10.675 LECTURE 7

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1. Today

→ Meaning of HF Eigenvalues (Koopman's Thereom).
→ Restricted HF (Roothan Equations).
→ Basis Sets
→ Orthoganalization
→ SCF procedure

2. Error Evaluation

Reminder, ϵ_a's are positive, ϵ_r's are negative.
Δ = true energy - approximation

Approximation	*Energy*	Δ	*Energy*	Δ
Frozen Orbitals (shell shifts)	ϵ_a	$-$	ϵ_r	$-$
No electron correlation (repulsion)	ϵ_a	$+$	ϵ_r	$-$
No Geometry Relaxation (sp3 to sp2)	ϵ_a	$-$	ϵ_r	$-$

Note, the errors in the "no electron" correlation cancel out.

3. "Restricted" (closed-shell paired electrons)

HF: The Roothan Equations.

Integrate out the degree's of freedom. $\chi(\vec{x}) = \begin{cases} \Psi_i(\vec{r})\alpha(\omega) \\ \Psi_j(\vec{r})\beta(\omega) \end{cases}$

$f(\vec{x})\chi_i(\vec{x}) = \epsilon_i\chi_i(\vec{x}) = f(\vec{x})\Psi_j(\vec{r})\alpha(\omega_1) = \epsilon_j\Psi_j(\vec{r})\alpha(\omega_1)$

solve for spin β

$[\int dw_q \alpha(w_1) f(\vec{x})\alpha(w_1)]\Psi_j(\vec{r}) = \epsilon_j\Psi_i(\vec{r})$

Plugin $f(\vec{x}_1) = h(\vec{r})\sum_c^N \int dx_2 \chi_1^*(\vec{x}_2) r_1^{-1}(1 - P_{12})\chi_2(\vec{x}_2)$

$\sum_c^N \to \sum_{c_\alpha}^{N/2} + \sum_{c_\beta}^{N/2}$

$f(\vec{r}_1)\Psi_j(\vec{r}) = h(\vec{r}_1)\Psi_j(\vec{r}_1) +$

$\sum_C^{N/2} \int dw_1 dw_2 dr_2 \alpha^*(w_1)\Psi_1^*(r_2)\alpha^*(w_2) r_{12}^{-1}\Psi_i(r_2)\alpha(w_2) alpha(w_1)\Psi_j(r_1) +$

Exchange terms

Cancel out orthogonal terms.

$\Rightarrow f(1) = h(1) + \sum_a^{N/2}[2J_a(1) - K_a(1)]$

$f\Psi_j(\vec{r}_1) = \epsilon_j\Psi_j(\vec{r}_1)$

Meaning only spatial orbitals are left after integrating.

Date: Fall 2004.

4. Basis Set

Functions are not necessarily orthonormal.
$\Psi_i \sum_{\mu=1}^{k} C_\mu \phi_{mu}$
$i = 1, 2, 3, 4, ...k$
Where Ψ_i is the spatial vector, and ϕ is the trial expansion.

5. Roothan Equations

$\bar{\bar{F}}\bar{\bar{C}} = \bar{\bar{S}}\bar{\bar{C}}\bar{\bar{\epsilon}}$
Where $\bar{\bar{\epsilon}}$ is the diagonal set.
Density Matrix $\rho(\vec{r}) = 2\sum_a^{N/2} |\Psi_1(\vec{r})|^2$
$= 2\sum_a^{N/2} \sum_\nu C^*_{v_o} \phi^*_r(\vec{r}) \sum_\mu C_{\mu_o}\phi_\mu(r)$
$= \sum_{\mu\nu} 2(\sum_a^{N/2} C_\mu C_n u)\phi_\mu(\vec{r})\phi^*_\nu(\vec{r})$
$= \sum_{\mu\nu} P_{\mu\nu}\phi_\mu(\vec{r})\phi^*_\nu(\vec{r})$
$P_{\mu\nu}$ is the density matrix $\bar{\bar{P}} \Rightarrow \bar{\bar{F}}(\bar{\bar{P}})$
$f\sum_\nu C_{\nu_i}\phi_\nu = \epsilon_i \sum C_{v_i}\phi_i$
Multiply by * and integrate.
$\Rightarrow \sum_\nu \int dr_1 \phi^*_\mu f \phi_\nu = \epsilon \sum_\nu C_{v_i} \int dr_1 \phi^*_\nu \phi_\mu$
The first term ($\int dr_1 \phi^*_\mu f \phi_\nu$) is the $F_{\mu\nu}$ "Fock" matrix. The second term ($dr_1 \phi^*_\nu \phi_\mu$) is the $S_{\mu\nu}$ overlap matrix.

