# 10.675 LECTURE 6

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## 1. Today

→ Variational Principle
→ Derive HF (Hartree-Fock) Equations
→ Interpretation of Solutions to HF equations

## 2. Variational Principle

Idea: The closer our guess of $C_i$'s of $\Psi_{trial}$, the lower our energy.
$\tilde{\Phi} \Rightarrow$ trial function
$E[\tilde{\Phi}] =< \tilde{\Phi}|H|\tilde{\Phi} >$
Functional Definition : maps functions to numbers

## 3. Functional Variation

vary $\tilde{\Phi} \rightarrow \tilde{\Phi} + \delta\tilde{\Phi}$
substitute in and solve
$E[\tilde{\Phi} + \delta\tilde{\Phi}] =< \tilde{\Phi} + \delta\tilde{\Phi}|H|\tilde{\Phi} + \delta\tilde{\Phi} >$
expand this via linear first order term.
$E[\tilde{\Phi} + \delta\tilde{\Phi}] = E[\tilde{\Phi}] + < \delta\tilde{\Phi}|H|\tilde{\Phi} > + < \tilde{\Phi}|H|\delta\tilde{\Phi} >$ + higher order terms.
$E[\tilde{\Phi} + \delta\tilde{\Phi}] = E[\tilde{\Phi}] + \delta E$
Trying to approach the true solution such that $H|\Phi >= E|\Phi > \Rightarrow \delta E = 0$
Normally, E will always be a min, so we don't have to worry about local/global max solutions.
There exists and infinite number of solutions.
$H|\tilde{\Phi}_\alpha >= E_\alpha|\tilde{\Phi}_\alpha >$
$\alpha = 0, 1, 2...$
$E_o \leq E_1 \leq E_2...$
H is hermitian
$H = H^\dagger$, and $E_\alpha$'s are real
$\tilde{\Phi}_\alpha$ 's are orthonormal.
$< \tilde{\Phi}_\alpha|\tilde{\Phi}_\beta >= \delta_{\alpha\beta}$
$< \tilde{\Phi}_\alpha|H|\tilde{\Phi}_\beta >= E_\alpha\delta_{\alpha\beta}$

## 4. Expansion

Expand trial wave function $\tilde{\Phi}$ in terms of the eigenstates $\Phi$.
$|\tilde{\Phi} >= \sum_\alpha C_\alpha|\Phi_\alpha >$
$|\tilde{\Phi} >= \sum_\alpha |\Phi_\alpha >< \Phi_\alpha|\tilde{\Phi} >$
$< \tilde{\Phi}| = \sum_\alpha C^*_\alpha < \Phi_\alpha|$

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$< \tilde{\Phi}| = \sum_\alpha < \tilde{\Phi}|\Phi_\alpha >< \Phi_\alpha|$
$< \tilde{\Phi}|\tilde{\Phi} >= 1 = \sum_\alpha < \tilde{\Phi}|\Phi_\alpha >< \Phi_\alpha|\tilde{\Phi} >= \sum_\alpha | < \Phi_\alpha|\tilde{\Phi} > |^2$
and
$< \tilde{\Phi}|H|\tilde{\Phi} >= \sum_{\alpha\beta} < \tilde{\Phi}|\Phi_\alpha >< \Phi_\alpha|H|\Phi_\beta >< \Phi_\beta|\tilde{\Phi} >= \sum_\alpha E_\alpha| < \Phi_\alpha|\tilde{\Phi} > |^2$
$E[\Phi] = \frac{<\tilde{\Phi}|H|\tilde{\Phi}>}{<\tilde{\Phi}|\tilde{\Phi}>} = \frac{\sum_\alpha E_\alpha|<\Phi_\alpha|\tilde{\Phi}>|^2}{\sum_\alpha |<\Phi_\alpha|\tilde{\Phi}>|^2} = \frac{\sum_\alpha E_\alpha|C_\alpha|^2}{\sum_\alpha |C_\alpha|^2} \geq E_o$
Use variational principle to derive HF equations given the determinant
$|\Psi_o >= |\chi_1, \chi_2\chi_3, \cdots\chi_N >$
$E_o =< \Psi_o|H||Psi_o >= E_o[\{\chi_\alpha\}]$
Minimize with respect to $\chi_\alpha$'s functions w/constraint of $\chi_\alpha$'s being orthonormal.
$\int d\vec{x}\chi_a^*(1)\chi_b(1) = [a|b] = \delta_{ab}$

