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 ψ_{nk}

- 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:

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

electron kinetic energy

e-e Coulomb repulsion

↑ fixed "external" potential from nuclei, etc.

  * Gives many-body energies and wavefunctions:

$$H\,\Psi(\vec{r}_1\sigma_1, \vec{r}_2\sigma_2, \cdots \vec{r}_N\sigma_N) = E\,\Psi(\vec{r}_1\sigma_1, \vec{r}_2\sigma_2, \cdots \vec{r}_N\sigma_N)$$

spin of electron 1

Position of electron 1

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

$$\psi_i(\vec{r}\sigma) = \phi_i(\vec{r})\,\chi_i(\sigma)$$

($\chi_i(\sigma)$: spin part; $\phi_i(\vec{r})$: orbital part)

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

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

($\vec{r}_1$: position of electron)

- Note: Two sets of indices: $\psi_1(\vec{r}_1, \sigma_1)$ — 1: Basis function number; 1: 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:

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

($N!$: number of possible permutations)

- where P_i is a permutation of electron coordinates
- $(-1)^{p_i} = -1$ if we permute odd number of indices, $+1$ " " " even " " "
- Simple example: Two orbitals, two electrons, one spin up one spin down

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

$$\mathcal{A}\{\psi_1(\vec{r}_1\uparrow)\,\psi_2(\vec{r}_2\downarrow)\} = \frac{1}{\sqrt{2}}\left[\psi_1(\vec{r}_1\uparrow)\,\psi_2(\vec{r}_2\downarrow) - \psi_1(\vec{r}_2\downarrow)\,\psi_2(\vec{r}_1\uparrow)\right]$$

permutate electron number

i.e., a singlet spin state.

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

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

$$\frac{1}{\sqrt{6}}\begin{vmatrix} \psi_1(\vec{r}_1) & \psi_1(\vec{r}_2) & \psi_1(\vec{r}_3) \\ \psi_2(\vec{r}_1) & \psi_2(\vec{r}_2) & \psi_2(\vec{r}_3) \\ \psi_3(\vec{r}_1) & \psi_3(\vec{r}_2) & \psi_3(\vec{r}_3) \end{vmatrix}$$

$$= \frac{1}{\sqrt{6}}\Big[\psi_1(\vec{r}_1)\,\psi_2(\vec{r}_2)\,\psi_3(\vec{r}_3) - \psi_1(\vec{r}_1)\,\psi_2(\vec{r}_3)\,\psi_3(\vec{r}_2) \quad (P)$$
$$- \psi_1(\vec{r}_2)\,\psi_2(\vec{r}_1)\,\psi_3(\vec{r}_3) \quad (P) + \psi_1(\vec{r}_2)\,\psi_2(\vec{r}_3)\,\psi_3(\vec{r}_1) \quad (P, P)$$
$$+ \psi_1(\vec{r}_3)\,\psi_2(\vec{r}_1)\,\psi_3(\vec{r}_2) \quad (P, P) - \psi_1(\vec{r}_3)\,\psi_2(\vec{r}_2)\,\psi_3(\vec{r}_1) \quad (P)\Big]$$

- we will use shorthand for Slater det: $\Psi_0 = \frac{1}{\sqrt{N!}}\det\{\psi_1\psi_2\cdots\psi_N\}$

- 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:

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

$$\langle\Psi_0|G_1|\Psi_0\rangle = \frac{1}{N!}\langle\det\{\psi_1\psi_2\cdots\psi_N\}|G_1|\det\{\psi_1\psi_2\cdots\psi_N\}\rangle$$

• consider element with nonpermuted terms:

$\langle \psi_1 \psi_2 \cdots \psi_N | G_1 | \psi_1 \psi_2 \cdots \psi_N \rangle$ ← write ordering to correspond to $\vec{r}_1, \vec{r}_2, \cdots \vec{r}_N$ electron coordinates

