

Recap - Chapter 3.2 Hartree-Fock

$$\Phi^{\text{trial}} = \begin{vmatrix} \phi_{o_1 s_1}(\underline{r}_1, \sigma_1) & \dots & \phi_{o_N s_N}(\underline{r}_1, \sigma_1) \\ \vdots & & \vdots \\ \phi_{o_1 s_1}(\underline{r}_N, \sigma_N) & \dots & \phi_{o_N s_N}(\underline{r}_N, \sigma_N) \end{vmatrix} \quad \text{Slater Determinant}$$

$$E^{\text{HF}}[\{\phi_{o_k s_k}\}] =$$

$$= \underbrace{\sum_{k=1}^N \int d^3r \phi_{o_k s_k}^*(\underline{r}) \left[-\frac{\nabla^2}{2} \right] \phi_{o_k s_k}(\underline{r})}_{\text{kinetic energy } T[\{\phi_{o_k s_k}\}]} + \underbrace{\sum_{k=1}^N \int d^3r \phi_{o_k s_k}^*(\underline{r}) V^{\text{nuc}}(\underline{r}) \phi_{o_k s_k}(\underline{r})}_{E^{\text{nuc-nuc}}}$$

$$+ \sum_{k, k'}^{N, N} \frac{1}{2} \int d^3r d^3r' \frac{\phi_{o_k s_k}^*(\underline{r}) \phi_{o_{k'} s_{k'}}^*(\underline{r}') \phi_{o_k s_k}(\underline{r}) \phi_{o_{k'} s_{k'}}(\underline{r}')}{|\underline{r} - \underline{r}'|} \quad \left. \vphantom{\sum_{k, k'}^{N, N}} \right\} \text{classical electrostatics}$$

$$- \sum_{k, k'}^{N, N} \frac{1}{2} \delta_{s_k s_{k'}} \int d^3r d^3r' \frac{\phi_{o_{k'} s_{k'}}^*(\underline{r}) \phi_{o_k s_k}^*(\underline{r}') \phi_{o_k s_k}(\underline{r}) \phi_{o_{k'} s_{k'}}(\underline{r}')}{|\underline{r} - \underline{r}'|} \quad \left. \vphantom{\sum_{k, k'}^{N, N}} \right\} \begin{array}{l} \text{"Exchange"} \\ \text{term"} \\ E^{\text{ex}} \\ \text{Consequence of} \\ \text{Pauli principle} \end{array}$$

3.3. The Hartree-Fock Equations

Next task: Find optimum $\{\phi_{o_k s_k}\}$ ("single-particle orbitals")

by: - minimizing $E^{\text{HF}}[\{\phi_{o_{k_1} s_{k_1}}, \phi_{o_{k_2} s_{k_2}}\}]$

- demanding orthonormality of $\{\phi_{o_k s_k}\}$:

$$\langle \phi_{o_{k_1} s_{k_1}} | \phi_{o_{k_2} s_{k_2}} \rangle = \delta_{o_{k_1} s_{k_1}, o_{k_2} s_{k_2}}$$

Variation: $\delta [E^{\text{HF}}[\{\phi_{o_{k_1} s_{k_1}}, \phi_{o_{k_2} s_{k_2}}\}] + \sum_{k, k'}^{N, N} [\lambda_{o_{k_1} s_{k_1}, o_{k_2} s_{k_2}} (\langle \phi_{o_{k_1} s_{k_1}} | \phi_{o_{k_2} s_{k_2}} \rangle - \delta_{o_{k_1} s_{k_1}, o_{k_2} s_{k_2}})]]$

= 0
 for any $\delta \phi_{\alpha s \alpha'}^*(r)$ away from the solution.

Leads to very similar Equations as Hartree, except for an extra "exchange term":

$$\left\{ -\frac{\nabla^2}{2} + V^{nuc}(r) + V_{es}^e(r) \right\} \phi_{\alpha s \alpha'}(r) - \sum_{k'=1}^N \delta_{s \alpha s \alpha'} \int d^3 r' \frac{\phi_{\alpha' s \alpha'}^*(r') \phi_{\alpha s \alpha'}(r')}{|r-r'|} \phi_{\alpha' s \alpha'}(r)$$

$$= \sum_{k'=1}^N \lambda_{\alpha s \alpha', \alpha' s \alpha'} \phi_{\alpha' s \alpha'}(r)$$

This does not look Schrödinger-like yet,

but can show that the matrix λ can be chosen to be diagonal (can be diagonalized because the LHS operator is Hermitian)

