

Beyond the one-electron approximation (G and P chapter IV)

- An approximation that we have been making implicitly and explicitly is that we can discuss electrons individually

* Approach that we took:

- Treat single electron in periodic potential via single-particle Schrödinger equation
- generates a band structure of allowed states in reciprocal space
- Fill bands with electrons in single-particle Bloch functions $\Psi_{\mathbf{k}}$
- But what about Coulomb interactions between electrons?
- Strictly speaking, we should solve Many-Body S.E.

* Recall, for fixed nuclear configuration (more later), electronic many-body H is:

$$H = \sum_i \frac{\vec{p}_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + V_{\text{ext}}(\vec{r})$$

electron kinetic energy \rightarrow
e-e Coulomb repulsion \uparrow

\uparrow Fixed "external" potential from nuclei, etc.

* Gives many-body energies and wave functions:
 \downarrow spin of electron

$$H \Psi(\vec{r}, \sigma_1, \vec{r}_2 \sigma_2, \dots \vec{r}_N \sigma_N) = E \Psi(\vec{r}, \sigma_1, \vec{r}_2 \sigma_2, \dots \vec{r}_N \sigma_N)$$

Position of electron \uparrow \uparrow N total electrons

- * Recall also that this is impossible to solve for more than a few electrons
- * We will discuss various approximations to solving the many-body problem.

Constructing the Many-body wavefunction

- First step: Choose a basis of single-electron orbitals $\phi_i(\vec{r})$

* Assume they are orthonormal and form a complete set

$$\Psi_i(\vec{r}_i \sigma_i) = \phi_i(\vec{r}) \chi_i(\sigma)$$

spin part
orbital part

* Consider expressing the G.S. many-body wavefunction:

$$\Psi_0(\vec{r}_1 \sigma_1, \vec{r}_2 \sigma_2, \dots, \vec{r}_N \sigma_N) = \psi_1(\vec{r}_1 \sigma_1) \psi_2(\vec{r}_2 \sigma_2) \dots \psi_N(\vec{r}_N \sigma_N)$$

position of electron

- Note: Two sets of indices: $\psi_i(\vec{r}, \sigma_i)$

orbital number ↑ electron number ↑

- Many issues with this including that Ψ does not have the correct antisymmetry (should pick up - when we swap e⁻ indices)

* We can make the RHS antisymmetric by applying operator A:

$$\Psi_0(\vec{r}_1 \sigma_1, \vec{r}_2 \sigma_2, \dots, \vec{r}_N \sigma_N) = A \{ \psi_1(\vec{r}_1 \sigma_1) \psi_2(\vec{r}_2 \sigma_2) \dots \psi_N(\vec{r}_N \sigma_N) \}$$

where:

$$A = \frac{1}{\sqrt{N!}} \sum_{i=1}^{N!} (-1)^{\rho_i} P_i$$

number of possible permutations

- Where P_i is a permutation of electron coordinates

- $(-1)^{\rho_i} = +1$ if we permute odd number of indices,
 -1 " " " even " "

- Simplest example, consider two electrons, one spin up, one spin down.

$$\psi_1(\vec{r}_1 \uparrow), \psi_2(\vec{r}_2 \downarrow)$$

$$A \{ \Psi_1(\vec{r}_1 \uparrow) \Psi_2(\vec{r}_2 \downarrow) \} = \frac{1}{\sqrt{2}} \left[\Psi_1(\vec{r}_1 \uparrow) \Psi_2(\vec{r}_2 \downarrow) - \Psi_1(\vec{r}_2 \downarrow) \Psi_2(\vec{r}_1 \uparrow) \right]$$

Permute electron number

i.e., a singlet spin state.

- Systematic way of generating antisymmetric combination of orbitals: **Slater determinant**

Take $\vec{r}_i \equiv \vec{r}_i \tau_i$, three orbitals ($i=1,2,3$):

$$\frac{1}{\sqrt{6}} \begin{vmatrix} \Psi_1(\vec{r}_1) & \Psi_1(\vec{r}_2) & \Psi_1(\vec{r}_3) \\ \Psi_2(\vec{r}_1) & \Psi_2(\vec{r}_2) & \Psi_2(\vec{r}_3) \\ \Psi_3(\vec{r}_1) & \Psi_3(\vec{r}_2) & \Psi_3(\vec{r}_3) \end{vmatrix}$$

$$= \frac{1}{\sqrt{6}} \left[\Psi_1(\vec{r}_1) \Psi_2(\vec{r}_2) \Psi_3(\vec{r}_3) - \Psi_1(\vec{r}_1) \Psi_2(\vec{r}_3) \Psi_3(\vec{r}_2) \right.$$

$$- \underbrace{\Psi_1(\vec{r}_2) \Psi_2(\vec{r}_1) \Psi_3(\vec{r}_3)}_P + \underbrace{\Psi_1(\vec{r}_2) \Psi_2(\vec{r}_3) \Psi_3(\vec{r}_1)}_{PP} \left. + \Psi_1(\vec{r}_3) \Psi_2(\vec{r}_1) \Psi_3(\vec{r}_2) - \Psi_1(\vec{r}_3) \Psi_2(\vec{r}_2) \Psi_3(\vec{r}_1) \right]$$