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

$$\langle \psi_1 \psi_2 \psi_3 | G_1 | \psi_1 \psi_2 \psi_3 \rangle =$$

$$\int \psi_1^*(\vec{r}_1)\, \psi_2^*(\vec{r}_2)\, \psi_3^*(\vec{r}_3) \left[h(\vec{r}_1) + h(\vec{r}_2) + h(\vec{r}_3) \right] \psi_1(\vec{r}_1)\, \psi_2(\vec{r}_2)\, \psi_3(\vec{r}_3)\, d\vec{r}_1\, d\vec{r}_2\, d\vec{r}_3$$

$$= \int \psi_1^*(\vec{r}_1)\, h(\vec{r}_1)\, \psi_1(\vec{r}_1)\, d\vec{r}_1 \cdot \int \psi_2^*(\vec{r}_2)\, \psi_2(\vec{r}_2)\, d\vec{r}_2 \cdot \int \psi_3^*(\vec{r}_3)\, \psi_3(\vec{r}_3)\, d\vec{r}_3$$

$$+ \left(\text{similar terms for } h(\vec{r}_2),\ h(\vec{r}_3) \right)$$

$$= \langle \psi_1 | h_1 | \psi_1 \rangle + \langle \psi_2 | h_2 | \psi_2 \rangle + \langle \psi_3 | h_3 | \psi_3 \rangle = \sum_i^N \langle \psi_i | h | \psi_i \rangle$$

What about, e.g.,

$$\langle \psi_1 \psi_2 \psi_3 | G_1 | \psi_2 \psi_1 \psi_3 \rangle =$$

$$\int \psi_1^*(\vec{r}_1)\, \psi_2^*(\vec{r}_2)\, \psi_3^*(\vec{r}_3) \left[h(\vec{r}_1) + h(\vec{r}_2) + h(\vec{r}_3) \right] \psi_1(\vec{r}_2)\, \psi_2(\vec{r}_1)\, \psi_3(\vec{r}_3)\, d\vec{r}_1\, d\vec{r}_2\, d\vec{r}_3$$

$$= \int \psi_1^*(\vec{r}_1)\, h(\vec{r}_1)\, \psi_2(\vec{r}_1)\, d\vec{r}_1 \cdot \int \cancel{\psi_2^*(\vec{r}_2)\, \psi_1(\vec{r}_2)\, d\vec{r}_2} \cdot \int \psi_3^*(\vec{r}_3)\, \psi_3(\vec{r}_3)\, d\vec{r}_3$$

= 0 b/c ψ_1, ψ_2 orthogonal

$$+ \left(\text{similarly for } h(\vec{r}_2),\ h(\vec{r}_3) \text{ terms} \right)$$

$$= 0$$

• 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.
  nonpermutated case:

$$\langle \psi_1 \psi_2 \psi_3 | \frac{e^2}{r_{12}} | \psi_1 \psi_2 \psi_3 \rangle =$$

$$\int \psi_1^*(\vec{r}_1)\, \psi_2^*(\vec{r}_2)\, \frac{e^2}{r_{12}}\, \psi_1(\vec{r}_1)\, \psi_2(\vec{r}_2)\, d\vec{r}_1 d\vec{r}_2 \cdot \underbrace{\int \psi_3^*(\vec{r}_3)\, \psi_3(\vec{r}_3)\, d\vec{r}_3}_{=1}$$

- What about $\langle \psi_1 \psi_2 \psi_3 | \frac{e^2}{r_{12}} | \psi_2 \psi_1 \psi_3 \rangle$

$$= -\int \psi_1^*(\vec{r}_1)\, \psi_2^*(\vec{r}_2)\, \frac{e^2}{r_{12}}\, \psi_1(\vec{r}_2)\, \psi_2(\vec{r}_1)\, d\vec{r}_1 d\vec{r}_2$$

- 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:

$$\langle \Psi_0 | G_2 | \Psi_0 \rangle = \frac{1}{2}\sum_{i\neq j}\left[\langle \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_j \psi_i \rangle\right]$$

↑ 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:

$$\Psi_0 = \det\{\psi_1 \psi_2 \cdots \psi_m \cdots \psi_N\},\ \Psi_{\mu m} = \det\{\psi_1 \psi_2 \cdots \psi_\mu \cdots \psi_N\}$$

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

- For G_1, any term that is not $\langle \psi_\mu | h | \psi_m \rangle$ is zero because $\langle \psi_\mu | \psi_i \rangle = \delta_{i\mu}$ and $\langle \psi_i | \psi_m \rangle = \delta_{im}$

so $\langle \Psi_{m,m} | G_1 | \Psi_0 \rangle = \langle \psi_\mu | h | \psi_m \rangle$

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:

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

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

- 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 antiparallel spins.