So we choose

$$\left\{ -\frac{\nabla^2}{2} + V^{nuc}(r) + V_{es}^e(r) \right\} \tilde{\phi}_{\alpha s \alpha'}(r) - \sum_{k'=1}^N \delta_{s \alpha s \alpha'} \left[\int d^3 r' \frac{\tilde{\phi}_{\alpha' s \alpha'}^*(r') \tilde{\phi}_{\alpha s \alpha'}(r')}{|r-r'|} \right] \tilde{\phi}_{\alpha' s \alpha'}(r)$$

$$= \epsilon_{\alpha s \alpha'} \tilde{\phi}_{\alpha s \alpha'}(r)$$

$\{ \tilde{\phi}_{\alpha s \alpha'} \}$ "canonical orbitals"

Hartree-Fock Equations

1. part: Hartree-like (up to V_{es}^e)

Exchange part [+ self-interaction corr.]:

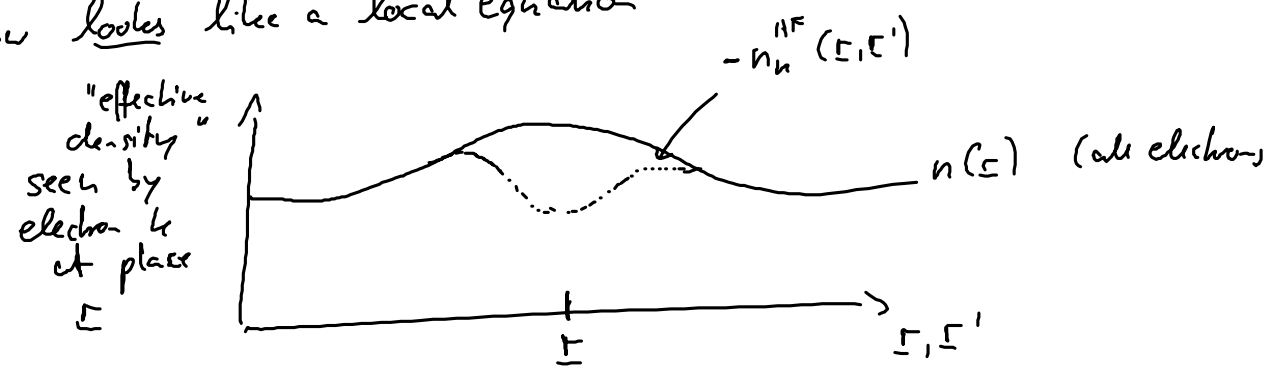
Non-local in $\tilde{\phi}_{\alpha s \alpha'}(r)$ - the above is an equation for $\phi_{\alpha s \alpha'}$ (α is only index not summed away)
 but integro-differential equation...

"Meaning" of the exchange term:

We could formally write:

$$\begin{aligned}
 & - \sum_{k' < k} \delta_{s_k s_{k'}} \int d^3 r' \frac{\tilde{\varphi}_{k's_{k'}}^*(r') \tilde{\varphi}_{k s_k}(r)}{|r - r'|} \tilde{\varphi}_{k's_{k'}}(r) \\
 & = - \sum_{k' < k} \delta_{s_k s_{k'}} \int d^3 r' \frac{1}{|r - r'|} \underbrace{\tilde{\varphi}_{k's_{k'}}^*(r') \tilde{\varphi}_{k s_k}(r') \tilde{\varphi}_{k's_{k'}}(r)}_{\varphi_{k s_k}(r)} \tilde{\varphi}_{k s_k}(r) \\
 & \quad \quad \quad \underbrace{\hspace{10em}}_{n_k^{HF}(r, r')} \\
 & = : V_k^x(r) \tilde{\varphi}_{k s_k}(r)
 \end{aligned}$$

now looks like a local equation



in short: An electron k at place r sees an electrostatic potential around itself that is effectively reduced: "Exchange hole"

This concept is physical! In the ME wave function, electrons move out of each others' way
Motion is "correlated"

Here (HF): Only electrons with same spin move out of each others' way

Reality (Full ME wave function): Electrons must move out of each others' way even in different spin channels due to $\frac{1}{|r - r'|}$ repulsion.

"Coulomb correlation"

"Chemists'" separation:

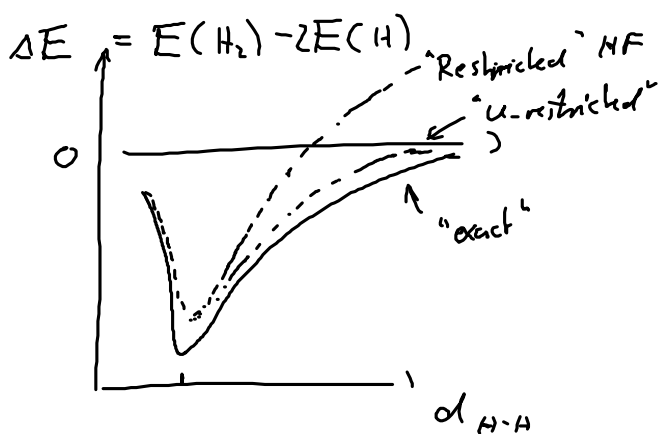
$$\text{Full correlation} = \text{Exchange} + \underbrace{\text{"Coulomb correlation"}_{\text{everything that cannot be captured with a single-determinant wave function.}}$$

