

# Concepts in Computational Materials Science

Recap:

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

Electrons & Nuclei: Adiabatic Approximation

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

with fixed nuclear coordinates  $\underline{R}_k$ :

$\Phi_\nu$  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

$$\Psi_{\text{trial}} = \Delta(\{\underline{R}_I\}) \cdot \Phi_\nu(\{\underline{R}_I\}, \{\underline{r}_k\})$$

would be an eigenfunction to  $\hat{T}$

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

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.

$$\sum_{\substack{\mu\nu \\ k \neq k'}} \frac{e^2}{|r_k - r_{k'}|}$$

How about one electron

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

This is something that we know.

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

Examples:

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

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

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

$$l = 0, \dots, n-1$$

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

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

$$\sim e^{-\frac{Zr}{n}} \left(\frac{Zr}{n}\right)^l \underbrace{L_{n-l-1}^{2l+1}\left(\frac{2Zr}{n}\right)}_{\uparrow}$$

- Isotropic harmonic oscillator

Lagrange

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

can separate for example in cartesian variables

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

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

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

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

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

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

$V_{\text{base}}$ : 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  $\{\varphi_i\}$

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

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

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

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

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

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

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

$$\text{Here } \Phi_\nu = \Phi_\nu(\{\underline{r}_I\}, \{\underline{r}_K\}) \equiv \bar{\Phi}_\nu(\{\underline{r}_K\})$$

↑  
for  $\nu$

But: Electrons are Fermions.

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

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)

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

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

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

Could produce a "many-electron" basis function

$$\text{by } \varphi_{\alpha_1}(\epsilon_1) \cdot \varphi_{\alpha_2}(\epsilon_2) \cdot \dots \cdot \varphi_{\alpha_N}(\epsilon_N)$$

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

Slater 1928 / Dirac 1927:

But the following form is automatically antisymmetric:

$$\bar{\Phi}_{SD}(\epsilon_1, \dots, \epsilon_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{\alpha_1}(\epsilon_1) & \dots & \varphi_{\alpha_N}(\epsilon_1) \\ \vdots & & \vdots \\ \varphi_{\alpha_1}(\epsilon_N) & \dots & \varphi_{\alpha_N}(\epsilon_N) \end{vmatrix} \leftarrow \begin{array}{l} \text{rows:} \\ \text{same} \\ \text{coordinates} \end{array}$$

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 converge,  
should get a complete set of many-electron  
basis functions.

Again, eigenvalue problem:

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

This could be done.

Goes by the name of "false 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  $\hat{H}^e \Phi_\nu(\{\zeta_k\}) = E_\nu \Phi_\nu(\{\zeta_k\})$

$$\hat{H}^e = -\sum_k \frac{\nabla_k^2}{2} + \sum_k \underbrace{V^{nuc-e}}_{V^{nuc}(\zeta) = -\sum_I \frac{Z_I}{|\mathbf{R}_I - \zeta|}}(\zeta_k) + \frac{1}{2} \sum_{\substack{k, k' \\ k \neq k'}}^{N} \frac{1}{|\zeta_k - \zeta_{k'}|}$$

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

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

we could use a product ansatz

$$\Phi_{total}(\{\zeta_k\}) = \prod_{k=1}^N \phi_{ok}(\zeta_k)$$

and would separate it to be different style-particle problems.  
 (particles would not interact explicitly).

### 3.1 Hartree Approximation

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

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

How does this help?

Ritz principle (variational principle) for the ground state  $\Phi_0, E_0$

$$\frac{\langle \Phi_0 | \hat{H}^e | \Phi_0 \rangle}{\langle \Phi_0 | \Phi_0 \rangle} = E_0 \leq \frac{\langle \Phi | \hat{H}^e | \Phi \rangle}{\langle \Phi | \Phi \rangle}$$

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

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

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

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

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

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

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

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

$$= \int d^3r_1 \dots d^3r_N \varphi_{\alpha_1}^*(r_1) \dots \varphi_{\alpha_N}^*(r_N) \left[ -\sum_k^N \left[ \frac{\nabla_k^2}{2} + v_{\text{elec}}(r_k) \right] \cdot \varphi_{\alpha_1}(r_1) \dots \varphi_{\alpha_N}(r_N) \right. \\ \left. + \frac{1}{2} \int d^3r_1 \dots d^3r_N \varphi_{\alpha_1}^*(r_1) \dots \varphi_{\alpha_N}^*(r_N) \left[ \sum_{\substack{k, k' \\ k \neq k'}}^N \frac{1}{|r_k - r_{k'}|} \right] \varphi_{\alpha_1}(r_1) \dots \varphi_{\alpha_N}(r_N) \right]$$

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

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

$$= : E^{\text{Hartree}} [\varphi_{\alpha_1}, \dots, \varphi_{\alpha_N}, \varphi_{\alpha_1}^*, \dots, \varphi_{\alpha_N}^*]$$

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

under the condition that  $\langle \varphi_{\alpha_k} | \varphi_{\alpha_k} \rangle \stackrel{!}{=} 1$

Minimize with Lagrangian constraints:

$$Q[\varphi_{\alpha_1}, \dots, \varphi_{\alpha_N}, \varphi_{\alpha_1}^*, \dots, \varphi_{\alpha_N}^*] = E^{\text{Hartree}}[\dots] - \sum_{k=1}^N \epsilon_{\alpha_k} (1 - \langle \varphi_{\alpha_k} | \varphi_{\alpha_k} \rangle) \\ \uparrow \\ \text{Lagrange parameters} \\ = \text{"minimal"}$$

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

$$\delta Q = Q[\varphi_{01}, \dots, \varphi_{0n}, \varphi_{0n}^*, \dots, \varphi_{0n}^* + \delta\varphi_{0n}^*, \dots, \varphi_{0n}^*] \\
 - Q[\varphi_{01}, \dots, \varphi_{0n}, \dots, \varphi_{0n}^*, \dots, \varphi_{0n}^*] = 0$$

Let's enter this into  $E^{\text{average}}$  :

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

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

This leads us to

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

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

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