- We will use shorthand for Slater det: $\Psi_0 = \frac{1}{\sqrt{N!}} \det \{ \Psi_1 \Psi_2 \dots \Psi_N \}$

- Now that we have an antisymmetric wave function, need to calculate matrix elements with H

* Kinetic energy and external potential can be written as sum over single-electron operators:

$$G_1 = \sum_i^N h_i = \sum_i^N h(r_i) \leftarrow h = \frac{p^2}{2m} + V_{\text{ext}} \leftarrow \begin{matrix} \text{nuclear-nuclear,} \\ \text{electron-nuclear} \end{matrix}$$

$$\langle \Psi_0 | G_1 | \Psi_0 \rangle = \frac{1}{N!} \langle \det \{ \Psi_1 \Psi_2 \dots \Psi_N \} | G_1 | \det \{ \Psi_1 \Psi_2 \dots \Psi_N \} \rangle$$

- consider element with nonpermuted terms:

$$\langle \Psi_1 \Psi_2 \dots \Psi_N | G_1 | \Psi_1 \Psi_2 \dots \Psi_N \rangle \xrightarrow{\text{write ordering to correspond to } \vec{r}_1, \vec{r}_2, \dots \vec{r}_N \text{ electron coordinates}}$$

for our example of three spin orbitals ($\vec{r}_i \equiv \vec{r}_i \sigma_i$):

$$\langle \Psi_1 \Psi_2 \Psi_3 | G_1 | \Psi_1 \Psi_2 \Psi_3 \rangle =$$

$$\begin{aligned} & \int \Psi_1^*(\vec{r}_1) \Psi_2^*(\vec{r}_2) \Psi_3^*(\vec{r}_3) [h(\vec{r}_1) + h(\vec{r}_2) + h(\vec{r}_3)] \Psi_1(\vec{r}_1) \Psi_2(\vec{r}_2) \Psi_3(\vec{r}_3) d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \\ &= \int \Psi_1^*(\vec{r}_1) h(\vec{r}_1) \Psi_1(\vec{r}_1) d\vec{r}_1 \cdot \int \Psi_2^*(\vec{r}_2) h(\vec{r}_2) \Psi_2(\vec{r}_2) d\vec{r}_2 \cdot \int \Psi_3^*(\vec{r}_3) h(\vec{r}_3) \Psi_3(\vec{r}_3) d\vec{r}_3 \\ &+ (\text{similar terms for } h(\vec{r}_2), h(\vec{r}_3)) \\ &= \langle \Psi_1 | h_1 | \Psi_1 \rangle + \langle \Psi_2 | h_2 | \Psi_2 \rangle + \langle \Psi_3 | h_3 | \Psi_3 \rangle = \sum_i^N \langle \Psi_i | h | \Psi_i \rangle \end{aligned}$$

What about, e.g.,

$$\langle \Psi_1 \Psi_2 \Psi_3 | G_1 | \Psi_2 \Psi_1 \Psi_3 \rangle =$$

$$\begin{aligned} & \int \Psi_1^*(\vec{r}_1) \Psi_2^*(\vec{r}_2) \Psi_3^*(\vec{r}_3) [h(\vec{r}_1) + h(\vec{r}_2) + h(\vec{r}_3)] \Psi_2(\vec{r}_2) \Psi_1(\vec{r}_1) \Psi_3(\vec{r}_3) d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \\ &= \int \Psi_1^*(\vec{r}_1) h(\vec{r}_1) \Psi_1(\vec{r}_1) d\vec{r}_1 \cdot \int \Psi_2^*(\vec{r}_2) h(\vec{r}_2) \Psi_2(\vec{r}_2) d\vec{r}_2 \cdot \int \Psi_3^*(\vec{r}_3) h(\vec{r}_3) \Psi_3(\vec{r}_3) d\vec{r}_3 \\ &+ (\text{similarly for } h(\vec{r}_2), h(\vec{r}_3) \text{ terms}) \\ &= 0 \end{aligned}$$

= 0 b/c Ψ_1, Ψ_2 orthogonal

- so only nonzero matrix elements are between terms with the same permutation!
- $N!$ of these terms (cancel $1/N!$)

$$\Rightarrow \langle \Psi_0 | G_1 | \Psi_0 \rangle = \sum_i \langle \Psi_i | h | \Psi_i \rangle$$

* Coulomb interaction requires two-particle operators:

$$G_2 = \frac{1}{2} \sum_{i \neq j}^N \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \equiv \frac{1}{2} \sum_{i \neq j}^N \frac{e^2}{r_{ij}}$$

- What terms of $\langle \Psi_0 | G_2 | \Psi_0 \rangle$ are nonzero?

