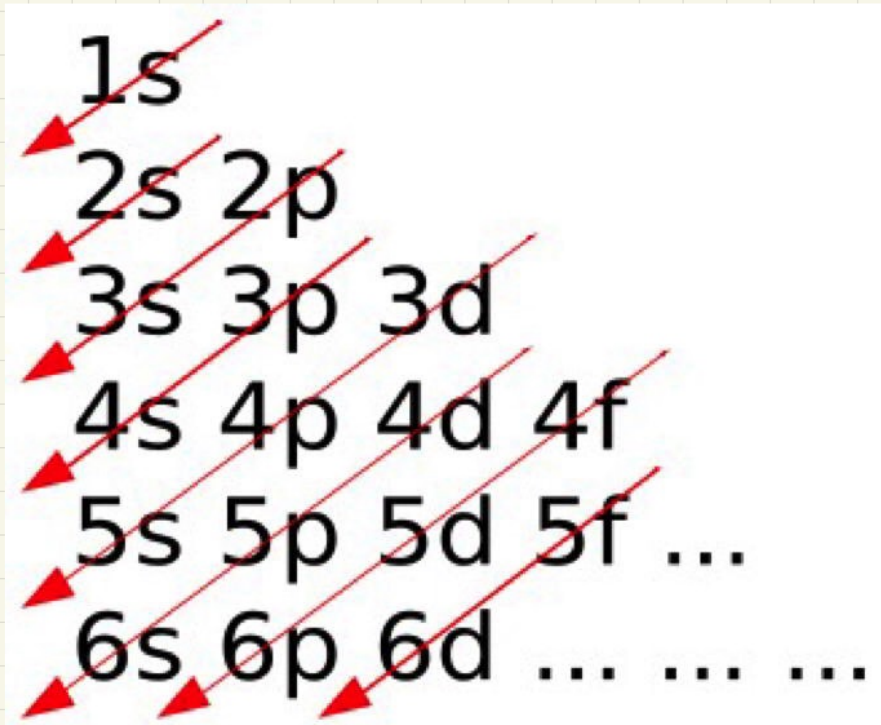


there are $(2s+1) \times (2l+1) = 4l+2$ degenerate states labeled by m and σ ; this group of orbitals is called a **shell**. Filling lower $n+l$ states first in the periodic table is



Filled shell atoms:

1s	² He	5s	³⁸ Sr
2s	⁴ Be	4d	⁴⁸ Cd
2p	¹⁰ Ne	5p	⁵⁴ Xe
3s	¹² Mg	6s	⁵⁶ Ba
3p	¹⁸ Ar	4f	⁷⁰ Yb
4s	²⁰ Ca	5d	⁸⁰ Hg
3d	³⁰ Zn	6p	⁸⁶ Rn
4p	³⁶ Kr	7s	⁸⁸ Ra
		5f/6d	¹⁰² No

known as the **Aufbau principle** (Aufbau (Ger.) = "construction").

Lecture 8 (Jan. 28): HF theory of the electron gas

The jellium model of the electron gas describes N electrons moving in a uniform neutralizing smeared ionic background. Since the system is translationally invariant, the HF single particle states must be plane waves: $\varphi_{\vec{k}}(\vec{x}) = V^{-1/2} e^{i\vec{k}\cdot\vec{x}}$.

The HF energies are

$$\varepsilon(\vec{k}) = \frac{\hbar^2 \vec{k}^2}{2m} - \int \frac{d^3 k'}{(2\pi)^3} \frac{4\pi e^2}{|\vec{k}-\vec{k}'|^2} \Theta(k_F - k') \equiv \varepsilon_0(\vec{k}) + \sum(\vec{k})$$

$\hbar^2 \vec{k}^2 / 2m$ "self-energy"
 \downarrow

\swarrow Hartree term cancelled by neutralizing background

The electron self-energy is computed to be

$$\Sigma(\mathbf{k}) = \frac{e^2 k_F}{2\pi} \left(\frac{k^2 - k_F^2}{k k_F} \ln \left| \frac{k + k_F}{k - k_F} \right| - 2 \right)$$

