

Chapter 3 continued

Recap: Hartree-Fock

Approximate the ME wave function itself: $\bar{\Phi}^{\text{trial}} = \text{single Slater Determinant}$

$$E^{\text{HF}}[\{\phi_{\sigma_k s_k}\}] = \langle \bar{\Phi}^{\text{trial}} | \hat{H}^e | \bar{\Phi}^{\text{trial}} \rangle$$

→ ground state $\bar{\Phi}^{\text{HF}}$ from Hartree-Fock Equations:

$$\left\{ -\frac{\nabla^2}{2} + V^{\text{nuc}}(r) + V_e^{\text{es}}(r) \right\} \phi_{\sigma_k s_k}(r) - \sum_{k'=1}^N \int d\mathbf{r}' \frac{\phi_{\sigma_{k'} s_{k'}}(r') \phi_{\sigma_k s_k}(r')}{|r-r'|} = \epsilon_{\sigma_k s_k} \phi_{\sigma_k s_k}(r)$$

Can be:

- Rewritten as a linear eigenvalue problem $\sum_j h_{ij}^{\text{HF}} c_{kj} = \sum_j (h_{ij}^{\text{eff}} + K_{ij}) c_{kj} = \epsilon_{\sigma_k s_k} \sum_j s_{ij} c_{kj}$

⇒ $\phi_{\sigma_k s_k} = \sum_j c_{kj} \phi_j(r)$ in some basis set $\{\phi_j\}$ - Effort $O(N^4)$

- solved self-consistently like Hartree (h^{eff}, K_{ij} depend on solutions $\{\phi_{\sigma_k s_k}\}$!)

... BUT:

... the real ME wavefunction $\Phi_{\nu}(\{\mathbf{r}_k, \sigma_k\})$ is not a single SD.

→ Adiabatic ground state energy $\langle \Phi_0 | \hat{H} | \Phi_0 \rangle < E^{\text{HF}}$

→ noticeable deviations of HF physical properties from reality in some cases (esp. metals)

→ Excited states $\nu > 0, E_{\nu} > E_0$?

Koopman's theorem for $\epsilon_{\sigma_k s_k} \rightarrow$ severe approximation needed.

How CAN WE DO BETTER?

- ① Do better on the ME wave fn Φ_V (cost!) ("Quantum Chemistry")
- ② Find way to "map" the exact physical problem onto something that we can solve more accurately at less cost
→ Density functional theory.

3.7 Beyond Hartree-Fock ①

a) Configuration interaction (CI)

If we had S single electron basis functions, N electrons

$$\rightarrow \text{can form } \binom{S}{N} = \frac{S!}{N!(S-N)!}$$

$$\text{Solve directly } \sum_j \binom{S}{N} \langle \Phi_{SD,j} | \hat{H}^e | \Phi_{SD,j} \rangle \langle \Phi_{SD,j} | \Phi_V \rangle = E_V \langle \Phi_i | \Phi_V \rangle$$

Obviously: Effort for full CI → "combinatorial explosion"

In practice: Already have "best" single Slater Determinant around: Φ^{HF}
... and the associated orbitals $\{\phi_{occ}\}$ (also $S > N$ orbitals
↳ general)

→ so what if we use Φ^{HF} plus afew relevant extra SD's
from $\{\phi_{occ}\}$

• $|\Phi^{HF}\rangle$

• $|\Phi_{k \rightarrow j}^{HF}\rangle \equiv \text{SD} \{ \phi_{l_1}(\epsilon_1) \cdots \phi_{l_{k-1}}(\epsilon_{k-1}) \cdot \phi_{l_{k+1}}(\epsilon_{k+1}) \cdots \phi_N(\epsilon_N) \cdot \phi_j(\epsilon_k) \}$
 "CI(S)"
 left out $k \leq N$
 entered $j > N$

• "double excited" SD's \rightarrow CI(SD)

• triple \rightarrow CI(SDT) ...

- ...

Advantage: Variational (at each level, E_{tot} goes down)

Disadvantage: still expensive

"not size-consistent"

Consider binding energy $E_b(\text{He}_2) = E_{\text{tot}}(\text{He}_2) - 2 E_{\text{tot}}(\text{He})$

if you do CI(SD):

He atom contains $\begin{array}{cccc} \text{---} & \uparrow & \downarrow & \uparrow\downarrow \\ \uparrow\downarrow & \downarrow & \uparrow & \text{---} \end{array}$

but He₂ does not contain $\begin{array}{c} \uparrow\downarrow \\ \text{He}_1 \end{array}$ $\begin{array}{c} \uparrow\downarrow \\ \text{He}_2 \end{array}$

... systematic error - could be large.