6. Solving Roothan Equations

Solve self consistently through basis set orthogonalization.
$\int dr \phi^*_\mu(r)\phi_\nu(r) = S_{\mu\nu}$
We want a transformation matrix $\bar{\bar{X}}$ that will orthogonalize S such that
$\phi'_\mu = \sum_\mu \phi_\nu$
$\mu = 1, 2, 3, 4, ...k$
$\int dr \phi^*_\nu(r)\phi_\nu(r) = \delta_{\mu\nu}$
$\delta_{\mu\nu} = \int dr[\sum_x x^*_{\lambda\mu}\phi^*_\lambda(r)][\sum_\sigma \chi_\sigma \phi_\sigma(r)]$
$= \sum_\lambda \sum_\sigma \chi^*_{\lambda\mu} \int ...$
$\bar{\bar{X}} + \bar{\bar{S}}\bar{\bar{X}} = 1$ with many possible choices of $\bar{\bar{X}}$
$\bar{\bar{X}} = \bar{\bar{S}}^{-1/2} \Rightarrow \bar{\bar{S}}^{-1/2}\bar{\bar{S}}\bar{\bar{S}}^{-1/2} = \bar{\bar{S}}^{-1/2}\bar{\bar{S}}^{1/2} = \bar{\bar{S}}^0 = 1$
$\bar{\bar{F}}\bar{\bar{C}} = \bar{\bar{S}}\bar{\bar{C}}\bar{\bar{\epsilon}}$ let $\bar{\bar{C}} = \bar{\bar{X}}\bar{\bar{C}}'\bar{\bar{F}}\bar{\bar{X}}\bar{\bar{C}}' = \bar{\bar{S}}\bar{\bar{X}}\bar{\bar{C}}'\bar{\bar{\epsilon}}$
Multiply by $\bar{\bar{X}}^*$ so $\bar{\bar{F}}'\bar{\bar{X}}^*\bar{\bar{F}}\bar{\bar{X}}$ then $\bar{\bar{F}}'\bar{\bar{C}}' = \bar{\bar{C}}\bar{\bar{\epsilon}}$
Transform to real C's.

7. SCF - Self Consistent Field Procedure

1) Specify System: Nuclear positions ($\vec{r}_k$'s), Atomic #'s (Z_k's), # electrons N, "basis set" (ϕ_μ)
2) Calculate $S_{\mu\nu}$, $H_{\mu\nu} = \int dr \phi^*_\mu h \phi_\nu$, and $(\mu\nu, \lambda\sigma)$
3) Diaganolize $\bar{\bar{S}} \Rightarrow \bar{\bar{X}} = \bar{\bar{S}}^{-1/2}$
4) Guess $\bar{\bar{P}}$ (density matrix)
5) Calculate $\bar{\bar{F}}$ (fock matrix)
6) $\bar{\bar{F}}' = \bar{\bar{X}}^*\bar{\bar{F}}\bar{\bar{X}}$
7) Diagonalize $\bar{\bar{F}}' \Rightarrow \bar{\bar{C}}' and \bar{\bar{\epsilon}}$
8) $\bar{\bar{C}} = \bar{\bar{X}}\bar{\bar{C}}'$

9) Calculate a new $\bar{\bar{P}}$ from $\bar{\bar{C}}$
10) Converged? Yes, done. No, goto step 5.