Expanding about $k = k_F$, we write $\mathbf{k} = (k_F + q) \hat{n}$, whence

$$\varepsilon(k_F + q) = \varepsilon_F + \frac{\hbar^2 k_F}{m} q + \frac{e^2}{\pi} q \ln \left| \frac{2k_F}{q} \right| + \mathcal{O}(q^2)$$

where $\varepsilon_F = \frac{\hbar^2 k_F^2}{2m} - \frac{e^2 k_F}{\pi}$ is the Fermi energy within

HF theory. The velocity in the vicinity of k_F is

$$v(q) = \frac{1}{\hbar} \frac{\partial \varepsilon(k_F + q)}{\partial q} = \frac{\hbar k_F}{m} + \frac{e^2}{\pi \hbar} \left(\ln \left| \frac{2k_F}{q} \right| - 1 \right)$$

which is logarithmically divergent as $q \rightarrow 0$. The reason for this is that the HF many-body WF does not incorporate electron screening. More on this later! The total kinetic energy per particle is

$$\frac{T}{N} = \frac{1}{N} \times 2 \sum_{|\mathbf{k}| < k_F} \varepsilon_0(\mathbf{k}) = \frac{2}{n} \int \frac{d^3 k}{(2\pi)^3} \frac{\hbar^2 k^2}{2m} \Theta(k_F - k) = \frac{3\hbar^2 k_F^2}{10m}$$

The total potential energy comes from four contributions:

(i) self-interaction of the neutralizing background, (ii) the interaction energy of the neutralizing background with the electron gas, (iii) the Hartree energy of the electron gas,

and (iv) the exchange (Fock) energy of the electron gas. The first three terms sum to zero, leaving

$$\frac{E_x}{N} = \frac{1}{2N} \times 2 \sum_{\substack{\mathbf{k} \\ |\mathbf{k}| < k_F}} \sum (\frac{\hbar}{k}) = \frac{1}{n} \int \frac{d^3k}{(2\pi)^3} \sum (\frac{\hbar}{k}) \Theta(k_F - k) = -\frac{3e^2 k_F}{4\pi}$$

It's convenient to define the dimensionless length r_s by

$$\frac{4}{3} \pi (r_s a_B)^3 n = 1$$

where $a_B = \hbar^2 / me^2 = 0.529 \text{ \AA}$ is the Bohr radius. Note

$$r_s = \left(\frac{3}{4\pi}\right)^{1/3} a_B^{-1} n^{-1/3}, \quad k_F = \left(\frac{9\pi}{4}\right)^{1/3} a_B^{-1} r_s^{-1}$$

Then we have

$$\frac{T}{N} = \frac{3}{5} \left(\frac{9\pi}{4}\right)^{2/3} \frac{e^2}{2a_B} \cdot \frac{1}{r_s^2} \approx \frac{2.21}{r_s^2} \text{ Ryd}$$

$$\frac{E_x}{N} = -\frac{3}{2\pi} \left(\frac{9\pi}{4}\right)^{1/3} \frac{e^2}{2a_B} \cdot \frac{1}{r_s} \approx -\frac{0.916}{r_s} \text{ Ryd}$$

We see that interaction contributions to the total energy dominate when r_s is large, where the density n is small. This is because the kinetic energy term involves two gradients, scaling as L^{-2} , while the Coulomb interaction scales as L^{-1} . Short-ranged interactions dominate at large densities.

Density functional theory

Recall that the many-electron Hamiltonian is $\hat{H} = \hat{T} + \hat{V} + \hat{U}$.