STM - CI used - e.g. excited states even in semiconductor nanostructures

3.8 Beyond Hartree Fock (QC - 5) = Perturbative Approach

$\Phi^{HF}(\{\epsilon_k, \sigma_k\})$ not the full solution to \hat{H}^e

but it is a solution to

$$\hat{H}^{\text{HF}} = \sum_k h_k^{\text{HF}}$$

$$\text{where } \langle \underline{r} | h_k^{\text{HF}} | \phi_{\underline{r}k} \rangle = \left\{ -\frac{\nabla^2}{2} + v^{\text{loc}}(\underline{r}) + v_{\text{es}}^e(\underline{r}) \right\} \phi_{\underline{r}k}(\underline{r}) \\ + \sum_{k'=1}^N \phi_{\underline{r}k'}(\underline{r}) \int d^{3-1} \frac{\phi_{\text{on}}^*(\underline{r}') \phi_{\text{on}}(\underline{r}')}{|\underline{r}-\underline{r}'|}$$

Could hope that $\hat{H}^e = \hat{H}^{\text{HF}} + \underbrace{(\hat{H}^e - \hat{H}^{\text{HF}})}_{\Delta \hat{H} \text{ and "pretty small"}$

Reminder: perturbation theory

$$\hat{H} = \hat{H}_0 + \lambda \Delta \hat{H} \quad \lambda = 0 \quad \text{"unperturbed system"}$$

(we know the solutions to that)

$$\lambda = 1 \quad \text{"full Hamiltonian"}$$

With $\hat{H}_0 \bar{\Phi}_\nu^{(0)} = E_\nu^{(0)} \bar{\Phi}_\nu^{(0)}$

we would like $\hat{H} \bar{\Phi}_\nu = E_\nu \bar{\Phi}_\nu \quad (*)$

Formally expand in terms λ :

$$\bar{\Phi}_\nu = \bar{\Phi}_\nu^{(0)} + \lambda \bar{\Phi}_\nu^{(1)} + \lambda^2 \bar{\Phi}_\nu^{(2)} + \dots$$

$$E_\nu = E_\nu^{(0)} + \lambda E_\nu^{(1)} + \lambda^2 E_\nu^{(2)} + \dots$$

if we place these expressions in (*) and simply equate powers of λ :

$$E_\nu^{(1)} = \langle \bar{\Phi}_\nu^{(0)} | \Delta \hat{H} | \bar{\Phi}_\nu^{(0)} \rangle$$

$$\bar{\Phi}_\nu^{(1)} = \sum_{\mu \neq \nu} \frac{\langle \bar{\Phi}_\mu^{(0)} | \Delta \hat{H} | \bar{\Phi}_\nu^{(0)} \rangle}{E_\nu^{(0)} - E_\mu^{(0)}} \bar{\Phi}_\mu^{(0)}$$

Sum over all other unperturbed states with weights given by how much $\Delta \hat{H}$ "couples"

μ, ν
 ... obviously must be extended
 for $E_\mu^{(1)} = E_\nu^{(1)}$ (degeneracy)

$$E_\nu^{(2)} = \langle \bar{\Phi}_\nu^{(0)} | \Delta \hat{H} | \bar{\Phi}_\nu^{(1)} \rangle$$

$$= \sum_{\mu \neq \nu} \frac{|\langle \bar{\Phi}_\mu^{(0)} | \Delta \hat{H} | \bar{\Phi}_\nu^{(0)} \rangle|^2}{E_\nu^{(0)} - E_\mu^{(0)}}$$

etc.

Application to MF Hamiltonian \hat{H}^e :

- Various paths along these lines (e.g., resum certain orders up to infinity etc.)

- Direct application: Møller/Plesset (1934)

$$\hat{H} = \hat{H}^e \quad \hat{H}_0 = \hat{H}^{HF}$$

$$\Delta \hat{H} = \hat{H}^e - \sum_{k=1}^N h_k^{HF} = \frac{1}{2} \sum_{\substack{k, k' \\ k \neq k'}}^{N, N} \frac{1}{|c-r|} - \sum_k (V_{cs}^e + V_k^x)$$

(single electron terms T, V_{int} already cancelled)