- Consider e^2/r_{12} in our three-orbital example.
nonpermuted case:

$$\langle \Psi_0 | \frac{e^2}{r_{12}} | \Psi_0 \rangle = \underbrace{\int \Psi_1^*(\vec{r}_1) \Psi_2^*(\vec{r}_2) \frac{e^2}{r_{12}} \Psi_1(\vec{r}_1) \Psi_2(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 \cdot \int \Psi_3^*(\vec{r}_3) \Psi_3(\vec{r}_3) d\vec{r}_3}_{=1}$$

- What about $\langle \Psi_0 | \frac{e^2}{r_{12}} | \Psi_0 \rangle$

$$= - \int \Psi_1^*(\vec{r}_1) \Psi_2^*(\vec{r}_2) \frac{e^2}{r_{12}} \Psi_1(\vec{r}_2) \Psi_2(\vec{r}_1) d\vec{r}_1 d\vec{r}_2$$

- Permutations involving Ψ_3 will vanish since $\int \Psi_3^*(\vec{r}_3) \Psi_i(\vec{r}_3) d\vec{r}_3 = \delta_{3i}$

- In general:

$$\langle \Psi_0 | G_2 | \Psi_0 \rangle = \frac{1}{2} \sum_{i \neq j} \langle \Psi_0 | \frac{e^2}{r_{ij}} | \Psi_0 \rangle - \langle \Psi_0 | \frac{e^2}{r_{12}} | \Psi_0 \rangle$$

*just two electron coordinates so
only need r_{12}*

* What if we have different Slater determinants?

- Consider $\Psi_{\mu, m}$ which differs from Ψ_0 by replacing Ψ_m by Ψ_μ :

$$\Psi_0 = \det \{ \Psi_1, \Psi_2, \dots, \Psi_m, \dots, \Psi_N \}, \quad \Psi_{\mu, m} = \det \{ \Psi_1, \Psi_2, \dots, \Psi_\mu, \dots, \Psi_N \}$$

(all other orbital the same and in the same order)

- For G_2 , any term that is not $\langle \Psi_\mu | h | \Psi_m \rangle$ is zero because $\langle \Psi_\mu | \Psi_i \rangle = \delta_{im}$ and $\langle \Psi_i | \Psi_m \rangle = \delta_{im}$

$$\text{so } \langle \Psi_{\mu, m} | G_2 | \Psi_0 \rangle = \langle \Psi_\mu | h | \Psi_m \rangle$$

Similarly,

$$\langle \Psi_{\mu,m} | G_2 | \Psi_0 \rangle = \sum_j \left[\langle \Psi_\mu \Psi_j | \frac{e^2}{r_{12}} | \Psi_m \Psi_j \rangle - \langle \Psi_\mu \Psi_j | \frac{e^2}{r_{12}} | \Psi_j \Psi_m \rangle \right]$$

[$\frac{1}{2}$ cancelled by, e.g., $\langle \Psi_\mu \Psi_j | \frac{e^2}{r_{12}} | \Psi_m \Psi_j \rangle = \langle \Psi_j \Psi_\mu | \frac{e^2}{r_{12}} | \Psi_j \Psi_m \rangle$]

- If we replace two spin-orbitals, matrix elements with G_1 vanish and:

$$\langle \Psi_{\mu\nu,mn} | G_2 | \Psi_0 \rangle = \langle \Psi_\mu \Psi_\nu | \frac{e^2}{r_{12}} | \Psi_m \Psi_n \rangle - \langle \Psi_\mu \Psi_\nu | \frac{e^2}{r_{12}} | \Psi_n \Psi_m \rangle$$

- If we replace three or more spin-orbitals, matrix elements with G_1, G_2 are zero

