

Concepts in Computational Materials Science

Recap:

$$\hat{H}(\underbrace{\Psi_n(\{\underline{R}_I\}, \{\underline{r}_k\})}_{\text{possibly } "10^{23}" \text{ coordinates?}}) = E_n \bar{\Psi}_n(\{\underline{R}_I\}, \{\underline{r}_k\})$$
$$\hat{H} = \hat{T}^e + \hat{T}^{nuc} + \hat{V}^{e-e} + \hat{V}^{e-nuc} + \hat{V}^{-nuc-nuc}$$

Electrons & Nuclei: Adiabatic Approximation

$$\hat{H}^e \bar{\Phi}_\nu(\{\underline{R}_I\}, \{\underline{r}_k\}) = E_\nu \bar{\Phi}_\nu(\{\underline{R}_I\}, \{\underline{r}_k\})$$

with fixed nuclear coordinates \underline{R}_k :

$\bar{\Phi}_\nu$ are "adiabatic" electron-only states.

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

perfectly legal definition (no approximation yet!)

Important part about B-O approximation:

"Hope" that electrons will stay in the same adiabatic eigenstate, regardless of the much slower nuclear motion.

If this were so, then

$$\Psi_{\text{trial}} = \Lambda(\{\underline{R}_I\}) \cdot \bar{\Phi}_\nu(\{\underline{R}_I\}, \{\underline{r}_k\})$$

would be an eigenfunction to \hat{H}

We saw: This is not strictly the case
because $\hat{T}^{nuc} = -\sum_I \frac{\nabla_I^2}{2M_I}$ acts on $\bar{\Phi}_\nu$!

If $M_I \equiv \frac{M_I}{m_e} \rightarrow \infty$, the of course BO approximation would hold.

2.3 The electronic problem (I) - one electron

$$(\hat{T} + \hat{V}^{e-nuc} + \hat{V}^{e-e}) \Phi_{\nu} = E_{\nu} \Phi_{\nu}$$

↓ couples the electrons.

$$\sum_{\substack{kk' \\ k \neq k'}} \frac{e^2}{|\epsilon_k - \epsilon_{k'}|}$$

How about one electron

$$\left[-\frac{\nabla^2}{2} + V(\underline{r}) \right] \Phi_{\nu}(\underline{r}) = E_{\nu} \Phi_{\nu}$$

This is something that we know.

Above (strictly): $V(\underline{r}) \equiv \hat{V}^{e-nuc}(\underline{r})$ Coulomb pot.
but in principle, $V(\underline{r})$ could be anything.

Examples:

• Hydrogen-like: $V(\underline{r}) = -\frac{Z}{r}$

Solutions $\Phi_{\nu}(\underline{r}) = R_{n,l}(r) \cdot Y_{lm}(\Omega)$
↑
solid angle

$$n = 1, 2, \dots$$

$$l = 0, \dots, n$$

$$m = -l, \dots, l$$

separable, and $R_{n,l}(r)$ analytically known

$$\sim e^{-\frac{Zr}{n}} \left(\frac{Zr}{n}\right)^l \binom{2l+1}{n-l-1} \left(\frac{Zr}{n}\right)^{n-l-1}$$

↑

- Isotropic harmonic oscillator

$$V(r) = \frac{1}{2} \omega^2 r^2$$

can separate for example in cartesian variables

$$\Phi_{\nu} = f_e(x) f_m(y) f_n(z)$$

$$f_e(x) \propto e^{-\frac{\beta x^2}{2}} \underbrace{H_e(\beta x)}_{\text{Hermite polynomial}} \quad \beta = \sqrt{m\omega}$$

- or even constant potential $V(r) = 0$

$$\Phi_{\nu}(r) \rightarrow \phi_{\underline{k}}(r) \sim e^{i\underline{k} \cdot r} \quad \text{plane waves, } \underline{k} \text{ continuous.}$$

Normalization? Often, work with finite "base region"
for example, unit cell in a periodic system.

$$\text{Then, convenient: } \phi_{\underline{k}}(r) = \frac{1}{\sqrt{V_{\text{base}}}} e^{i\underline{k} \cdot r}$$

V_{base} : Volume of base region

Useful: Sets of solutions $\{\Phi_{\nu}\}$ for a given potential $V(r)$
are

• orthonormal: $\langle \Phi_{\nu} | \Phi_{\mu} \rangle = \delta_{\nu\mu}$

• complete: $\sum_{\nu} |\Phi_{\nu}\rangle \langle \Phi_{\nu}| = \mathbb{1}$

\Rightarrow can use such a set (e.g., plane waves) as basis sets to solve Schrödinger Equation for any other potential $\tilde{V}(r)$.