## 5. Lagrange Method of Undetermined Multipliers

$L[\{\chi_\alpha\}] = E_o[\{\chi_\alpha\}] - \sum_{a=1}^N \sum_{b=1}^N \epsilon_{ab}([a|b] - \delta_{ab})$
Where $\epsilon_{ab}$ are the undetermined multipliers.
$\frac{\delta L}{\delta \epsilon_{ab}} = 0$
$\frac{\delta L}{\delta \chi_a} = 0$
vary: $\chi_a \rightarrow \chi_a + \delta\chi_a$
$\delta L = 0\delta E_o - \sum_a^N \sum_b^N \epsilon_{ab}\delta[a|b] = 0$
$\delta[a|b] = [\delta\chi_a|\chi_b] + [\chi_a|\delta\chi_b]$
$\delta E_o = \sum_{a=q}^N([\delta\chi_a|h|\chi_a] + [\chi_a|h|\delta\chi_a]$
$+\frac{1}{2}\sum_a \sum_b([\delta\chi_a\chi_a|\chi_b\chi_b] + [\chi_a\delta\chi_a|\chi_b\chi_b] + [\chi_a\chi_a|\delta\chi_b\chi_b] + [\chi_a\chi_a|\chi_b\delta\chi_b])$
$+\frac{1}{2}\sum_a \sum_b([\delta\chi_a\chi_b|\chi_b\chi_a] + [\chi_a\delta\chi_b|\chi_b\chi_a] + [\chi_a\chi_b|\delta\chi_b\chi_a] + [\chi_a\chi_b|\chi_b\delta\chi_a])$
$= \sum_a^N = [\delta\chi_a|h|\chi_a] + \sum_a \sum_b([\delta\chi_a chi_a|\chi_b\chi_b] - [\delta\chi_a\chi_b|\chi_b\chi_a])$+ the complex conjugate terms.
$\delta L = 0 = \sum_1^N [\delta\chi_a|1|\chi_a] + \sum_{ab}[\delta\chi_a\chi_a|\chi_b\chi_b] - [\delta\chi_a\chi_b|\chi_b\chi_a] - \sum |ab\epsilon_a[\delta\chi_a| = \chi_b]$+ the complex conjugate terms.
$\delta L = \sum_{a=1}^N \int dx\delta\chi_a(1)[h(1)\chi)a(1) + \sum_{b=1}^N (J_b(1) - K_b(1)\chi_a(1) - \sum_{b=1}^N \epsilon_{ba}\chi_b(1)] = 0$
+ Complex conjugate terms.

## 6. Continued...

$[h(1) + \sum_b^N J_b(1) - K_b(1)]\chi_a(1) = \sum_b^N \epsilon_{ab}\chi(1)$
"Canonical Form" via unitary transformation to diaganolize $f|\chi_a >= \epsilon|\chi_a >$
Canonical HF equations.
$\epsilon_a =< \chi_a|f|\chi_a >=< \chi_a|h + \sum_b(J_b - K_b)|\chi_a >$
$=< a|h|a > + \sum_b < ab|ab| - < ab|ba >$
$=< a|h|a > + \sum_b < ab||ab >$ where $|a >$'s are occupied spin orbitals
$\epsilon_r =< r|h|r > + \sum_b < rb||rb >$ where $|r >$'s are "virtual" spin orbitals
$\sum_a^N \epsilon_a = \sum_a^N < a|h|a > + \sum_a^N \sum_b^N < ab||ab >$
$E_o \sum_a^N < a|h|a > +1/2 \sum \sum < ab||ab > \neq \sum_a^N \epsilon_a$
because of the coefficients on the double summation.
Example: $\epsilon_a$ includes interactions with all other orbitals, as does $\epsilon_b$, so they are being double counted in SCF.

## 7. Significance of orbital energies (Koopman's Thereom)

$E_o^N = \sum_a < a|h|a > +1/2 \sum_a \sum_b < ab||ab >$
when you take out one electron

$E_c^{N-1} = \sum_{anec} < a|h|a > +1/2 \sum_{anec} \sum_{bnec} < ab||ab >$
Ionization potential $= E_c^{N-1} - E_o^N$
$= - < c|h|c > -1/2 \sum_a < ac||ac > -1/2 \sum_b < cb||cb >$
$= - < c|h|c > - \sum_b < cb||cb >= \epsilon_c$
"Electron Affinity" $= E_A = E_o^N - E_r^{N+1} = \epsilon_r =$ the energy of the system with an additional electron in the virtual levels.
This is the "frozen" orbital approximation.