* Let's analyze the spin part for an arbitrary two-electron integral:

$$\langle \Psi_\alpha \Psi_\beta | \frac{e^2}{r_{12}} | \Psi_\gamma \Psi_\delta \rangle = \int \Psi_\alpha(\vec{r}_1, \sigma_1) \Psi_\beta(\vec{r}_2, \sigma_2) \frac{e}{r_{12}} \Psi_\gamma(\vec{r}_1, \sigma_1) \Psi_\delta(\vec{r}_2, \sigma_2) d(\vec{r}_1, \sigma_1) d(\vec{r}_2, \sigma_2)$$

$$= \underbrace{\int \chi_\alpha(\vec{r}_1) \chi_\beta(\vec{r}_1) d\sigma_1}_{\delta \chi_\alpha \chi_\beta} \underbrace{\int \chi_\beta(\vec{r}_2) \chi_\delta(\vec{r}_2) d\sigma_2}_{\delta \chi_\beta \chi_\delta} \int \Phi_\alpha(\vec{r}_1) \Phi_\beta(\vec{r}_2) \frac{e}{r_{12}} \Phi_\gamma(\vec{r}_1) \Phi_\delta(\vec{r}_2) d\vec{r}_1 d\vec{r}_2$$

- So for integrals of the form: $\langle \Psi_\alpha \Psi_\beta | \frac{e^2}{r_{12}} | \Psi_\alpha \Psi_\beta \rangle$, the delta functions are satisfied automatically regardless of spin.

→ known as "direct" Coulomb, classical electrostatic interaction between charge densities:

$$e^2 \int \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2, \quad \rho(\vec{r}_1) = \Phi_\alpha^*(\vec{r}_1) \Phi_\alpha(\vec{r}_1), \quad \rho(\vec{r}_2) = \Phi_\beta^*(\vec{r}_2) \Phi_\beta(\vec{r}_2)$$

- For integrals of the form $\langle \Psi_\alpha \Psi_\beta | \frac{e^2}{r_{12}} | \Psi_\beta \Psi_\alpha \rangle$, only nonzero if χ_α and χ_β are the same spin!

→ "Exchange interaction," can be thought of as energy of parallel versus anti-parallel spins.

Hartree - Fock equations

- Idea: Describe the ground state of system with N interacting electrons as a single Slater determinant of optimized orbitals

* Note: Exact solution is generally made up of many Slater determinants

* We will optimize the orbital part of the wavefunction for a given fixed spin configuration.

* Energy for given Slater determinant Ψ_0 is

$$E_0 = \langle \Psi_0 | H | \Psi_0 \rangle = \sum_i^{\text{occ}} \langle \Psi_i | h | \Psi_i \rangle + \frac{1}{2} \sum_{ij}^{\text{occ}} \left[\langle \Psi_i | \Psi_j | \frac{e^2}{r_{ij}} | \Psi_i \Psi_j \rangle - \langle \Psi_i | \Psi_j | \frac{e^2}{r_{ij}} | \Psi_j \Psi_i \rangle \right]$$

"Direct" Coulomb "Exchange"

• We will vary the N contributing spin orbitals $\{\Psi_i\}$ to minimize E_0

• Add constraint that $\langle \Psi_i | \Psi_i \rangle = \delta_{ij}$:

$$G(\{\Psi_i\}) = \sum_i \langle \Psi_i | h | \Psi_i \rangle + \frac{1}{2} \sum_{ij} \left[\langle \Psi_i | \Psi_j | \frac{e^2}{r_{ij}} | \Psi_i \Psi_j \rangle - \langle \Psi_i | \Psi_j | \frac{e^2}{r_{ij}} | \Psi_j \Psi_i \rangle \right] - \sum_{ij} \varepsilon_{ij} \langle \Psi_i | \Psi_j \rangle$$

Unknown multiplet

• Consider just the variation in Ψ_i^* :

$$\delta G = \sum_i \langle \delta \Psi_i | h | \Psi_i \rangle + \frac{1}{2} \sum_{ij} \left[\langle \delta \Psi_i | \Psi_j | \frac{e^2}{r_{ij}} | \Psi_i \Psi_j \rangle - \langle \delta \Psi_i | \Psi_j | \frac{e^2}{r_{ij}} | \Psi_j \Psi_i \rangle \right] - \sum_{ij} \varepsilon_{ij} \langle \delta \Psi_i | \Psi_j \rangle = 0$$

two terms from i and j

Since this needs to be true for any $\delta \Psi_i^*$, we have that

$$\sum_i h | \Psi_i \rangle + \sum_{ij} \left[\langle \Psi_i | \frac{e^2}{r_{ij}} | \Psi_i \Psi_j \rangle - \langle \Psi_i | \frac{e^2}{r_{ij}} | \Psi_j \Psi_i \rangle \right] = \sum_{ij} \varepsilon_{ij} | \Psi_i \rangle$$

so for each Ψ_i we can write:

$$\left[\frac{p^2}{2m} + V_{\text{ext}} + V_{\text{coulomb}} + V_{\text{exchange}} \right] | \Psi_i \rangle = \varepsilon_i | \Psi_i \rangle$$