For any two systems of electrons, the \hat{T} and \hat{U} terms are the same, respectively. What distinguishes the electronic energy spectra in La_2CuO_4 from that of Pb or even styrofoam is the \hat{V} term. Recall

$$\begin{aligned}\hat{V} &= \sum_i v^{\text{ext}}(\vec{r}_i) \cong \sum_{\alpha, \beta} \langle \alpha | \hat{v}^{\text{ext}} | \beta \rangle \psi_{\alpha}^{\dagger} \psi_{\beta} \\ &= \int d^3x v^{\text{ext}}(\vec{x}) \sum_{\sigma} \psi_{\sigma}^{\dagger}(\vec{x}) \psi_{\sigma}(\vec{x})\end{aligned}$$

It's the ionic potential $v^{\text{ext}}(\vec{r})$ which distinguishes one material from another. The one-body number density of electrons of spin polarization σ is given by

$$\begin{aligned}n_{\sigma}(\vec{x}) &= \langle \Psi | \psi_{\sigma}^{\dagger}(\vec{x}) \psi_{\sigma}(\vec{x}) | \Psi \rangle \\ &= N \sum_{\sigma_2} \cdots \sum_{\sigma_N} \int d^2x_2 \cdots \int d^2x_N |\Psi_{\sigma\sigma_2\cdots\sigma_N}(\vec{x}, \vec{x}_2, \dots, \vec{x}_N)|^2\end{aligned}$$

We call $\hat{n}_{\sigma}(\vec{x}) = \psi_{\sigma}^{\dagger}(\vec{x}) \psi_{\sigma}(\vec{x})$ the one-body density operator for electrons of spin polarization σ . Then $\hat{n}(\vec{x}) = \sum_{\sigma} \hat{n}_{\sigma}(\vec{x})$ is the total one-body density operator. We call $n_{\sigma}(\vec{x}) = \langle \hat{n}_{\sigma}(\vec{x}) \rangle$ and $n(\vec{x}) = \langle \hat{n}(\vec{x}) \rangle$ the corresponding expectation values in a particular ground state or thermal ensemble.

Remarkably, it turns out that the entire ground state wavefunction $\Psi_{\sigma_1 \cdots \sigma_N}(\vec{x}_1, \dots, \vec{x}_N)$ is in fact a functional

of the one-body density $n(\vec{x})$. This seems completely crazy! The many-body WF is a function of $N = \mathcal{O}(10^{23})$ positions, while $n(\vec{x})$ is a function of just one. Still, it is true!

Hohenberg - Kohn theorems:

- 1) The ground state energy of a many-electron system is a functional of the total electron density $n(\vec{x})$.
- 2) The ground state energy may be expressed as a functional of the density, $E[n(\vec{x})]$, such that minimizing $E[n(\vec{x})]$ with respect to $n(\vec{x})$ yields the true ground state density.

Proofs:

1) This is a statement that $n(\vec{x})$ uniquely determines $|\Psi\rangle$.

The proof is quite simple. Let $|\Psi\rangle$ and $|\Psi'\rangle$ be the ground states corresponding to $v_{\text{ext}}(\vec{x})$ and $v'_{\text{ext}}(\vec{x})$. The respective Hamiltonians are $\hat{H} = \hat{T} + \hat{V} + \hat{U}$ and $\hat{H}' = \hat{T} + \hat{V}' + \hat{U}$. Regarding $|\Psi\rangle$ as a variational ground state for H' , we have

$$\langle \Psi' | H' | \Psi' \rangle < \langle \Psi | H' | \Psi \rangle = \langle \Psi | H | \Psi \rangle + \langle \Psi | (V' - V) | \Psi \rangle$$

where $\hat{V} = \int d^3x \hat{n}(\vec{x}) v_{\text{ext}}(\vec{x})$ and $\hat{V}' = \int d^3x \hat{n}(\vec{x}) v'_{\text{ext}}(\vec{x})$