How is this done? Consider some basis set $\{\varphi_i\}$

$$\left[-\frac{\nabla^2}{2} + \tilde{V}(r) \right] \Phi_{\nu}(r) = \tilde{E}_{\nu} \Phi_{\nu}(r)$$

$$\hat{H}|\Phi_\nu\rangle = E_\nu |\Phi_\nu\rangle$$

$$\langle \varphi_i | \hat{H} | \Phi_\nu \rangle = E_\nu \langle \varphi_i | \Phi_\nu \rangle$$

$$(*) \quad \sum_j \langle \varphi_i | \hat{H} | \varphi_j \rangle \langle \varphi_j | \Phi_\nu \rangle = E_\nu \langle \varphi_i | \Phi_\nu \rangle$$

$$\begin{aligned} \text{Then } \Phi_\nu(\underline{r}) &= \langle \underline{r} | \Phi_\nu \rangle = \sum_j \langle \underline{r} | \varphi_j \rangle \underbrace{\langle \varphi_j | \Phi_\nu \rangle}_{c_{j\nu}} \\ &= \sum_j c_{j\nu} \varphi_j(\underline{r}) \end{aligned}$$

$$\text{and } (*) \quad \underline{H} \underline{c}_\nu = E_\nu \underline{c}_\nu$$

In practice: Matrix algebra in a basis set

Can do if we take finite part (S functions)
of a complete $\{\varphi_i\}$

→ get $\Phi_\nu^{(S)}(\underline{r}), E_\nu^{(S)}(\underline{r})$

... and then take successively larger basis
subsets to "prove" convergence

e.g. plane waves: use finite $E_{\text{cut}} = \frac{k_{\text{cut}}^2}{2}$ to define finite
basis set.

2.4 Properties of a "real" many-electron system

$$\text{Here } \Phi_\nu = \Phi_\nu(\{\underline{r}_I\}, \{\underline{r}_k\}) \equiv \Phi_\nu(\{\underline{r}_k\})$$

↑
for now

But: Electrons are Fermions.

Simple rule: Observables should not change if we
switch out $\underline{r}_i, \underline{r}_j$ in Φ_ν

This means

$$\bar{\Phi}(\epsilon_1, \dots, \epsilon_i, \dots, \epsilon_j, \dots, \epsilon_N) = \pm \bar{\Phi}(\epsilon_1, \dots, \epsilon_j, \dots, \epsilon_i, \dots, \epsilon_N)$$

in particular

$$\bar{\Phi}(\epsilon_1, \dots, \epsilon_N) = 0 \quad \text{for } \epsilon_i = \epsilon_j, \quad i \neq j.$$

Pauli principle: " - " for electrons (Fermions)

→ $\bar{\Phi}_\nu$ "antisymmetric" against exchange of two coordinates.

What does this mean for $\bar{\Phi}_\nu$ if written down in a "basis set"

Define single-particle basis set $\{\varphi_i(\epsilon)\}$.

Could produce a "many-electron" basis function

$$\text{by } \varphi_{\epsilon_1}(\epsilon_1) \cdot \varphi_{\epsilon_2}(\epsilon_2) \cdot \dots \cdot \varphi_{\epsilon_N}(\epsilon_N)$$

But a simple product does not tell us how to fulfill antisymmetry requirement.

Slater 1928 / Dirac 1927:

But the following form is automatically antisymmetric:

$$\bar{\Phi}_{SD}(\epsilon_1, \dots, \epsilon_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{\epsilon_1}(\epsilon_1) & \dots & \varphi_{\epsilon_N}(\epsilon_1) \\ \vdots & & \vdots \\ \varphi_{\epsilon_1}(\epsilon_N) & \dots & \varphi_{\epsilon_N}(\epsilon_N) \end{vmatrix} \leftarrow \begin{array}{l} \text{rows:} \\ \text{same} \\ \text{coordinates} \end{array}$$

For 2 electrons:

$$\bar{\Phi}_{SD}(\underline{r}_1, \underline{r}_2) = \frac{1}{2} (\varphi_1(\underline{r}_1)\varphi_2(\underline{r}_2) - \varphi_1(\underline{r}_2)\varphi_2(\underline{r}_1))$$

antisymmetric

"Slater Determinant".