diagonalized: $\sum_j \varepsilon_{ij} = \sum_i \delta_{ij}$

"Hartree" part

$$\text{Where: } \langle \vec{r}_i | V_{\text{coulomb}} | \Psi_i \rangle = \sum_j \Psi_i(\vec{r}_i, \sigma_i) \int \Psi_j^*(\vec{r}_j, \sigma_j) \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \Psi_j(\vec{r}_j, \sigma_j) d(\vec{r}_j, \sigma_j)$$

$$\langle \vec{r}_i | V_{\text{exchange}} | \Psi_i \rangle = \sum_j \Psi_i(\vec{r}_i, \sigma_i) \int \Psi_j^*(\vec{r}_j, \sigma_j) \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \Psi_i(\vec{r}_j, \sigma_j) d(\vec{r}_j, \sigma_j)$$

* Note: Subtlety about the total energy

- We can write the Hartree-Fock equation as

$$F \Psi_i = \varepsilon_i \Psi_i, \quad F = h + V_{\text{Coulomb}} + V_{\text{exchange}}$$

$$\Rightarrow \varepsilon_i = \langle \Psi_i | h | \Psi_i \rangle + \sum_j^{\text{occ}} \left[\langle \Psi_i | \Psi_j | \frac{e^2}{r_{ij}} | \Psi_i \Psi_j \rangle - \langle \Psi_i | \Psi_j | \frac{e^2}{r_{ij}} | \Psi_j \Psi_i \rangle \right]$$

- But before we said the energy was:

$$E_0 = \langle \Psi_0 | H | \Psi_0 \rangle = \sum_i^{\text{occ}} \langle \Psi_i | h | \Psi_i \rangle + \frac{1}{2} \sum_{ij}^{\text{occ}} \left[\langle \Psi_i | \Psi_j | \frac{e^2}{r_{ij}} | \Psi_i \Psi_j \rangle - \langle \Psi_i | \Psi_j | \frac{e^2}{r_{ij}} | \Psi_j \Psi_i \rangle \right]$$

SD:

$$E_0^{\text{HF}} = \sum_i^{\text{occ}} \varepsilon_i - \frac{1}{2} \sum_{ij}^{\text{occ}} \underbrace{\left[\langle \Psi_i | \Psi_j | \frac{e^2}{r_{ij}} | \Psi_i \Psi_j \rangle - \langle \Psi_i | \Psi_j | \frac{e^2}{r_{ij}} | \Psi_j \Psi_i \rangle \right]}_{\text{"Double counting" term}}$$

- What is the physical meaning of ε_i ? Consider an ionization process where we remove an electron from orbital Ψ_m

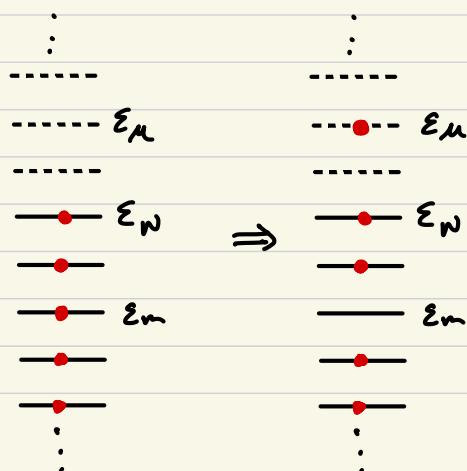
$$* E_0^{\text{HF}}(N) - E_0^{\text{HF}}(N-1) = \langle \Psi_m | h | \Psi_m \rangle + \sum_j^{\text{occ}} \left[\langle \Psi_m | \Psi_j | \frac{e^2}{r_{ij}} | \Psi_m \Psi_j \rangle - \langle \Psi_m | \Psi_j | \frac{e^2}{r_{ij}} | \Psi_j \Psi_m \rangle \right]$$

↑ Factor of 2
from Ψ_j first or second
position

$$= \varepsilon_m$$

- Koopmans' theorem: ε_m is the energy required to remove an electron from spin-orbital Ψ_m

- Excitation energies: Consider moving an electron from a filled orbital to an empty ("virtual") one