Intermediate summary

- HF by construction the "best" single SD approximation to full ME wave function
- proper Fermion symmetry
- self-interaction free
- traditional starting point for "quantum chemistry"

3.5 The relevance of spin - "restricted" vs. "unrestricted" HF

Consider (last time) H_2 binding curve



If we had no spin-polarization overlap

- N electrons, $N_{\uparrow} = N_{\downarrow} = \frac{N}{2}$

in this case we could try -


$$\phi_{0_{k,\uparrow}}(\mathbf{r}) = \phi_{0_{k,\downarrow}}(\mathbf{r}) \equiv \phi_k(\mathbf{r})$$

where two electrons occupy each $\phi_k(\mathbf{r})$

Result =

$$\left\{ -\frac{\nabla^2}{2} + V^{nuc}(\mathbf{r}) + V^{es}(\mathbf{r}) \right\} \phi_{0_k}(\mathbf{r}) - \sum_{k' \neq k} \int d^3r' \frac{\phi_{0_{k'}}^*(\mathbf{r}') \phi_{0_k}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \phi_{0_{k'}}(\mathbf{r}) = \epsilon_{0_k} \phi_{0_k}(\mathbf{r})$$

"restricted HF"

So for H_2  twice the same, extended $\phi_{0_{k,\uparrow}} = \phi_{0_{k,\downarrow}}$ for H_2

but for long distances: What we want is



separate H atoms where each has its own separate spin polarization, $\phi_{0_{k,\uparrow}} \neq \phi_{0_{k,\downarrow}}$
can do if we keep spin ...
 (although, within the single SD, even this is an approximation)

3.6 Hartree-Fock in practice - basis sets (Restricted HF for simplicity)

Remember (single electron case, e.g. Hartree Eq)

$$\hat{h}^{\text{eff}} \phi_{0k}(\underline{r}) = \epsilon_{0k} \phi_{0k}(\underline{r})$$

with basis set

$$\{\phi_i(\underline{r})\}$$

$$\text{then } \phi_{0k}(\underline{r}) = \sum_j c_{kj} \phi_j(\underline{r})$$

$$\int d^3r \phi_i^*(\underline{r}) \hat{h}^{\text{eff}} \sum_j c_{kj} \phi_j(\underline{r}) = \int d^3r \phi_i^*(\underline{r}) \epsilon_{0k} \sum_j c_{kj} \phi_j(\underline{r})$$

$$\Rightarrow \sum_j h_{ij}^{\text{eff}} c_{kj} = \epsilon_{0k} \sum_j s_{ij} c_{kj}$$

$$\text{where } h_{ij}^{\text{eff}} = \int d^3r \phi_i^*(\underline{r}) \hat{h}^{\text{eff}} \phi_j(\underline{r}) \quad \text{if } \{\phi_i(\underline{r})\} \text{ ON}$$

$$s_{ij} = \int d^3r \phi_i^*(\underline{r}) \phi_j(\underline{r}) = \delta_{ij}$$

"Generalized" Eigenvalue problem for vectors c_k , Eigenvalues ϵ_{0k} .

up to $V_e^{\text{es}}(\underline{r})$, could write HF equations like that.

How about the exchange term?

$$\int d^3r \phi_i^*(\underline{r}) \sum_{k'=1}^{N/2} \int d^3r' \frac{\phi_{0k'}^*(\underline{r}') \phi_{0k}(\underline{r}')}{|\underline{r}-\underline{r}'|} \phi_{0k'}(\underline{r})$$

$$= \sum_j \sum_l \sum_m \underbrace{\sum_{k'}^{N/2} c_{k'l}^* c_{k'm} c_{kj}}_{\frac{1}{2} P_{lm} \text{ "density matrix" (} k' \text{ summed away)}} \underbrace{\int d^3r \int d^3r' \frac{\phi_i^*(\underline{r}) \phi_l(\underline{r}) \phi_l^*(\underline{r}') \phi_j(\underline{r}')}{|\underline{r}-\underline{r}'|}}_{\substack{\text{4 basis fun, 6 i-ketel dimensional matrix} \\ \text{shorthand (im | l j) "Coulomb" matrix}}}$$

l, m are also summed away

$$= \sum_j \frac{1}{2} \sum_{lm} P_{lm} (im | l j) c_{kj}$$

K_{ij} ... matrix like everything else ... does not depend on k anymore.

