

# Chapter 3.1 Hartree Method - Continued

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We have: "Adiabatic" many-electron problem

$$\hat{H}^e = \hat{T}^e + \hat{V}^{nuc} + \hat{V}^{e-e}$$

Hartree Ansatz: "If only we had a separable problem"

$$\bar{\Phi}^{trial} \equiv \bar{\Phi}^{Hartree}(\{\underline{r}_k\}) = \varphi_{o_1}(\underline{r}_1) \cdot \dots \cdot \varphi_{o_N}(\underline{r}_N)$$

(not a Slater Determinant)

Variational principle: Minimize

$$E^{trial} = \frac{\langle \bar{\Phi}^{Hartree} | \hat{H}^e | \bar{\Phi}^{Hartree} \rangle}{\langle \bar{\Phi}^{Hartree} | \bar{\Phi}^{Hartree} \rangle}$$

$$\Rightarrow \left[ \underbrace{-\frac{\nabla^2}{2}}_{(1)} + \underbrace{V^{nuc}(\underline{r})}_{(2)} + \sum_{\substack{k'=1 \\ k \neq k'}}^N \int d^3r' \frac{\varphi_{o_{k'}}^*(\underline{r}') \varphi_{o_{k'}}(\underline{r}')}{|\underline{r} - \underline{r}'|} \right] \varphi_{o_k}(\underline{r}) = \epsilon_{o_k} \varphi_{o_k}(\underline{r})$$

(3)

WHAT HAVE WE HERE?

... an effective single-particle Hamiltonian

$$\underline{\hat{h}_k^{eff} \varphi_{o_k}(\underline{r}) = \epsilon_{o_k} \varphi_{o_k}(\underline{r})}$$

(1) kinetic energy term ✓

(2) nuclear potential ✓

(3) e-e - interaction term

• depends on  $k$  (why?)

• depends on all other  $\phi_{0k'}(\underline{r})$

... VGH - full Hamiltonian depends on its solutions.

• explicitly depends only on  $\underline{r}$

→ local effective potential  $V_k^{\text{eff}}(\underline{r})$ .

Remark:

$$V_k^{\text{eff}}(\underline{r}) = \sum_{\substack{k'=1 \\ k \neq k'}}^N \int d^3r' \frac{\phi_{0k'}^*(\underline{r}') \phi_{0k'}(\underline{r}')}{|\underline{r} - \underline{r}'|}$$

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

$$- \int d^3r' \frac{|\phi_{0k}(\underline{r}')|^2}{|\underline{r} - \underline{r}'|} \quad (\text{B})$$

(A) note:  $n(\underline{r}) = \sum_{k'=1}^N |\phi_{0k'}(\underline{r})|^2$  density of the electrons

→  $\int d^3r' \frac{n(\underline{r}')}{|\underline{r} - \underline{r}'|} = V_{\text{es}}^e(\underline{r})$  classical electrostatic potential

numerically, lots of good ways to compute this

from Poisson Eq.  $\Delta V_{\text{es}}^e(\underline{r}) = -4\pi n(\underline{r})$

also called "Hartree potential" ...

(B) " $n_{0k}$ "  $(\underline{r}) = |\phi_{0k}(\underline{r})|^2$  classical density of electron  $k$

basically, removes the interaction of electron  $k$  with

itself.

Hartree method: "self-interaction free"

Complete single-particle like recipe for:

-  $n(\epsilon)$  (approx.)

- approx. for  $E_0 < E_0^{[Hartree]}$   
 $\uparrow$   
 g.s. of full ME system

Meaning of  $\phi_{0k}(\epsilon)$ ,  $E_{0k}$  ... later

But note:

$$E_0^{[Hartree]} \neq \sum_{k=1}^N E_{0k}$$

Reason: ME interaction

$$\hat{V}^{ee} = \frac{1}{2} \sum_{\substack{k,k' \\ k \neq k'}}^{NV} \frac{1}{|\epsilon_k - \epsilon_{k'}|}$$

but no  $\frac{1}{2}$  in  $V_{es}^e(\epsilon)$ !

"Double-counting"

### Practical aspects

$$V_k^{eff}(\epsilon) \equiv V_k^{eff}[\{\phi_{0k}\}](\epsilon)$$

depends on its solutions

"Method of the self-consistent field" (SCF)

o Guess an approximate solution

$$- V_k^{eff(0)} \equiv \sum_{I=1}^M V_{free atom}^{eff}(\epsilon)$$

$$n^{(0)}(\underline{r}) \equiv \sum_{I=1}^M n_{\text{free atom}}(\underline{r}) \quad \text{etc}$$

$$(a) \left[ -\frac{\nabla^2}{2} + V_k^{\text{eff}(i-1)}(\underline{r}) \right] \varphi_{0k}^{(i)}(\underline{r}) = \epsilon_{0k}^{(i)} \varphi_{0k}^{(i)}(\underline{r})$$

$$(b) \text{ update density } n^{(i)}(\underline{r}) = \sum_{k=1}^N |\varphi_{0k}^{(i)}(\underline{r})|^2 \quad \Leftarrow \text{but this update could be more sophisticated}$$