* Excitation energy:

$$\Delta E = \langle \Psi_{\mu, m} | H | \Psi_{\mu, m} \rangle - \langle \Psi_0 | H | \Psi_0 \rangle$$

$$= \langle \Psi_\mu | h | \Psi_\mu \rangle - \langle \Psi_m | h | \Psi_m \rangle$$

$$+ \sum_j^{\text{occ}} \left[\langle \Psi_\mu \Psi_j | \frac{e^2}{r_{12}} | \Psi_\mu \Psi_j \rangle - \langle \Psi_\mu \Psi_j | \frac{e^2}{r_{12}} | \Psi_j \Psi_\mu \rangle \right] \quad \text{Extra term from occupying } \Psi_\mu$$

$$- \left[\langle \Psi_\mu \Psi_m | \frac{e^2}{r_{12}} | \Psi_\mu \Psi_m \rangle - \langle \Psi_\mu \Psi_m | \frac{e^2}{r_{12}} | \Psi_m \Psi_\mu \rangle \right] \quad \text{Remove term between } \Psi_\mu \text{ and } \Psi_m$$

$$- \sum_j^{\text{occ}} \left[\langle \Psi_j \Psi_m | \frac{e^2}{r_{12}} | \Psi_j \Psi_m \rangle - \langle \Psi_j \Psi_m | \frac{e^2}{r_{12}} | \Psi_m \Psi_j \rangle \right] \quad \text{Remove all other } \Psi_m \text{ terms}$$

$$= \varepsilon_\mu - \varepsilon_m - \underbrace{\left[\langle \Psi_\mu \Psi_m | \frac{e^2}{r_{12}} | \Psi_\mu \Psi_m \rangle - \langle \Psi_\mu \Psi_m | \frac{e^2}{r_{12}} | \Psi_m \Psi_\mu \rangle \right]}_{\text{Coulomb interaction between electron in } \Psi_\mu \text{ and "hole" in } \Psi_m.}$$

Energy difference
between states

Density functional theory (DFT)

- By far the most popular way of describing the electronic structure of solids
- A different philosophy than Hartree-Fock
 - * HF: approximate the ground-state **wavefunction**
 - * DFT: Focus on the ground-state **density**
- Does the density contain less information than the wavefunction?

* Hohenberg-Kohn theorem says no!

* Write many-body H as $H = H_{\text{int}} + V_{\text{ext}}$ where:

$$H_{\text{int}} = T + V_{\text{ee}} = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

(drop nuclei-nuclei interaction for now)

$$V_{\text{ext}} = - \sum_{i,I} \frac{z_I e^2}{|\vec{r}_i - \vec{R}_I|}$$

NOTE: V_{ext} defines the system you are considering; operator H_{int} is always the same.

- Assume ground-state wavefunction Ψ_G is non-degenerate

- One-body ground-state density is:

$$n(\vec{r}) = \langle \Psi_G | \sum_i \delta(\vec{r} - \vec{r}_i) | \Psi_G \rangle$$

- Since V_{ext} is a local potential, $V_{\text{ext}} = \sum_i \int v_{\text{ext}}(\vec{r}) \delta(\vec{r} - \vec{r}_i) d^3r$

$$\text{so: } \langle \Psi_G | V_{\text{ext}} | \Psi_G \rangle = \int n(\vec{r}) v_{\text{ext}}(\vec{r}) d^3r$$

- Therefore, if we know Ψ_G and given $v_{\text{ext}}(\vec{r})$, we can determine $n(\vec{r})$

- So we can write: $F[V_{\text{ext}}] = n(\vec{r})$
 \uparrow some "functional," i.e., a function F of a function $V_{\text{ext}}(\vec{r})$

- Question: Can we invert this equation to get
 $V_{\text{ext}}(\vec{r}) \stackrel{?}{=} G[n(\vec{r})]$?
 \uparrow a different functional

- ⇒ If we can, that means there is a one-one mapping between ground-state density and external potential
- ⇒ A system (e.g., crystalline solid) is defined by V_{ext} , so this would imply that all properties of system can be defined in terms of $n(\vec{r})$

- Let's prove it!

Consider two Hamiltonians with different external potentials:

$$H = H_{\text{int}} + V_{\text{ext}}, \quad \bar{H} = H_{\text{int}} + \bar{V}_{\text{ext}}$$

With ground-state wave functions $|\Psi_G\rangle, |\bar{\Psi}_G\rangle$
 " " " energies E_G, \bar{E}_G

Now we write:

$$\begin{aligned} \langle \bar{\Psi}_G | H | \bar{\Psi}_G \rangle &= \langle \bar{\Psi}_G | H_{\text{int}} + V_{\text{ext}} | \bar{\Psi}_G \rangle = \langle \bar{\Psi}_G | H_{\text{int}} + V_{\text{ext}} + \bar{V}_{\text{ext}} - \bar{V}_{\text{ext}} | \bar{\Psi}_G \rangle \\ &= \bar{E}_G + \langle \bar{\Psi}_G | V_{\text{ext}} - \bar{V}_{\text{ext}} | \bar{\Psi}_G \rangle \\ &= \bar{E}_G + \int \bar{n}(\vec{r}) [V_{\text{ext}}(\vec{r}) - \bar{V}_{\text{ext}}(\vec{r})] d^3r \end{aligned}$$

since the true ground-state energy of H must be lower than $\langle \bar{\Psi}_G | H | \bar{\Psi}_G \rangle$:

$$E_G < \bar{E}_G + \int \bar{n}(\vec{r}) [V_{\text{ext}}(\vec{r}) - \bar{V}_{\text{ext}}(\vec{r})] d^3r$$

