Chapter 3.1 Hartree Method - Continued

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We have: "Adiabatic" many-electron problem

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

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

$$\Phi^{trial} \equiv \Phi^{Hartree}(\{\underline{r}_k\}) = \varphi_{\sigma_1}(\underline{r}_1) \cdot \ldots \cdot \varphi_{\sigma_N}(\underline{r}_N)$$

(not a Slater Determinant)

Variational principle: Minimize

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

$$\Rightarrow \left[-\frac{\nabla^2}{2} + v^{ne}(\underline{r}) + \sum_{\substack{k'=1 \\ k \neq k'}}^{N} \int d^3r' \frac{\varphi^*_{\sigma_{k'}}(\underline{r}') \varphi_{\sigma_{k'}}(\underline{r}')}{|\underline{r} - \underline{r}'|} \right] \varphi_{\sigma_k}(\underline{r}) = \epsilon_{\sigma_k} \varphi_{\sigma_k}(\underline{r})$$

① ② ③

WHAT HAVE WE HERE?

... an effective single-particle Hamiltonian

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

① kinetic energy term ✓

② nuclear potential ✓

(3) e-e - interaction term

- depends on k (why?)
- depends on all other $\varphi_{\sigma_{k'}}(\underline{r})$

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

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

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

Rewrite:

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

$$= \sum_{k'=1}^{N} \int d^3r' \, \frac{|\varphi_{\sigma_{k'}}(\underline{r}')|^2}{\underline{r} - \underline{r}'} \qquad (A)$$

$$- \int d^3r' \, \frac{|\varphi_{\sigma_k}(\underline{r})|^2}{|\underline{r} - \underline{r}'|} \qquad (B)$$

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

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

numerically, lots of good ways to compute this from Poisson Eq. $\Delta V_{es}^{e}(\underline{r}) = -4\pi n(\underline{r})$

also called "Hartree potential" ...

(B) $"n_{\sigma_k}"(\underline{r}) = |\varphi_{\sigma_k}(\underline{r})|^2$ 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:

- $n(\vec{r})$ (approx.)
- approx. for $E_0 < E_0^{[\text{Hartree}]}$

E_0: g.s. of full ME system

Meaning of $\varphi_{0k}(\vec{r})$, ϵ_{0k} ... later

But note: $E_0^{[\text{Hartree}]} \neq \sum_{k=1}^{N} \epsilon_{0k}$

Reason: ME interaction $\hat{V}^{ee} = \frac{1}{2} \sum_{\substack{k,k' \\ k \neq k'}}^{NN} \frac{1}{|\vec{r}_k - \vec{r}_{k'}|}$

but no $\frac{1}{2}$ in $v_{es}^{e}(\vec{r})$!

"Double-counting"

Practical aspects

$$V_k^{\text{eff}}(\vec{r}) \equiv V_k^{\text{eff}}[\{\varphi_{0k'}\}](\vec{r})$$

depends on its solutions

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

- Guess an approximate solution

$$V_k^{\text{eff}(0)} \equiv \sum_{I=1}^{M} V_{\text{free atom}}^{\text{eff}}(\vec{r})$$

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

Iterate: $i \to i+1$

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

(b) update density $n^{(i)}(\underline{r}) = \sum_{k=1}^{N} |\varphi_{ok}^{(i)}(\underline{r})|$ ⇐ 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"

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

α: mixing factor, $0 \le \alpha \le 1$

(d) back to (a), unless

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

$$\left| \epsilon_{ok}^{(i)} - \epsilon_{ok}^{(i-1)} \right| < \delta_2 \quad (**)$$

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 will proper Fermionic
(anti) symmetry — Slater determinant.

$$\Phi^{\text{trial}} \equiv \Phi^{\text{HF}}(\{\vec{r}_k, \sigma_k\}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{o_1 s_1}(\vec{r}_1, \sigma_1) & \cdots & \varphi_{o_N s_N}(\vec{r}_1, \sigma_1) \\ \vdots & & \\ \varphi_{o_1 s_1}(\vec{r}_N, \sigma_N) & \cdots & \varphi_{o_N s_N}(\vec{r}_N, \sigma_N) \end{vmatrix}$$

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

$$\Phi_\nu(\{\vec{r}_k, \sigma_k\}) \equiv \Phi_\nu(\{\vec{r}_k\}) \cdot \chi_\nu(\sigma_k)$$

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

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 independent components $\Phi^{\text{Hartree}} = \begin{pmatrix} \Phi_\uparrow^{\text{Hartree}}(\vec{r}_k, \sigma_k = \frac{1}{2}) \\ \Phi_\downarrow^{\text{Hartree}}(\vec{r}_k, \sigma_k = -\frac{1}{2}) \end{pmatrix}$

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 $\underline{r}_k = \underline{r}_{k'}$ would be possible.