Could: - Postulate $\{\varphi_i(\underline{r})\}$ (subset, size S)

- For N electrons, construct all possible Slater Determinants $\bar{\Phi}_{SD}$ from $\{\varphi_i(\underline{r})\}$

$$\Rightarrow \binom{S}{N} = \frac{S!}{N!(S-N)!} \text{ possible determinants}$$

but if we increase S systematically to convergence, should get a complete set of many-electron basis functions.

Again, eigenvalue problem:

$$\sum_j \langle \bar{\Phi}_{SD,i} | \hat{H}^{el} | \bar{\Phi}_{SD,j} \rangle \langle \bar{\Phi}_{SD,j} | \bar{\Phi}_v \rangle = E_v \langle \bar{\Phi}_{SD,i} | \bar{\Phi}_v \rangle$$

This could be done.

Goes by the name of "full configuration interaction" (FCI)

Matrix dimension $\frac{S!}{N!(N-S)!}$

for example $S = 2N \rightarrow \frac{(2N)!}{N! N!}$

4 electrons	6	SD's
8 electrons	70	
40 electrons	10^{11}	SD's

Full is nice for many purposes (including to show that a solution can actually be produced) but unfortunately, not realistic for a real ME system all the way from first principles.

Chapter 3 Effective single particles (I): Hartree and Hartree-Fock

We know $\hat{H}^e \Phi_N(\{\epsilon_k\}) = E_N \Phi_N(\{\epsilon_k\})$

$$\hat{H}^e = -\sum_k \frac{\nabla_k^2}{2} + \sum_k \underbrace{V^{nuc-e}}_{V^{nuc}(r) = -\sum_I \frac{Z_I}{|R_I - r|}}(\epsilon_k) + \frac{1}{2} \sum_{\substack{k, k' \\ k+k'}}^{N,N} \frac{1}{|\epsilon_k - \epsilon_{k'}|}$$

\hat{V}^{e-e} ruins our day.

If only $V^{e-e} \approx \sum_k V_{eff}(\epsilon_k)$ then $H^e \approx \sum_k h^{eff}(\epsilon_k)$

we could use a product ansatz

$$\Phi_{trial}(\{\epsilon_k\}) = \prod_{k=1}^N \phi_{ok}(\epsilon_k)$$

and would separate i-to k different single-particle problems.
 (particles would not interact explicitly).

3.1 Hartree Approximation

What happens if we just use a product wave function Ansatz anyway?

$$\bar{\Phi}^{\text{Hartree}}(\{\underline{r}_k\}) = \varphi_{o_1}(\underline{r}_1) \cdot \dots \cdot \varphi_{o_N}(\underline{r}_N) \quad \text{Hartree's total function}$$

How does this help?

Ritz principle (variational principle) for the ground state $\bar{\Phi}_0, E_0$

$$\frac{\langle \bar{\Phi}_0 | \hat{H}^e | \bar{\Phi}_0 \rangle}{\langle \bar{\Phi}_0 | \bar{\Phi}_0 \rangle} = E_0 \leq \frac{\langle \bar{\Phi} | \hat{H}^e | \bar{\Phi} \rangle}{\langle \bar{\Phi} | \bar{\Phi} \rangle}$$

for all possible many-electron wave functions $|\bar{\Phi}\rangle$.

We also know that $\bar{\Phi}^{\text{Hartree}}$ can not be the ground state.

$$\text{But } \frac{\langle \bar{\Phi}^{\text{Hartree}} | \hat{H}^e | \bar{\Phi}^{\text{Hartree}} \rangle}{\langle \bar{\Phi}^{\text{Hartree}} | \bar{\Phi}^{\text{Hartree}} \rangle} > E_0 \quad \text{upper bound to } E_0.$$

$$\text{We require } \langle \bar{\Phi}^{\text{Hartree}} | \bar{\Phi}^{\text{Hartree}} \rangle = 1$$

$$\int d^3r_1 \dots \int d^3r_N \bar{\Phi}^{\text{Hartree}}(\{\underline{r}_k\}) \bar{\Phi}^{\text{Hartree}}(\{\underline{r}_k\})$$

$$= \left[\int d^3r_1 \varphi_{o_1}^*(\underline{r}_1) \varphi_{o_1}(\underline{r}_1) \right] \cdot \dots \cdot \left[\int d^3r_N \varphi_{o_N}^*(\underline{r}_N) \varphi_{o_N}(\underline{r}_N) \right]$$

$$\stackrel{!}{=} 1 \quad \rightarrow \text{require } \langle \varphi_{o_k} | \varphi_{o_k} \rangle \stackrel{!}{=} 1$$