So we conclude that $E' < E + \langle \Psi | (V' - V) | \Psi \rangle$. But exactly the same reasoning may be deployed, mutatis

mutandis, to show $E < E' + \langle \Psi' | (V - V') | \Psi' \rangle$ (i.e. switch primed and unprimed quantities). Adding these inequalities,

$$0 < \langle \Psi | (V' - V) | \Psi \rangle - \langle \Psi' | (V' - V) | \Psi' \rangle \\ = \int d^3x (n(\vec{x}) - n'(\vec{x})) (v'_{\text{ext}}(\vec{x}) - v_{\text{ext}}(\vec{x}))$$

Thus if $n(\vec{x}) = n'(\vec{x})$ we arrive at a contradiction: $0 < 0$. We conclude that if $v_{\text{ext}}(\vec{x}) \neq v'_{\text{ext}}(\vec{x})$, then $n(\vec{x}) \neq n'(\vec{x})$.

2) The second HK theorem establishes a variational principle. Define the functional

$$E[n] = \underbrace{\langle \Psi[n] | \hat{T} + \hat{U} | \Psi[n] \rangle}_{E_{\text{jel}}[n]} + \int d^3x v_{\text{ext}}(\vec{x}) n(\vec{x})$$

Here $E_{\text{jel}}[n]$ is the energy functional for jellium, for which $v_{\text{ext}} = 0$. Note $|\Psi[n]\rangle$ here is the ground state WF of the electron gas with density $n(\vec{x})$, corresponding to some $v_{\text{ext}}(\vec{x})$. The presumption $n(\vec{r}) \rightarrow |\Psi[n]\rangle, v_{\text{ext}}(\vec{r})$ is highly nontrivial, and indeed it is false for noninteracting electrons ($e=0$): no density $n(\vec{x})$ which vanishes at any given location can correspond to an exact ground state in any external potential $v_{\text{ext}}(\vec{r})$ due to the Perron-Frobenius "no nodes theorem". Functions $n(\vec{x})$ which do correspond to the ground state density for an interacting electron

system in an external potential $v_{\text{ext}}(\vec{r})$ are called V -representable. But this is just giving a fancy name to what we don't really understand. What is the domain of V -representable functions $n(\vec{x})$? Nobody knows!

We redefine the two-body interaction \hat{U} as

$$\hat{U} = \frac{1}{2} \int d^d x \int d^d x' (\hat{n}(\vec{x}) - n_0) \frac{e^2}{|\vec{x} - \vec{x}'|} (\hat{n}(\vec{x}') - n_0)$$

where there is a uniform neutralizing background of charge density $\rho_{\text{back}} = +en_0$. Total charge neutrality then requires

$$\lim_{N \rightarrow \infty} \frac{1}{N} \int d^d x (n(\vec{x}) - n_0) = 0$$

If this condition is violated, the energy per particle diverges. Finally, if $n'(\vec{x}) \neq n(\vec{x})$, then

$$E[n'] = \langle \Psi[n'] | \hat{H} | \Psi[n'] \rangle > E[n]$$

which follows from treating $|\Psi[n']\rangle$ as a variational gs WF for a Hamiltonian whose gs density is $n(\vec{x})$. So we conclude $E[n]$ is minimized when $n(\vec{x})$ corresponds to the true ground state density for external potential $v_{\text{ext}}(\vec{x})$.

Kohn-Sham equations:

For the electron gas, $E_{\text{el}}[n]$ is a universal functional,

given by

$$E_{\text{Jel}}[n] = \min_{|\Psi\rangle \rightarrow n(\vec{x})} \langle \Psi[n] | \hat{T} + \hat{U} | \Psi[n] \rangle$$

where minimization is wrt all totally antisymmetric N -body WFs which yield a one-body density $n(\vec{x})$.