Zero order: $E^{(0)} = \sum_{k=1}^N \epsilon_{0k} s_k + E^{HF}$
 by def. of $\Phi_0^{(0)}, \hat{H}^{HF}$

$$E_{MP2} = E^{(0)} + E^{(1)} = \sum_{k=1}^N \epsilon_{0k} s_k + \frac{1}{2} V^{ee} - V^{ee}$$

$$= \sum_{k=1}^N \epsilon_{0k} s_k - \frac{1}{2} V^{ee} = E^{HF}$$

$V^{ee} = \langle \Phi^{HF} | \frac{1}{2} \sum_{\substack{k, k' \\ k \neq k'}} \frac{1}{|c-r|} | \Phi^{HF} \rangle$
 double-counting

First order: Corrects double-counting in sum of eigenvalues

$$E^{(2)} = \sum_{\substack{\text{excited} \\ \text{states} \\ \mu \neq 0}} \frac{|\langle \Phi_0^{\text{HF}} | \Delta \hat{H} | \Phi_\mu^{\text{HF}} \rangle|^2}{E_0^{\text{HF}} - E_\mu^{\text{HF}}}$$

can be calculated (all expectation values known)

by constructing all excited CI Slater Determinants from Φ_0^{HF}

Because of V^{ee} , only two-electron 1-terms survive!

$$\int d\tau_1 \dots d\tau_n \bar{\Phi}_0^{\text{HF}} \hat{V}^{e-e} \Phi_\mu^{\text{HF}}$$

\hat{V}^{e-e} can only couple two pairs of occupied & unoccupied orbitals

Result: MP2

- straightforward way: $O(S^5)$ for numerical effort
- good for many molecular systems
- not good for systems where Φ^{HF} is inappropriate
(if the ground state of the HE is near-degenerate)
"multireference"
- no good for metals

There are many more methods:

CCSD(T)

MRSEF

MRCI

CASSEF

CASPT2

YOUR FAVORITE - ALL PARENTS

ETC.

4. Density Functional Theory

So far $\Phi_v \equiv \Phi_v(\{\underline{r}_k\})$ determines all properties of the adiabatic electronic system
 ... but must know this for 10^{23} electrons in real 'solid state' physics

Have also seen: Large part of effective potential is given by

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

depends on $n(\underline{r})$ - density (3D)

Wouldn't it be good ...

if we could express everything we want to know (physical properties) exactly through $n(\underline{r})$ [3D] instead of $\Phi_v(\{10^{23} \text{ dir}\})$?

Historically (approximate chronology)

- Thomas (1926) / Fermi (1928) - Heuristic description $E^{ME}[\Phi_v] \approx E[n(\underline{r})]$

- Dirac (1930) "... whole state of atom determined by density, not necessarily by specific Ψ "
 ... but he meant density matrix $\hat{n}(\underline{r}, \underline{r}')$
 not just $n(\underline{r})$

- Slater (1951) "X α " method - "A simplification of Hartree-Fock"
 essentially, replace \hat{V}_k^x by an effective local potential $V_{x\alpha}(\underline{r})$.

- Hohenberg-Kohn theorem (1964)
rigorous proof ^{that} $n(\underline{r})$ contains all information on physical observables of ME system

- Kohn-Shan equations (1965) - In principle, NE system is rigorously replaceable by an effective single-particle system to obtain $n(\underline{r})$, $E[n]$.
 [with an effective potential that needs to be found]

3.1 Hohenberg-Kohn theorem

- (A) The ground state density $n(\underline{r})$ uniquely determines the many-electron wave function $|\Phi_0\rangle$. The ground state energy E_0 and all phys. observables $\langle O \rangle$ are functionals of $n(\underline{r})$ alone.
- (B) There exists a universal functional $F_{HK}[n]$ such that
 $E_0 = E[n] = F_{HK}[n] + \int d^3r v^{\text{ext}}(\underline{r}) n(\underline{r})$ is variational in $n(\underline{r})$ [minimum energy for ground state density $n_0(\underline{r})$]