$$\langle \bar{\Phi}^{\text{Hartree}} | \hat{H}^e | \bar{\Phi}^{\text{Hartree}} \rangle$$

$$= \int d^3r_1 \dots d^3r_N \phi_{o_1}^*(r_1) \dots \phi_{o_N}^*(r_N) \left[-\sum_k \left[\frac{\nabla_k^2}{2} + v_{\text{huc}}(r_k) \right] \cdot \phi_{o_1}(r_1) \dots \phi_{o_N}(r_N) \right. \\ \left. + \frac{1}{2} \int d^3r_1 \dots d^3r_N \phi_{o_1}^*(r_1) \dots \phi_{o_N}^*(r_N) \left[\sum_{\substack{k, k' \\ k \neq k'}} \frac{1}{|r_k - r_{k'}|} \right] \phi_{o_1}(r_1) \dots \phi_{o_N}(r_N) \right]$$

$$= \sum_{k=1}^N \int d^3r_k \phi_{o_k}^*(r_k) \left[-\frac{\nabla_k^2}{2} + v_{\text{huc}}(r_k) \right] \phi_{o_k}(r_k)$$

$$+ \frac{1}{2} \sum_{\substack{k, k' \\ k \neq k'}}^{NN} \int d^3r_k d^3r_{k'} \phi_{o_k}^*(r_k) \phi_{o_{k'}}^*(r_{k'}) \left[\frac{1}{|r_k - r_{k'}|} \right] \phi_{o_k}(r_k) \phi_{o_{k'}}(r_{k'})$$

$$= : E^{\text{Hartree}} [\phi_{o_1}, \dots, \phi_{o_N}, \phi_{o_1}^*, \dots, \phi_{o_N}^*]$$

This is an "energy functional", and we now seek the set $\{\phi_{o_k}\}$ which minimizes $E^{\text{Hartree}}[\dots]$.

under the condition that $\langle \phi_{o_k} | \phi_{o_k} \rangle \stackrel{!}{=} 1$

Minimize with Lagrangian constraints:

$$Q[\phi_{o_1}, \dots, \phi_{o_N}, \phi_{o_1}^*, \dots, \phi_{o_N}^*] = E^{\text{Hartree}}[\dots] - \sum_{k=1}^N \epsilon_{o_k} (1 - \langle \phi_{o_k} | \phi_{o_k} \rangle) \\ \uparrow \\ \text{Lagrange parameters}$$

= "minimal"

Functional minimization : Seek stationary point
 so that the change $\delta Q = 0$
 if we vary any of the ϕ_{0k} by any small
 $\delta\phi_{0k}$.

$$\delta Q = Q[\phi_{01}, \dots, \phi_{0N}, \phi_{01}^*, \dots, \phi_{0N}^* + \delta\phi_{0k}^*, \dots, \phi_{0N}^*] \\
 - Q[\phi_{01}, \dots, \phi_{0N}, \dots, \phi_{0k}^*, \dots, \phi_{0N}^*] = 0$$

Let's enter this into E^{Dirac} :

$$\int d^3r_k \delta\phi_{0k}^* \left[-\frac{\nabla_k^2}{2} + V^{\text{unc}}(\underline{r}_k) \right] \phi_{0k}(\underline{r}_k) \\
 + 2 \cdot \frac{1}{2} \sum_{\substack{k'=1 \\ k' \neq k}}^N \int d^3r_k d^3r_{k'} \delta\phi_{0k}^*(\underline{r}_k) \phi_{0k'}(\underline{r}_{k'}) \frac{1}{|\underline{r}_k - \underline{r}_{k'}|} \phi_{0k}(\underline{r}_k) \phi_{0k'}(\underline{r}_{k'}) \\
 - E_{0k} \int d^3r_k \delta\phi_{0k}^*(\underline{r}_k) \phi_{0k}(\underline{r}_k) \stackrel{!}{=} 0$$

Everywhere we have $\int d^3r_k \delta\phi_{0k}^*(\underline{r}_k) [\dots]$
 this is not zero in general this must be zero.

This leads us to

$$\left[-\frac{\nabla^2}{2} + V^{\text{unc}}(\underline{r}) + \sum_{\substack{k'=1 \\ k' \neq k}}^N \int d^3r' \frac{\phi_{0k'}^*(\underline{r}') \phi_{0k'}(\underline{r}')}{|\underline{r}' - \underline{r}|} \right] \cdot \phi_{0k}(\underline{r}) = \\
 = E_{0k} \phi_{0k}(\underline{r}) .$$

How nice. An effective single-particle
 equation for $\phi_{0k}(\underline{r})$.