(c) update es. potential

$$V_{\text{Hartree}}^{(i)}(\underline{r}) = \int d^3r' \frac{n^{(i)}(\underline{r}')}{|\underline{r} - \underline{r}'|}$$

simplest: "linear mixing"

$$n_{\text{next}}^{(i)} = \alpha n^{(i)} + (1-\alpha)n^{(i-1)}$$

↑  
mixing factor  
 $0 \leq \alpha \leq 1$

(d) back to (a), unless

$$\|n^{(i)} - n^{(i-1)}\| < \delta_1 \quad (*)$$

$$|\epsilon_{0k}^{(i)} - \epsilon_{0k}^{(i-1)}| < \delta_2 \quad (**)$$

etc.

if (\*, \*\*) fulfilled:

"self-consistent"

NOTE: • Full SCF problem is non-linear

• not even (at this point) guaranteed that a solution exists

• or there could even be more than one solution.

• and convergence not guaranteed from given starting point

### 3.2 "Proper Fermions" - Exchange and "Hartree-Fock"

Idea: Use same principle as Hartree method,

but trial function with proper Fermion  
(anti) symmetry - Slater determinant.

$$\Phi^{\text{trial}} \equiv \bar{\Phi}^{\text{HF}}(\{\Gamma_k, \sigma_k\}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{o_1 s_1}(\Gamma_1, \sigma_1) & \dots & \varphi_{o_N s_N}(\Gamma_N, \sigma_N) \\ \vdots & & \vdots \\ \varphi_{o_1 s_1}(\Gamma_N, \sigma_N) & \dots & \varphi_{o_N s_N}(\Gamma_1, \sigma_1) \end{vmatrix}$$

$o_k$  "orbital index" of el.  $k$

$s_k$  "spin index"

So far, we (somewhat incorrectly) ignored the fact  
that electrons carry spin -  $s = \pm \frac{1}{2}$

Could have included this through

$$\bar{\Phi}_\nu(\{\Gamma_k, \sigma_k\}) \equiv \bar{\Phi}_\nu(\{\Gamma_k\}) \cdot \chi_\nu(\{\sigma_k\})$$

For  $\hat{H}^e$  as defined so far: Separation possible since  $\hat{H}^e$  does  
not depend on spin  
(no spin-orbit coupling.)

For example,  $\chi_\nu(\{\sigma_k\}) = \chi_{s_1}(\sigma_1) \cdot \dots \cdot \chi_{s_N}(\sigma_N)$

e.g.  $\chi_\uparrow = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ ,  $\chi_\downarrow = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

For Hartree Ansatz, could have led to two indep

components  $\bar{\Phi}^{\text{Hartree}} \equiv \begin{pmatrix} \bar{\Phi}_\uparrow^{\text{Hartree}}(\Gamma_k, \sigma_k = \frac{1}{2}) \\ \bar{\Phi}_\downarrow^{\text{Hartree}}(\Gamma_k, \sigma_k = -\frac{1}{2}) \end{pmatrix}$

Hartree-Fock: Keep spin indices right here because

Pauli principle states

"two electrons can not be in same state"

if  $\sigma_{k'} \neq \sigma_k$ , then  $\underline{\Gamma}_k = \underline{\Gamma}_{k'}$  would be possible.

In particular, write orthonormality requirement for

$\phi_{\sigma_k s_k}(\underline{\Gamma}_{k'} \sigma_k)$  in SD as:

$$\begin{aligned} \langle \phi_{\sigma_k, s_k} | \phi_{\sigma_{k'}, s_{k'}} \rangle &= \int d^3r \sum_{\sigma} \phi_{\sigma_k s_k}^*(\underline{\Gamma}_{\sigma}) \phi_{\sigma_{k'} s_{k'}}(\underline{\Gamma}, \sigma) \\ &= \delta_{\sigma_k, \sigma_{k'}} \delta_{s_k, s_{k'}} \end{aligned}$$

Next task:

Compute & minimize

$$\begin{aligned} E^{HF}[\Phi^{HF}] &= \langle \bar{\Phi}^{HF} | \hat{H}^e | \Phi^{HF} \rangle \\ &= \langle \bar{\Phi}^{HF} | \sum_k \left( -\frac{\nabla_k^2}{2} + V^{unc}(\underline{r}) \right) + \frac{1}{2} \sum_{\substack{k, k' \\ k \neq k'}} \frac{1}{|\underline{r}_k - \underline{r}_{k'}|} | \Phi^{HF} \rangle \end{aligned}$$

Note:  $\Phi^{HF}$  is Slater Determinant

→  $N!$  terms, all multiplied together, lots of book-keeping.

in fact: Most terms are 0 due to orthonormality requirement, except a few which we can group together.