Hartree - Fock equations

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

"Direct" Coulomb, "Exchange"

$$E_0 = \langle \Psi_0 | H | \Psi_0 \rangle = \sum_i^{occ} \langle \psi_i | h | \psi_i \rangle + \frac{1}{2} \sum_{ij}^{occ} \left[\langle \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_j \psi_i \rangle \right]$$

(i: occupied orbital)

- We will vary the N contributing spin orbitals $\{\psi_i\}$ to minimize E_0

- Add constraint that $\langle \psi_i | \psi_j \rangle = \delta_{ij}$:

unknown Lagrange multiplier

$$G(\{\psi_i\}) = \sum_i \langle \psi_i | h | \psi_i \rangle + \frac{1}{2} \sum_{ij} \left[\langle \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_j \psi_i \rangle \right] - \sum_{ij} \varepsilon_{ij} \langle \psi_i | \psi_j \rangle$$

- Consider just the variation in ψ_i^*:

two terms from ij and ji

$$\delta G = \sum_i \langle \delta\psi_i | h | \psi_i \rangle + \frac{2}{2} \sum_{ij} \left[\langle \delta\psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_i \psi_j \rangle - \langle \delta\psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_j \psi_i \rangle \right] - \sum_{ij} \varepsilon_{ij} \langle \delta\psi_i | \psi_j \rangle = 0$$

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

$$\sum_i h | \psi_i \rangle + \sum_{ij} \left[\langle \psi_j | \frac{e^2}{r_{12}} | \psi_i \psi_j \rangle - \langle \psi_j | \frac{e^2}{r_{12}} | \psi_j \psi_i \rangle \right] = \sum_{ij} \varepsilon_{ij} | \psi_j \rangle$$

So for each ψ_i we can write:

Fock operator; diagonalized: $\sum_{ij} \varepsilon_{ij} = \varepsilon_i \delta_{ij}$

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

"Hartree" part

Where:

$$\langle \vec{r}_1 | V_{coulomb} | \psi_i \rangle = \sum_j \psi_i(\vec{r}_1 \sigma_1) \int \psi_j^*(\vec{r}_2 \sigma_2) \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \psi_j(\vec{r}_2 \sigma_2) \, d(\vec{r}_2 \sigma_2)$$

$$\langle \vec{r}_1 | V_{exchange} | \psi_i \rangle = -\sum_j \psi_j(\vec{r}_1 \sigma_1) \int \psi_j^*(\vec{r}_2 \sigma_2) \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \psi_i(\vec{r}_2 \sigma_2) \, d(\vec{r}_2 \sigma_2)$$

* Note: Subtlety about the total energy

- We can write the Hartree-Fock equation as

$$F\psi_i = \varepsilon_i \psi_i \quad , \quad F = h + V_{coulomb} + V_{exchange}$$

$$\Rightarrow \varepsilon_i = \langle \psi_i | h | \psi_i \rangle + \sum_j^{occ} \left[\langle \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_j \psi_i \rangle \right]$$

- But before we said the energy was:

$$E_0 = \langle \Psi_0 | H | \Psi_0 \rangle = \sum_i^{occ} \langle \psi_i | h | \psi_i \rangle + \frac{1}{2} \sum_{ij}^{occ} \left[\langle \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_j \psi_i \rangle \right]$$

SD:

$$E_0^{HF} = \sum_i^{occ} \varepsilon_i - \underbrace{\frac{1}{2} \sum_{ij}^{occ} \left[\langle \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \frac{e^2}{r_{12}} | \psi_j \psi_i \rangle \right]}_{\text{"Double counting" term}}$$

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

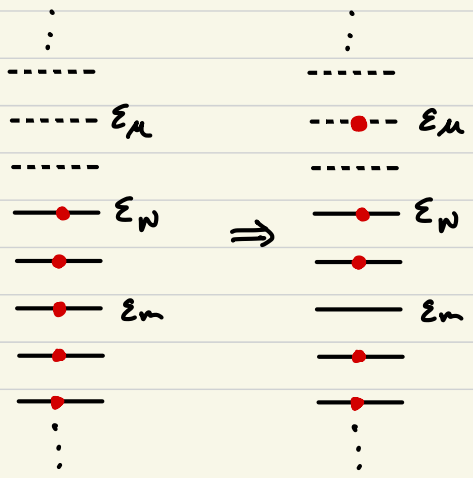
$$* \quad E_0^{HF}(N) - E_0^{HF}(N-1) = \langle \psi_m | h | \psi_m \rangle + \sum_j^{occ} \left[\langle \psi_m \psi_j | \frac{e^2}{r_{12}} | \psi_m \psi_j \rangle - \langle \psi_m \psi_j | \frac{e^2}{r_{12}} | \psi_j \psi_m \rangle \right]$$

