1. TODAY

→ Meaning of HF Eigenvalues (Koopman’s Theorem).
→ Restricted HF (Roothan Equations).
→ Basis Sets
→ Orthogonalization
→ SCF procedure

2. ERROR EVALUATION

Reminder, $\epsilon_a$’s are positive, $\epsilon_r$’s are negative.
$\Delta = \text{true energy} - \text{approximation}$

<table>
<thead>
<tr>
<th>Approximation</th>
<th>$\epsilon_a$</th>
<th>$\Delta$</th>
<th>$\epsilon_a$</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frozen Orbitals (shell shifts)</td>
<td>$\epsilon_a$</td>
<td></td>
<td>$\epsilon_r$</td>
<td></td>
</tr>
<tr>
<td>No electron correlation (repulsion)</td>
<td>$\epsilon_a$</td>
<td>+</td>
<td>$\epsilon_r$</td>
<td></td>
</tr>
<tr>
<td>No Geometry Relaxation (sp3 to sp2)</td>
<td>$\epsilon_a$</td>
<td></td>
<td>$\epsilon_r$</td>
<td></td>
</tr>
</tbody>
</table>

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. $\chi(\vec{x}) = \begin{pmatrix} \Psi_i(\vec{r})\alpha(\omega) \\ \Psi_j(\vec{r})\beta(\omega) \end{pmatrix}$

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

solve for spin $\beta$

$[\int dw_0\alpha(w_1)f(\vec{x})\alpha(w_1)]\Psi_j(\vec{r}) = \epsilon_j\Psi_j(\vec{r})$

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

$\sum_{c}^{N} \rightarrow \sum_{c_1}^{N/2} + \sum_{c_2}^{N/2}$

$f(\vec{r}_1)\Psi_j(\vec{r}) = h(\vec{r}_1)\Psi_j(\vec{r}_1) + 
\sum_{c}^{N/2} \int dw_1\int dw_2\int dx_2\alpha^*(w_1)\Psi_i^*(r_2)\alpha(w_2)r_1^{-1}\Psi_i(r_2)\alpha(w_1)alpha(w_1)\Psi_j(r_1) +$

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.
Functions are not necessarily orthonormal.
\[ \Psi_{i} \sum_{\mu=1}^{k} C_{\mu} \phi_{\mu i} \]
i = 1, 2, 3, 4, ...k
Where \( \Psi_{i} \) is the spatial vector, and \( \phi \) is the trial expansion.

5. Roothan Equations

\[ \vec{F} \vec{C} = \vec{S} \vec{C} \vec{e} \]
Where \( \vec{e} \) is the diagonal set.
Density Matrix \( \rho(r) = 2 \sum_{a}^{N/2} |\Psi_{1}(\vec{r})|^{2} \)
\[ = 2 \sum_{a}^{N/2} \sum_{\mu} C_{\mu}^{*} \phi_{\mu \tau}(\vec{r}) \sum_{\mu} C_{\mu \tau} \phi_{\mu}(r) \]
\[ = \sum_{\mu \nu} 2(\sum_{a}^{N/2} C_{\mu}^{*} C_{\nu \tau}) \phi_{\mu \tau}(\vec{r}) \phi_{\mu \tau}(\vec{r}) \]
\[ = \sum_{\mu \nu} P_{\mu \nu} \phi_{\mu}(\vec{r}) \phi_{\mu}(\vec{r}) \]

\( P_{\mu \nu} \) is the density matrix \( \vec{P} \Rightarrow \vec{F}(\vec{P}) \)
\[ f \sum_{\nu} C_{\nu \tau} \phi_{\nu}(r) = \epsilon_{i} \sum_{\nu} C_{\nu \tau} \phi_{\nu}(r) \]
Multiply by \( * \) and integrate.
\[ \Rightarrow \sum_{\nu} \int dr_{1} \phi_{\nu}^{*}(r) \phi_{\nu} = \epsilon_{i} \sum_{\nu} C_{\nu \tau} \int dr_{1} \phi_{\nu}^{*}(r) \phi_{\nu} \]
The first term \( (\int dr_{1} \phi_{\nu}^{*}(r) \phi_{\nu}) \) is the \( F_{\nu \nu} \) "Fock" matrix. The second term \( (dr_{1} \phi_{\nu}^{*}(r) \phi_{\nu}) \) is the \( S_{\mu \nu} \) overlap matrix.

6. Solving Roothan Equations

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

7. SCF - Self Consistent Field Procedure

1) Specify System: Nuclear positions \( (r_{k}'s) \), Atomic \#’s \( (Z_{k}'s) \), \# electrons \( N \),
"basis set" \( (\phi_{\mu}) \)
2) Calculate \( S_{\mu \nu}, H_{\mu \nu} = \int dr \phi_{\mu}^{*} h \phi_{\nu} \), and \( (\mu \nu, \lambda \sigma) \)
3) Diagonalize \( \tilde{S} \Rightarrow \tilde{X} = \tilde{S}^{-1/2} \)
4) Guess \( \tilde{P} \) (density matrix)
5) Calculate \( \tilde{F} \) (fock matrix)
6) \( \tilde{F}' = \tilde{X}^{*} \tilde{F} \tilde{X} \)
7) Diagonalize \( \tilde{F}' \Rightarrow \tilde{C}' and \tilde{e} \)
8) \( \tilde{C} = \tilde{X} \tilde{C}' \)
9) Calculate a new $\ddot{P}$ from $\ddot{C}$