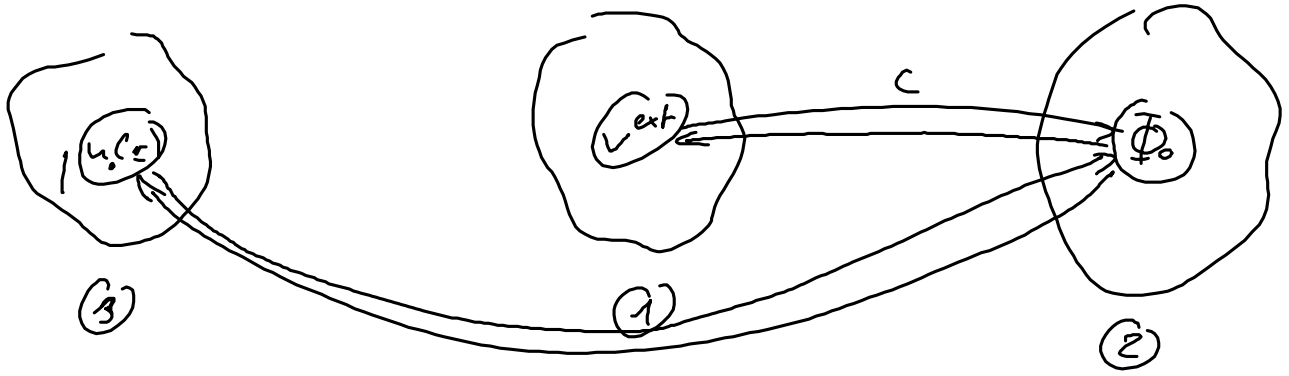
Proof: Consider $\hat{H}^e = \frac{1}{I} + \hat{V}^{\text{ext}} + \hat{V}^{\text{e-e}}$
 with a non-degenerate ground state $|\Phi_0\rangle$, $E_0 = \langle \Phi_0 | \hat{H}^e | \Phi_0 \rangle$

$$\text{Density } n_0(\underline{r}) = \langle \Phi_0 | \sum_{k=1}^N \delta(\underline{r} - \underline{r}_k) | \Phi_0 \rangle$$

$$= N \int \prod_{i=1}^N d^3r_i | \Phi_0(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N) |^2$$

Consider the following three sets:

- (1) all possible external potentials $\{v^{\text{ext}}(\underline{r})\}$
- (2) all possible ground state wf. $\{|\Phi_0\rangle\}$
- (3) all possible ground state densities $\{n_0\}$



Obviously, there exists map

$$C: \{v^{ext}\} \rightarrow \{\Phi_0\}$$

each Φ_0 must have at least one v^{ext} that defines it

there exists a map $D: \{\Phi_0\} \rightarrow \{\psi_0(\epsilon)\}$

each ψ_0 must have at least one Φ_0 that defines it

If $v^{ext}(\epsilon) \neq v^{ext'}(\epsilon) + \text{const}$ then $\Phi_0 \neq \Phi_0'$

Proof: $(\hat{T} + \hat{V}^{ext} + \hat{V}^{cc}) \Phi_0 = E_0 \Phi_0$

$$(\hat{T} + \hat{V}^{ext'} + \hat{V}^{cc}) \Phi_0' = E_0' \Phi_0'$$

Assume that $\Phi_0 = \Phi_0'$

$$\Rightarrow (\hat{V}^{ext} - \hat{V}^{ext'}) \Phi_0 = \underbrace{(E_0 - E_0')}_{\text{constant}} \Phi_0 \quad \Downarrow$$

\Rightarrow Map C is injective.

If $\Phi_0 \neq \Phi_0'$ then $\psi_0(\epsilon) \neq \psi_0'(\epsilon)$

where Φ_0 g.s. to \hat{H}^e
 Φ_0' g.s. to $\hat{H}^{e'}$ with different $V^{ext'}$

Proof: $E_0 = \langle \Phi_0 | \hat{H}^e | \Phi_0 \rangle \stackrel{\text{Ritz}}{\leftarrow} \langle \Phi_0' | \hat{H}^e | \Phi_0' \rangle$
 $= \langle \Phi_0' | \hat{H}^{e'} + \hat{H}^e - \hat{H}^{e'} | \Phi_0 \rangle$

$$= E_0' + \int d^3r \psi_0(\epsilon) (v^{ext}(\epsilon) - v^{ext'}(\epsilon)) \quad (i)$$

similarly $E_0' \leftarrow E_0 + \int d^3r \psi_0'(\epsilon) (v^{ext'}(\epsilon) - v^{ext}(\epsilon)) \quad (ii)$

$$\int u_0(\epsilon) = u_0'(\epsilon)$$

$$\rightarrow (i) + (ii) \quad E_0 + E_0' < E_0' + E_0 \quad \Downarrow$$

\Leftrightarrow Map D is injective.

Thus: $(CD)^{-1}$ exists, connects $u_0(\epsilon)$ uniquely to $v^{\text{ext}}(\epsilon)$
 thus to \hat{H}^e , $\Phi_0[u_0]$,
 and thus to all expectation values $\langle \Phi_0 | \hat{O} | \Phi_0 \rangle$
 of any observable, $\hat{O} = O[u_0]$

HK theorem, variational principle (8) \rightarrow next line.