen wave function explicitly

$$\phi_{nlm}(\vec{r}) = R_{nl}Y_l^m(\phi, \theta)$$

NOTE: the solution neglects or doesn't include the effects of spin.

7. Spin

Electrons have an intrinsic spin $+/- \frac{1}{2}$ or $\uparrow\downarrow$. This spin is a consequence of the SE in its relativistic formulation, *i.e.* the Dirac equation. Thus, degeneracy of the atomic orbitals exists.
Let ω be the spin coordinate. $\vec{x} = (\vec{r}, \omega)$.
Ψ = Total wave functions of the many body N electron system
$= \Psi(\vec{x_1}, \vec{x_2}, \vec{x_3}...\vec{x_N})$

8. Pauli Principle

Ψ must be anti symmetric with respect to exchange.
$\hat{P}_i j \rightarrow$ Permutation operator, which exchanges electron i with j.
$\hat{P}_{12}\Psi(\vec{x_1}, \vec{x_2}, \vec{x_3}) = \Psi(\vec{x_2}, \vec{x_1}, \vec{x_3}) = -\Psi(\vec{x_1}, \vec{x_2}, \vec{x_3})$

9. Helium Atom

Introduce spin orbital concept $\chi(\vec{x})$ where $\vec{x} = (\vec{r}, \vec{\omega})$
The ground state wave function is the lowest state.
$\Psi_0 = \chi_\alpha(\vec{x_1})\chi_\beta(\vec{x_2})$ which is our "trial" wavefunction.

10. Slater Determinant

$\Psi_0 = \chi_\alpha(\vec{x_1})\chi_\beta(\vec{x_2}) \rightarrow$ Not anti-symmetric, so it's a poor trial wave function. Try this instead.
$\Psi_0 = \frac{1}{\sqrt{2}}\left(\chi_\alpha(\vec{x_1})\chi_\beta(\vec{x_2}) - \chi_\alpha(\vec{x_2})\chi_\beta(\vec{x_1})\right)$
Which is anti-symmetric AND coupled.
A more convenient format is a slater determinant.

$$\Psi = \frac{1}{\sqrt{2}}\begin{vmatrix} \chi_\alpha(\vec{x_1}) & \chi_\alpha(\vec{x_2}) \\ \chi_\beta(\vec{x_1}) & \chi_\beta(\vec{x_2}) \end{vmatrix}$$

11. Spatial Functions

$\phi(r_1)\phi(r_2)$ abbreviate as $\phi(1)\phi(2)$
Spin Function α or β.
$\alpha(1)\alpha(2)$ and $\beta(1)\beta(2)$ are symmetric
$\alpha(1)\beta(2)$ and $\beta(1)\alpha(2)$ violates indistinguishability. Implies we have an independent measure of spins.

12. Combined Spin and Spatial Functions

Now that we have the electronic and spatial wave functions, we combine to get a complete trial wave function for helium.

$$\Psi(\vec{\chi_1}\vec{\chi_2}) = \frac{1}{\sqrt{2}}\phi(1)\phi(2)\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$$

Note that $\int \phi(1)\phi(1)dr = \int \phi(2)\phi(2)dr = 1$ from the overlap integral
$S = \int \phi_a\phi_b d(\vec{r})$

13. Hydrogen Gas

Valence bond theory, so valence bond wave function.
Choose a trial wave function (Heiter and London).
$\Psi = \phi_a(1)\phi_b(2)$ or $\phi_b(1)\phi_a(2)$
So, we need to create an overall anti-symmetric wave function of both electronic and spatial wave functions.

$$\Psi = \frac{1}{\sqrt{2 + 2S^2}}\left[\phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2)\right]\frac{1}{\sqrt{2}} * (\chi_\alpha(\vec{x}_1)\chi_\beta(\vec{x}_2) - \chi_\alpha(\vec{x}_2)\chi_\beta(\vec{x}_1))$$

which is overall anti-symmetric (both spatially and electronically).

14. Hydrogen Hamiltonian

The complete Hamiltonian is as follows.

$$H = \frac{-1}{2}\nabla_1^2 - \frac{-1}{2}\nabla_2^2 - \frac{1}{\vec{r_1} - \vec{R_a}} - \frac{1}{\vec{r_2} - \vec{R_b}} + \frac{1}{\vec{r_1} - \vec{r_2}} - \frac{1}{\vec{r_2} - \vec{R_a}} - \frac{1}{\vec{r_1} - \vec{R_b}}$$

Where $\vec{r}$ denotes electron position vector, $\vec{R}$ denotes nucleus position vector.

15. Perturbation Theory

Summary on pg 68 of S&O
Dissociation Energy
H_2 System
Calculated De = 3.15 eV Re=0.87$\mathring{A}$
Experimental De = 4.75 Re = 0.741 $\mathring{A}$
Major approximations
$\rightarrow$ Form of the trial wavefunction
$\rightarrow$BO approximation
$\rightarrow$ Perturbation Theory (how we solve it)

16. Molecular Orbital Approach

Trial Wave Function

$$\Psi = \frac{1}{\sqrt{2 + 2S^2}}\left[(\phi_a + \phi_b)(1)(\phi_a + \phi_b)(2)\right]\frac{1}{\sqrt{2}} * (\alpha(1)\beta(2) - \beta(1)\alpha(2))$$

The spatial orbital section is symmetric, and the electronic orbitals are antisymmetric. A symmetric function times a antisymmetric function leads to an overall anti symmetric function.
This is essentially a linear combination of spatial orbitals $\Psi(1)$ and $\Psi(2)$.

If we multiply out the spatial terms, we get the following.

$$\phi_a(1)\phi_a(2) + \phi_b(1)\phi_b(2) + \phi_a(1)\phi_a(2) + \phi_b(1)\phi_a(2)$$

The first two terms are "ionic" because both electrons are centered on 1 atom. The 2nd two terms are "covalent", as the electrons are shared. Unfortunately, if we maintain this balance, this implies that ionic-covalent characteristics should occur 50/50. This is obviously not the case. Thus, a fudge factor λ can be used to reduce the ionic content of the wave function. Then we can solve variationally. Typically, λ is set to 0.26.