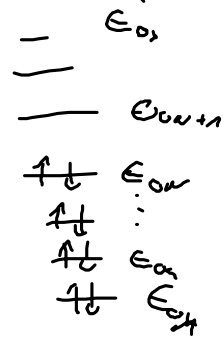
In full: $\sum_j (h_{ij}^{\text{eff}} - k_{ij}) c_{kj} = E_{0k} \sum_j c_{kj}$ like before
 "Roothaan Equations"

Note: need $(i|1|j)$ and sum over them
 If $\{\phi_i(\xi)\}$ has S basis functions $\rightarrow S^4$ matrix elements
 (without special tricks)
 " $O(S^4)$ " summations as written above (compare $O(S^3)$ for solution of ELP) for computational effort (= time)

Note also: Full solution of Roothaan Eq's yields
 S eigenvalues/eigenvectors.
 E_{0k}/c_{kj} for $k > N$ "unoccupied" orbitals

3.6 "Meaning" of HF (II): Koopman's Theorem

What can we learn from E_{0k} ?



Consider N -electron system,
 Hartree-Fock wave function Φ^N

$\rightarrow N$ "filled" single-electron orbitals $\phi_{0k s_k}(\xi)$

Consider next ionization energy; take one electron out of orbital $j \leq N$
 imagine that the remaining $\phi_{0k s_k}$ don't change

Then, HF determinant for $N-1$ electron system

$$\Phi_j^{N-1} = \text{SD} \{ \phi_1(\xi_1) \cdots \phi_{j-1}(\xi_{j-1}) \cdot \phi_{j+1}(\xi_{j+1}) \cdots \phi_N(\xi_N) \}$$

(i.e. remove column j , row j from SD Φ^N)

ionization energy

$$\begin{aligned}
 I_j &= E_j^{N-1} - E^N = \langle \bar{\Phi}_j^{N-1} | \hat{H}_{N-1}^e | \bar{\Phi}_j^{N-1} \rangle - \langle \bar{\Phi}^N | \hat{H}_N | \bar{\Phi}^N \rangle \\
 &= \langle \bar{\Phi}^{N-1} | \sum_{\substack{k=1 \\ k \neq j}}^N (-\frac{\nabla_k^2}{2} + V^{nuc}) | \bar{\Phi}^{N-1} \rangle + \frac{1}{2} \langle \bar{\Phi}_j^{N-1} | \sum_{\substack{k_1, k_2 \\ k_1 \neq k_2 \\ k_1 \neq j \\ k_2 \neq j}}^{N-1} \frac{1}{|\mathbf{r}_{k_1} - \mathbf{r}_{k_2}|} | \bar{\Phi}_j^{N-1} \rangle \\
 &\quad - \langle \bar{\Phi}^N | \sum_{k=1}^N (-\frac{\nabla_k^2}{2} + V^{nuc}) | \bar{\Phi}^N \rangle + \frac{1}{2} \langle \bar{\Phi}^N | \sum_{\substack{k_1, k_2 \\ k_1 \neq k_2}}^{N-1} \frac{1}{|\mathbf{r}_{k_1} - \mathbf{r}_{k_2}|} | \bar{\Phi}^N \rangle \\
 &= - \langle \phi_{j, s_j} | -\frac{\nabla^2}{2} + V^{nuc} | \phi_{j, s_j} \rangle - \sum_{\substack{k=1 \\ k \neq j}}^N \int d^3r_1 d^3r_2 \frac{\phi_{j, s_j}^*(\mathbf{r}_1) \phi_{k, s_k}(\mathbf{r}_1) \phi_{k, s_k}(\mathbf{r}_2) \phi_{j, s_j}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \\
 &\quad + \sum_{\substack{k=1 \\ k \neq j}}^N \int d^3r_1 d^3r_2 \frac{\phi_{j, s_j}^*(\mathbf{r}_1) \phi_{k, s_k}(\mathbf{r}_1) \phi_{k, s_k}(\mathbf{r}_2) \phi_{j, s_j}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}
 \end{aligned}$$

see orig derivation of Hartree, esp especially the

factors $\frac{1}{2}$ are gone

because same term appears twice (double counting)

$$= - \epsilon_{j, s_j} [= \langle \phi_{j, s_j} | \hat{h}_j^{HF} | \phi_{j, s_j} \rangle]$$

↑ single electron operator from HF eqns.

Total energy difference $E_j^{N-1} - E^N$ can be converted to a "single-particle eigenvalue"

if we assume that $\{\phi_{k, s_k}\}$ do not change if we take out one electron from the problem.

In practice, sometimes a reasonable, never a great approximation for I_j .

Could do similar for excitations e.g. $j < N \xrightarrow{\text{excited}} i > N$
to

$$E_{j \rightarrow i} \approx \epsilon_i - \epsilon_j \dots \text{but progressively worse approximation.}$$