In particular, write orthonormality requirement for $\varphi_{\sigma_k s_k}(\underline{r}_k, \sigma_k)$ in SD as:

$$\langle \varphi_{\sigma_k, s_k} | \varphi_{\sigma_{k'}, s_{k'}} \rangle = \int d^3r \sum_\sigma \varphi^*_{\sigma_k s_k}(\underline{r}, \sigma) \varphi_{\sigma_{k'} s_{k'}}(\underline{r}, \sigma)$$

$$= \delta_{\sigma_k, \sigma_{k'}} \delta_{s_k, s_{k'}}$$

Next task:

Compute & minimize

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

$$= \langle \Phi^{HF} | \sum_k \left(-\frac{\nabla_k^2}{2} + V^{ions}(\underline{r}) \right) + \frac{1}{2} \sum_{\substack{k,k' \\ k \neq k'}}^{N} \frac{1}{|\underline{r}_k - \underline{r}_{k'}|} | \Phi^{HF} \rangle$$

Note: Φ^{HF} is Slater Determinant

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

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

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

$$\Phi_{SD,2} = \frac{1}{\sqrt{2}} \left(\varphi_1(1) \varphi_2(2) - \varphi_1(2) \varphi_2(1) \right)$$

$\underline{r}_1, \sigma_1$

$$\langle \Phi_{SD,2} | \Phi_{SD,2} \rangle = \frac{1}{2} \sum_{\sigma_1 \sigma_2} \int d^3r_1 d^3r_2 \cdot$$

$$\left[\varphi_1^*(1) \varphi_2^*(2) \varphi_1(1) \varphi_2(2) \right] \to 1$$

$$- \varphi_1^*(1) \varphi_2^*(2) \varphi_1(2) \varphi_2(1) \to 0$$

$$- \varphi_1^*(2)\,\varphi_2^*(1)\,\varphi_1(1)\,\varphi_2(2) \;\to\; 0$$
$$+ \varphi_1^*(2)\,\varphi_2^*(1)\,\varphi_1(2)\,\varphi_2(1)\,] \;\to\; 1$$

$$= 1$$

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

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

$$= \sum_{k=1}^{N} \sum_{\sigma} \int d^3r \; \varphi^*_{\sigma_k s_k}(r,\sigma) \left[-\frac{\nabla^2}{2} + V^{ion}(r) \right] \varphi_{\sigma_k s_k}(r,\sigma) \qquad (1)$$

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

$$\cdot \Big[\varphi^*_{\sigma_k s_k}(r,\sigma)\, \varphi^*_{\sigma_{k'} s_{k'}}(r'\sigma')\, \varphi_{\sigma_k s_k}(r,\sigma)\, \varphi_{\sigma_{k'} s_{k'}}(r',\sigma') \qquad (2)$$

$$- \varphi^*_{\sigma_{k'} s_{k'}}(r,\sigma)\, \varphi^*_{\sigma_k s_k}(r'\sigma')\, \varphi_{\sigma_k s_k}(r,\sigma)\, \varphi_{\sigma_{k'} s_{k'}}(r'\sigma') \Big] \qquad (3)$$

(switched.)

Simplify this beast.

1) spin-separate $\varphi_{\sigma_k s_k}(r_k,\sigma_k) = \varphi_{\sigma_k,s_k}(r_k)\,\chi_{s_k}(\sigma)$

(1) $\sum_{\sigma} \chi^*_{s_k}(\sigma)\,\chi_{s_k}(\sigma) = 1$

(2) 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) 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.

$$\tilde{E}^x = -\frac{1}{2} \sum_{\substack{k,k' \\ k \neq k'}}^{NN} \delta_{s_k s_{k'}} \int d^3r\, d^3r' \frac{\varphi^*_{\sigma_k s_k}(\vec{r})\, \varphi^*_{\sigma_{k'} s_{k'}}(\vec{r}')\, \varphi_{\sigma_{k'} s_{k'}}(\vec{r}')\, \varphi_{\sigma_k s_k}(\vec{r})}{|\vec{r} - \vec{r}'|}$$

$$= -\frac{1}{2} \sum_{k,k'}^{NN} \; - \; \frac{1}{2} \sum_{k=k'}^{N} \int d^3r\, d^3r' \frac{\varphi^*_{\sigma_k s_k}(\vec{r})\, \varphi^*_{\sigma_k s_k}(\vec{r}')\, \varphi_{\sigma_k s_k}(\vec{r}')\, \varphi_{\sigma_k s_k}(\vec{r})}{|\vec{r} - \vec{r}'|}$$

(+) same sign as ②

→ group this in ② to get rid of $k \neq k'$ there.

(this is precisely the self-interaction term)

Finally:

$$E^{HF}[\{\varphi_{\sigma_k s_k}\}] = T_s[\{\varphi_{\sigma_k s_k}\}] + E^{e\text{-ion}}[\{\varphi_{\sigma_k s_k}\}]$$

$$+ \underbrace{E^e_{es}[\{\varphi_{\sigma_k s_k}\}]}_{\text{"Hartree term" (classical electrostatics, see before)}} + \underbrace{E^x[\{\varphi_{\sigma_k s_k}\}]}_{\text{"Exchange term" Results from Pauli principle also contains self-interaction by construction.}}$$

$\Rightarrow$ on the whole, of course "self-interaction free"

3.3 Hartree-Fock Equations:

Idea: Take E^{HF} as before (for Helium)

and vary with constraints, minimal for an $\delta\varphi_{a,\sigma_a}(x)$...