But we can obtain a similar version by considering $\langle \Psi_G | \bar{H} | \Psi_G \rangle$:

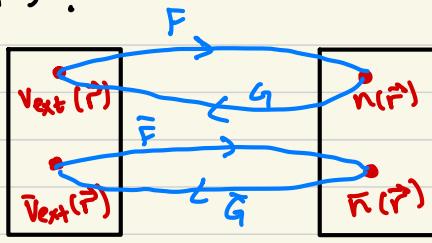
$$\bar{E}_G < E_G + \int n(\vec{r}) [\bar{V}_{\text{ext}}(\vec{r}) - V_{\text{ext}}(\vec{r})] d^3 r$$

$$\bar{E}_G < E_G - \int n(\vec{r}) [V_{\text{ext}}(\vec{r}) - \bar{V}_{\text{ext}}(\vec{r})] d^3 r$$

$$\Rightarrow E_G > \bar{E}_G + \int n(\vec{r}) [V_{\text{ext}}(\vec{r}) - \bar{V}_{\text{ext}}(\vec{r})] d^3 r !$$

so we find that for $V_{\text{ext}}(\vec{r}) \neq \bar{V}_{\text{ext}}(\vec{r})$,
 $n(\vec{r}) \neq \bar{n}(\vec{r})$!

* Schematic:



\Rightarrow Ground state density "one-to-one" with V_{ext} , so uniquely determines H , Ψ_G , and all properties of the system

* This means we can define a functional of n that gives the energy so that:

$$E[n_{\text{GS}}] = E_{\text{GS}}$$
, where n_{GS} , E_{GS} are GS density and energy

* Written in another form:

$$E[n(\vec{r}); V_{\text{ext}}(\vec{r})] = T[n(\vec{r})] + V_{\text{ee}}[n(\vec{r})] + \int V_{\text{ext}}(\vec{r}) n(\vec{r}) d^3 r$$

↑ electro-electron
interaction energy
functional
 ↑ K.E. functional
of n ↑ external potential
energy

- The problem: Even though we know $E[n]$, $T[n]$, $V_{\text{ee}}[n]$ exist we do not know what they are.

Kohn-Sham equations

- We need to figure out an expression for energy functionals
- We also need to obtain the density
- * Of course we can get n via: $n = \langle \Psi | \sum_i \delta(\vec{r} - \vec{r}_i) | \Psi \rangle$ but then we would need to know Ψ and would have solved the problem anyway
- Kohn-Sham approach to these two problems:
 - * Write $n(\vec{r})$ has sum over some set of orthonormal orbitals:

$$n(\vec{r}) = \sum_i \Phi_i^*(\vec{r}) \Phi_i(\vec{r})$$

single-particle orbitals

GS many-body density
 - * Note: $\Phi_i(\vec{r})$ are single-particle orbitals, only depend on 3 coordinates (\vec{r}) not $3N$ ($\vec{r}_1 \dots \vec{r}_N$)
 - * Note: We could construct an approximate GS many-body wavefunction like: $\Psi = \det \{\Phi_1 \dots \Phi_N\}$ but it would not correspond to a true many-body GS in any rigorous sense

* Now we write down some contributions to $E[n]$ that we know:

- Classical Coulomb, i.e., Hartree energy:

$$E_H[n] = \frac{1}{2} \int n(\vec{r}) \frac{e^2}{|\vec{r} - \vec{r}'|} n(\vec{r}') d\vec{r} d\vec{r}' = \frac{1}{2} \sum_{ij} \langle \Phi_i \Phi_j | \frac{e^2}{\vec{r}_{ij}} | \Phi_i \Phi_j \rangle$$

(note that in general, $E_{ee}[n] \neq E_H[n]$)

- Single-particle kinetic energy:

$$T_0[n] = \sum_i \langle \Phi_i | \frac{p^2}{2m} | \Phi_i \rangle$$

(note, in general $T[n] \neq T_0[n]$)

* Now we write the energy functional as:

$$E[n, v_{ext}] = T_0[n] + E_H[n] + \int v_{ext}(\vec{r}) n(\vec{r}) d^3r + E_{xc}[n]$$