↑ 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:

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

$$= \langle \psi_\mu | h | \psi_\mu \rangle - \langle \psi_m | h | \psi_m \rangle$$

$$+ \sum_j^{occ} \left[\langle \psi_\mu \psi_j | \frac{e^2}{r_{12}} | \psi_\mu \psi_j \rangle - \langle \psi_\mu \psi_j | \frac{e^2}{r_{12}} | \psi_j \psi_\mu \rangle \right]$$ ← Extra term from occupying ψ_μ

$$- \left[\langle \psi_\mu \psi_m | \frac{e^2}{r_{12}} | \psi_\mu \psi_m \rangle - \langle \psi_\mu \psi_m | \frac{e^2}{r_{12}} | \psi_m \psi_\mu \rangle \right]$$ ← Remove term between ψ_μ and ψ_m

$$- \sum_j^{occ} \left[\langle \psi_j \psi_m | \frac{e^2}{r_{12}} | \psi_j \psi_m \rangle - \langle \psi_j \psi_m \frac{e^2}{r_{12}} | \psi_m \psi_j \rangle \right]$$ ← Remove all other ψ_m terms

$$= \varepsilon_\mu - \varepsilon_m - \left[\langle \psi_\mu \psi_m | \frac{e^2}{r_{12}} | \psi_\mu \psi_m \rangle - \langle \psi_\mu \psi_m | \frac{e^2}{r_{12}} | \psi_m \psi_\mu \rangle \right]$$

Energy difference between states

Coulomb interaction between electron in ψ_μ and "hole" in ψ_m.

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

  * Why? Many body wavefunction $\Psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)$ function of 3N electron coordinates. The density $n(\vec{r})$ is a function of 3 coordinates!

- Does the density contain less information than the wavefunction?

  * Hohenberg-Kohn theorem says no!

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

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

(drop nuclei-nuclei interaction for now)

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

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

- Assume ground-state wavefunction Ψ_G is nondegenerate

- 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, $V_{ext} = \sum_i \int v_{ext}(\vec{r}) \delta(\vec{r} - \vec{r}_i) \, d^3r$

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

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

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

- Question: can we invert this equation to get $v_{ext}(\vec{r}) \stackrel{?}{=} G[n(\vec{r})]$?
  ↑ 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:

  $$H = H_{int} + v_{ext} \quad , \quad \bar{H} = H_{int} + \bar{v}_{ext}$$

  with ground-state wavefunctions $|\Psi_G\rangle$, $|\bar{\Psi}_G\rangle$

  " " " energies E_G, $\bar{E}_G$

  Now we write:

$$\langle \bar{\Psi}_G | H | \bar{\Psi}_G \rangle = \langle \bar{\Psi}_G | H_{int} + v_{ext} | \bar{\Psi}_G \rangle = \langle \bar{\Psi}_G | H_{int} + v_{ext} + \bar{v}_{ext} - \bar{v}_{ext} | \bar{\Psi}_G \rangle$$

$$= \bar{E}_G + \langle \bar{\Psi}_G | v_{ext} - \bar{v}_{ext} | \bar{\Psi}_G \rangle$$

$$= \bar{E}_G + \int \bar{n}(\vec{r}) \left[v_{ext}(\vec{r}) - \bar{v}_{ext}(\vec{r}) \right] d^3r$$

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

$$E_G < \bar{E}_G + \int \bar{n}(\vec{r}) \left[v_{ext}(\vec{r}) - \bar{v}_{ext}(\vec{r}) \right] d^3r$$

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

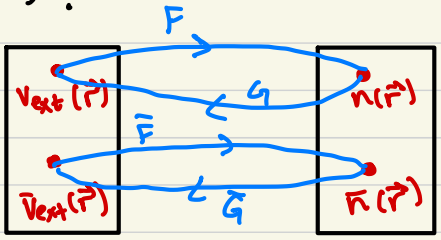
$$\bar{E}_G < E_G + \int n(\vec{r}) \left[\bar{v}_{ext}(\vec{r}) - v_{ext}(\vec{r}) \right] d^3r$$

$$\bar{E}_G < E_G - \int n(\vec{r}) \left[v_{ext}(\vec{r}) - \bar{v}_{ext}(\vec{r}) \right] d^3r$$

$$\Rightarrow \quad E_G > \bar{E}_G + \int n(\vec{r}) \left[v_{ext}(\vec{r}) - \bar{v}_{ext}(\vec{r}) \right] d^3r \; !$$