For noninteracting systems, the ground state is a Slater determinant $|\Psi_S[n]\rangle$. Define the functional

$$T_S[n] = \min_{|\Psi_S\rangle \rightarrow n(\vec{x})} \langle \Psi_S | \hat{T} | \Psi_S \rangle$$

where $|\Psi_S\rangle$ is an N -particle Slater determinant, with

$$\langle \vec{x}_1, \sigma_1, \dots, \vec{x}_N, \sigma_N | \Psi_S \rangle = \frac{1}{\sqrt{N!}} \det \{ \varphi_{\alpha_i}(\vec{x}_j, \sigma_j) \}$$

We can write

$$n(\vec{x}) = \sum_{\alpha} \sum_{\sigma} n_{\alpha} |\varphi_{\alpha}(\vec{x}, \sigma)|^2$$

with $n_{\alpha} \in \{0, 1\}$ and $N = \sum_{\alpha} n_{\alpha}$. Then

$$T_S[n] = -\frac{\hbar^2}{2m} \sum_{\alpha} n_{\alpha} \langle \varphi_{\alpha} | \nabla^2 | \varphi_{\alpha} \rangle = \frac{\hbar^2}{2m} \sum_{\alpha} n_{\alpha} \langle \nabla \varphi_{\alpha} | \nabla \varphi_{\alpha} \rangle$$

We now define the exchange-correlation functional $E_{xc}[n]$:

$$E_{\text{Jel}}[n] = T_S[n] + E_H[n] + E_{xc}[n]$$

where $E_H[n]$ is the Hartree functional,

$$E_H[n] = \frac{1}{2} \int d^3x \int d^3x' (n(\vec{x}) - n_0) \frac{e^2}{|\vec{x} - \vec{x}'|} (n(\vec{x}') - n_0)$$

Note that :

- $E_{\text{jel}}[n]$ is universal, but unknown
- $T_s[n]$ is defined above
- $E_H[n]$ is defined above

Thus our ignorance of $E_{\text{jel}}[n]$ has been transferred to the exchange-correlation functional $E_{\text{xc}}[n]$. We may extremize by varying wrt the $\{\varphi_\alpha^*(\vec{x}, \sigma)\}$ with $n_\alpha = 1$. This results in the Kohn-Sham equations:

$$\left\{ -\frac{\hbar^2}{2m} \vec{\nabla}^2 + v_{\text{ext}}(\vec{x}) + v_H(\vec{x}) + v_{\text{xc}}(\vec{x}) \right\} \varphi_\alpha(\vec{x}, \sigma) = \varepsilon_\alpha \varphi_\alpha(\vec{x}, \sigma)$$

where $n_\alpha = 1$ and $v_{\text{ext}}(\vec{x} \rightarrow 0) \equiv 0$

$$v_H(\vec{x}) = \frac{\delta E_H[n]}{\delta n(\vec{x})} = \int d^3x' \frac{e^2}{|\vec{x} - \vec{x}'|} (n(\vec{x}') - n_0)$$

and where

$$v_{\text{xc}}(\vec{x}) = \frac{\delta E_{\text{xc}}[n]}{\delta n(\vec{x})}$$

Note we have set $\delta F = 0$ where

$$F[n] = T_s[n] + \langle \Psi_S[n] | \hat{V} | \Psi_S[n] \rangle + E_H[n] + E_{\text{xc}}[n]$$

and we've used the chain rule,

$$\frac{\delta F[n]}{\delta \varphi^*(\vec{x}, \sigma)} = \frac{\delta F[n]}{\delta n(\vec{x})} \cdot \frac{\delta n(\vec{x})}{\delta \varphi^*(\vec{x}, \sigma)} = \frac{\delta F[n]}{\delta n(\vec{x})} \varphi_{\alpha}(\vec{x}, \sigma) \quad (n_{\alpha} = 1)$$

Important difference vis-a-vis HF theory: $v_{xc}(\vec{x})$ is local, unlike $v^F(\vec{x}, \vec{x}')$. Some caveats:

- the KS orbitals $\varphi_{\alpha}(\vec{x}, \sigma)$ themselves have no obvious physical significance
- still they are often interpreted as WFs for Bloch bands
- the KS eigenvalues ϵ_{α} do not in general correspond to physical excitation energies of the system
- the Slater determinant $\det \{ \varphi_{\alpha_i}(\vec{x}_j, \sigma_j) \}$ is not in general a good approximation to the actual gs WF; the HF WF is often better!
- As $N \rightarrow \infty$, for gapless systems, the highest eigenvalue ϵ_N corresponds to the Fermi energy.