Or:

$$E[n, v_{ext}] = \sum_i \langle \phi_i | \frac{\vec{p}^2}{2m} + v_{ext} | \phi_i \rangle + \frac{1}{2} \sum_{ij} \langle \phi_i | \phi_j | \frac{e^2}{r_{ij}} | \phi_i | \phi_j \rangle + E_{xc}[n]$$

where $E_{xc}[n] \equiv T[n] - T_0[n] + E_{ee}[n] - E_H[n]$

- E_{xc} is call "exchange-correlation" functional

- Basically all of the stuff we don't know

* Now we minimize E WRT ϕ_i as we did for Hartree-Fock to get an equation for ϕ_i :

$$\left[\frac{\vec{p}^2}{2m} + V_{ext} + V_{coulomb} + V_{xc} \right] |\phi_i\rangle = \varepsilon_i |\phi_i\rangle$$

Kohn-Sham
equation

- $V_{coulomb}$ is Hartree Coulomb interaction potential, same as HF

- V_{xc} is defined as:

$$SE_{xc}[n] \equiv \int V_{xc}(\vec{r}) \delta n(\vec{r}) d^3r = \int V_{xc}(\vec{r}) \delta \sum_i \phi_i^*(\vec{r}) \phi_i(\vec{r}) d^3r$$

so: $V_{xc}(\vec{r}) = \frac{\delta E_{xc}[n]}{\delta n(\vec{r})}$

- Similar to HF, exact GS energy is:

$$E_{GS} = \sum_i \varepsilon_i - \frac{1}{2} \sum_{ij} \langle \phi_i | \phi_j | \frac{e^2}{r_{ij}} | \phi_i | \phi_j \rangle + \underbrace{E_{xc}[n] - \int V_{xc}(\vec{r}) n(\vec{r}) d^3r}_{\text{"Double counting" of Hartree potential}}$$

"Double counting"
of Hartree potential

Not zero since V_{xc}
is defined by functional
derivative WRT

How to
↓ CEST
This

- Note: No Koopmans' theorem for DFT ϕ_i and ε_i . Rigorously they have no physical meaning, but are often associated with the band structure

- we still have not really made any progress since we don't know E_{xc} !
- Kohn and Sham did propose an approximate E_{xc} : **Local Density Approximation (LDA)**

* Consider a solid as a "nonuniform electron gas"



position \vec{r}
has density $n(\vec{r}) = n_0$
map to
uniform electron
gas w/ density n_0



$$\bullet E_{xc}^{LDA}[n] = \int \epsilon_{xc}(n(\vec{r})) n(\vec{r}) d^3r$$

↑ many-body exchange-correlation energy
per e^- of uniform gas of density $N(\vec{r})$

$$V_{xc}^{LDA}(\vec{r}) \equiv \frac{\delta E_{xc}^{LDA}}{\delta n(\vec{r})} = \epsilon_{xc}(n(\vec{r})) + n(\vec{r}) \frac{d \epsilon_{xc}(n(r))}{d n(r)}$$

• Total energy is thus:

$$E_0^{LDA} = \sum_i \epsilon_i - \frac{1}{2} \int n(\vec{r}) \frac{e^2}{|\vec{r} - \vec{r}'|} n(\vec{r}') d\vec{r} d\vec{r}' - \int n(\vec{r}) \frac{d \epsilon_{xc}(n(\vec{r}))}{d n(r)} n(\vec{r}) d\vec{r}$$

* This is useful because there are high-accuracy calculations of ϵ_{xc} for uniform electron gas at different densities

• See Leperley and Alder Phys. Rev. Lett. 45, 566 (1980)
or Fig. 6 in Sec. IV. 7 in G and F

Beyond one-electron approximation Summary

- We had been neglecting explicit electron-electron Coulomb interactions
- Discussed two ways of including approximate interactions (Note: there are many more)
 - * Hartree - Fock: Approximate the many-body wave function with a single Slater determinant made up of single-particle orbitals which are solutions to:
$$\left[\frac{\mathbf{p}^2}{2m} + V_{\text{ext}} + V_{\text{Coulomb}} + V_{\text{exchange}} \right] |\Psi_i\rangle = \varepsilon_i |\Psi_i\rangle$$

- HF often used in chemistry for molecules

* Density functional theory: From Hohenberg - Kohn, we know that the many-body density contains all information about a system with a given V_{ext} .

- To get density, solve auxiliary single-particle problem:

$$\left[\frac{\mathbf{p}^2}{2m} + V_{\text{ext}} + V_{\text{Coulomb}} + V_{\text{xc}} \right] |\Phi_i\rangle = \varepsilon_i |\Phi_i\rangle$$

- where many-body density is $n(\vec{r}) = \sum_i \Phi_i^*(\vec{r}) \Phi_i(\vec{r})$
- All approximations reside in exchange-correlation potential, LDA is one approximation to XC
- DFT is the most popular way of describing the electronic structure of solids!