Example: 2-particles,  $\langle \bar{\Phi}_{SD,2} | \Phi_{SD,2} \rangle$

$$\bar{\Phi}_{SD,2} = \frac{1}{\sqrt{2!}} \left( \phi_{\sigma_1}(\underline{r}_1) \phi_{\sigma_2}(\underline{r}_2) - \phi_{\sigma_1}(\underline{r}_2) \phi_{\sigma_2}(\underline{r}_1) \right)$$

$$\begin{aligned} \langle \bar{\Phi}_{SD,2} | \Phi_{SD,2} \rangle &= \frac{1}{2} \sum_{\sigma_1, \sigma_2} \int d^3r_1 d^3r_2 \cdot \\ &\quad \left[ \phi_{\sigma_1}^*(\underline{r}_1) \phi_{\sigma_2}^*(\underline{r}_2) \phi_{\sigma_1}(\underline{r}_1) \phi_{\sigma_2}(\underline{r}_2) \rightarrow 1 \right. \\ &\quad \left. - \phi_{\sigma_1}^*(\underline{r}_1) \phi_{\sigma_2}^*(\underline{r}_2) \phi_{\sigma_1}(\underline{r}_2) \phi_{\sigma_2}(\underline{r}_1) \rightarrow 0 \right] \end{aligned}$$

$$- \phi_1^*(z) \phi_2^*(1) \phi_1(1) \phi_2(z) \rightarrow 0$$

$$+ \phi_1^*(z) \phi_2^*(1) \phi_1(z) \phi_2(1) \rightarrow 1$$

= 1

Similar diligent counting for  $E^{HF}$  leads to:

$$\langle \Phi^{HF} | \hat{H}^e | \Phi^{HF} \rangle = E^{HF} =$$

$$= \sum_{k=1}^N \sum_{\sigma} \int d^3r \phi_{0k s_k}^*(\underline{r}, \sigma) \left[ -\frac{\nabla^2}{2} + v^{nucl}(\underline{r}) \right] \phi_{0k s_k}(\underline{r}, \sigma) \quad (1)$$

$$+ \frac{1}{2} \sum_{\substack{k, k' \\ k \neq k'}}^N \sum_{\sigma, \sigma'} \int d^3r \int d^3r' \frac{1}{|\underline{r} - \underline{r}'|} \cdot$$

$$\cdot \left[ \phi_{0k s_k}^*(\underline{r}, \sigma) \phi_{0k' s_{k'}}^*(\underline{r}', \sigma') \phi_{0k s_k}(\underline{r}, \sigma) \phi_{0k' s_{k'}}(\underline{r}', \sigma') \right] \quad (2)$$

$$- \phi_{0k' s_{k'}}^*(\underline{r}, \sigma) \phi_{0k s_k}^*(\underline{r}', \sigma') \phi_{0k s_k}(\underline{r}, \sigma) \phi_{0k' s_{k'}}(\underline{r}', \sigma') \quad (3)$$

switched.

Simplify this beast.

1) spin - separate  $\phi_{0k s_k}(\underline{r}_k, \sigma_k) = \phi_{0k s_k}(\underline{r}_k) \chi_{s_k}(\sigma)$

$$(1) \quad \sum_{\sigma} \chi_{s_k}(\sigma) \chi_{s_k}(\sigma) = 1$$

$$(2) \quad \text{similar: } \sum_{\sigma, \sigma'} \chi_{s_k}^*(\sigma) \chi_{s_k}(\sigma) \chi_{s_{k'}}^*(\sigma') \chi_{s_{k'}}(\sigma') = \delta_{s_k s_k} \delta_{s_{k'} s_{k'}} =$$

$$(3) \quad \text{not quite } \sum_{\sigma, \sigma'} \chi_{s_{k'}}^*(\sigma) \chi_{s_k}^*(\sigma') \chi_{s_k}(\sigma) \chi_{s_{k'}}(\sigma')$$

$$= \delta_{s_k s_{k'}} \delta_{s_k s_{k'}} = \delta_{s_k s_{k'}}$$

Compare with Hartree theory:

All same, except for term (3)

(3) Reorganize a bit.

$$\tilde{E}^x = -\frac{1}{2} \sum_{\substack{N,N \\ k,k' \\ k \neq k'}} \delta_{s_k s_{k'}} \int d^3r d^3r' \frac{\phi_{0k s_k}^*(r) \phi_{0k s_k}^*(r) \phi_{0k s_k}(r') \phi_{0k s_{k'}}(r')}{|r-r'|}$$

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

same sign as (2)  
 → group this in to (2) to get rid of  $k \neq k'$  here.  
 (this is precisely the self-interaction term)

Finally 3

$$E^{HF} [\{\phi_{0k s_k}\}] = T_S [\{\phi_{0k s_k}\}] + E^{e-l.e.e} [\{\phi_{0k s_k}\}] + E_e^e [\{\phi_{0k s_k}\}] + E^x [\{\phi_{0k s_k}\}]$$

"Hartree term"  
 (classical electrostatics see before)

"Exchange term"  
 Results from Pauli principle also contains self-interaction by convention

on the whole, of course "self-interaction free"

### 3.3 Hartree-Fock Equations:

Idea: Take  $E^{HF}$  as before (for Halsee)  
and vary with constraints, minimal for an  $\delta \varphi_{\sigma_k, \rho_k}(\varepsilon) \dots$