The problem now focuses on finding the best approximation to the unknown functional $E_{xc}[n]$.

Local density approximation (LDA):

Write $E_{xc}[n] = \int d^3x n(\vec{x}) \epsilon_{xc}(n(\vec{x}))$. Then

$$U_{xc}(\vec{x}) = \mu_{xc}(n(\vec{x})) = \frac{\delta E_{xc}[n]}{\delta n(\vec{x})} = \epsilon_{xc}(n(\vec{x})) + n(\vec{x}) \left. \frac{\partial \epsilon_{xc}(n)}{\partial n} \right|_{n(\vec{x})}$$

In the HF approximation for $d=3$, $\frac{E_x}{V} = -\frac{3e^2}{4\pi} n k_F \propto n^{4/3}$
and thus

$$\mu_{xc}(n) = \frac{4}{3} \epsilon_{xc}(n) = -\frac{e^2}{\pi} k_F(n)$$

where $k_F(n) = (3\pi^2 n)^{1/3}$.

Gradient expansions:

Expanding about the jellium density n_0 , we have

$$E_{xc}^{GEA}[n_0 + \delta n] = \frac{1}{2} \int d^3x \left\{ A(n_0) (\delta n(\vec{x}))^2 + B(n_0) (\vec{\nabla} \delta n(\vec{x}))^2 + \dots \right\}$$

GEA = Gradient Expansion Approximation

SGEA = Spin Gradient Expansion Approximation

$$E_{xc}^{SGEA}[n_{0\uparrow} + \delta n_{\uparrow}, n_{0\downarrow} + \delta n_{\downarrow}] = \frac{1}{2} \int d^3x \left\{ A_{\sigma\sigma'}(n_{0\sigma}, n_{0\sigma'}) \delta n_{\sigma} \delta n_{\sigma'} + B_{\sigma\sigma'}(n_{0\sigma}, n_{0\sigma'}) \vec{\nabla} \delta n_{\sigma} \cdot \vec{\nabla} \delta n_{\sigma'} + \dots \right\}$$

In real materials applications, LDA is often better than GEA.

Applications of DFT (see Girvin and Yang):

- **structural determination**: the external potential is

$$v_{\text{ext}}(\vec{x}) = - \sum_l \frac{z_l e^2}{|\vec{x} - \vec{R}_l|}$$

The total energy is

$$E_{\text{tot}}[\{\vec{R}_l\}, n] = E_{\text{jel}}[n] + \int d^3x n(\vec{x}) v_{\text{ext}}(\vec{x}) + \sum_{l \neq l'} \frac{z_l z_{l'} e^2}{|\vec{R}_l - \vec{R}_{l'}|}$$

Given $\{\vec{R}_l\}$, extremize $E_{\text{tot}}[\{\vec{R}_l\}, n(\vec{x})]$ wrt $n(\vec{x})$ to obtain an energy $\Phi(\{\vec{R}_l\})$. Then minimize wrt nuclear positions $\{\vec{R}_l\}$. Typically use pbc, large xtal unit cell.

- **cohesive energy**: $E_{\text{coh}} = E_{\text{crystal}} - E_{\text{atomic}}$ is the crystalline binding energy (when $E_{\text{coh}} < 0$)
- **elastic constants**: vary $\Phi(\{\vec{R}_l\})$ wrt nuclear positions
- **phase diagram under pressure**: At $T=0$, $G = H = E + pV$
Including pV term, obtain G at finite pressure.

Lecture 9 (Feb. 1): Linear response theory

Response functions of jellium system to an external

potential: expand $E_{\text{jel}}[n_0 + \delta n]$ about uniform density n_0 :