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

* Schematic:



⇒ 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:

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

* Written in another form:

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

$T[n(\vec{r})]$: K.E. functional of n

$V_{ee}[n(\vec{r})]$: electron-electron interaction energy functional

$\int v_{ext}(\vec{r})\, n(\vec{r})\, d^3r$: external potential energy

- The problem: Even though we know $E[n]$, $T[n]$, $V_{ee}[n]$ 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 theses two problems:

  * Write $n(\vec{r})$ as sum over some set of orthonormal orbitals:

GS many-body density ← $n(\vec{r}) = \sum_i \phi_i^*(\vec{r})\,\phi_i(\vec{r})$ ← single-particle orbitals

  - Note: $\phi_i(\vec{r})$ are single-particle orbitals, only depend on 3 coordinates $(\vec{r})$ not $3N$ $(\vec{r}_1 \cdots \vec{r}_N)$

  - Note: We could construct an approximate GS many-body wavefunction like: $\Psi = \det\{\phi_1 \cdots \phi_N\}$ 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:

$$E_H[n] = \frac{1}{2}\int n(\vec{r})\,\frac{e^2}{|\vec{r}-\vec{r}'|}\,n(\vec{r}')\,d\vec{r}\,d\vec{r}' = \frac{1}{2}\sum_{ij}\langle \phi_i\phi_j \left| \frac{e^2}{r_{12}} \right| \phi_i\phi_j \rangle$$

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

  - Single-particle kinetic energy:

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

  (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:

$$E[n, v_{ext}] = \sum_i \langle \phi_i | \frac{p^2}{2m} + v_{ext} | \phi_i \rangle + \frac{1}{2} \sum_{ij} \langle \phi_i \phi_j | \frac{e^2}{r_{12}} | \phi_i \phi_j \rangle + E_{xc}[n]$$

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:

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

Kohn-Sham equation

- $v_{coulomb}$ is Hartree Coulomb interaction potential, same as HF
- v_{xc} is defined as:

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

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

- Similar to HF, exact GS energy is:

$$E_{GS} = \sum_i \varepsilon_i - \frac{1}{2} \sum_{ij} \langle \phi_i \phi_j | \frac{e^2}{r_{12}} | \phi_i \phi_j \rangle + E_{xc}[n] - \int v_{xc}(\vec{r})\, n(\vec{r})\, d^3r$$

↑ "Double counting" of Hartree potential

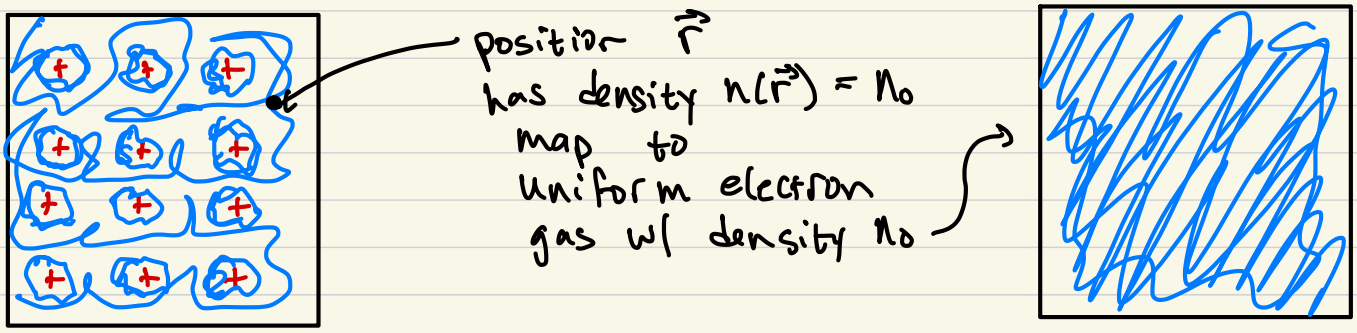
Not zero since v_{xc} is defined by functional derivative WRT n

- 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 progess 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"



- $E_{xc}^{LDA}[n] = \int \varepsilon_{xc}[n(\vec{r})]\, n(\vec{r})\, d^3r$

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

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

- Total energy is thus!

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

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

- See Ceperley and Alder Phys. Rev. Lett. 45, 566 (1980) or Fig. 6 in Sec. IV. 7 in G and P

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 wavefunction with a single Slater determinant made up of single-particle orbitals which are solutions to:

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

- 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:

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

- 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!