

## Chap 9 Electron-electron interactions

- e-e interaction and Pauli exclusion principle (chap 17)
- Hartree approximation
- Hartree-Fock approximation
  - Exchange-correlation hole
- Density functional theory

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## What's missing with the non-interacting electrons?

- exchange effect
- screening effect
- normalization of band gap (and band structure, FS)
- quasiparticle, collective excitation
- superconductivity
- ...

## Beyond non-interacting electron

$$H = \sum_{i=1}^N \left( \frac{p_i^2}{2m} + U_{ion}(\vec{r}_i) \right) + \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} V_{ee}(\vec{r}_i - \vec{r}_j),$$

$$V_{ee}(\vec{r}_i - \vec{r}_j) = \frac{e^2}{|\vec{r}_i - \vec{r}_j|},$$

$$H\Psi(\vec{r}_1, \vec{r}_2, \dots) = E\Psi(\vec{r}_1, \vec{r}_2, \dots)$$

This is a differential eq. with  $N=10^{23}$  degrees of freedom.  
We need approximations.

## Hartree approximation (1928):

$$\text{assume } \Psi(\vec{r}_1, \vec{r}_2, \dots) = \psi_1(\vec{r}_1)\psi_2(\vec{r}_2)\cdots\psi_N(\vec{r}_N)$$

No quantum correlation  
~ classical particles

$$H\Psi(\vec{r}_1, \vec{r}_2, \dots) = E\Psi(\vec{r}_1, \vec{r}_2, \dots)$$

$$\Rightarrow \left[ -\frac{\hbar^2}{2m} \nabla^2 + U_{ion}(\vec{r}) \right] \psi_i(\vec{r}) + \left[ \underbrace{e^2 \int d^3r' \frac{\sum_j |\psi_j(\vec{r}')|^2}{|\vec{r} - \vec{r}'|}}_j \right] \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r})$$

Hartree (or direct) potential  $V_{ee}^H(\vec{r})$

Each electron moves in the potential from all the other electrons,

- Need to be solved self-consistently (by iteration).
- Self-consistency doesn't mean the result is correct.

What's wrong with the HA?

- The manybody wave function violates the Pauli principle
- The calculated total energy is positive (means the electron gas is unstable)

## Self-consistent Hartree approximation

1. choose initial  $\{\psi_i\}$



2. construct  $n(\vec{r}) = \sum_i |\psi_i(\vec{r})|^2 \rightarrow V_{ee}^H(\vec{r}) = e^2 \int d^3r' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|}$



3. solve  $\left[ -\frac{\hbar^2}{2m} \nabla^2 + U_{ion}(\vec{r}) + V_{ee}^H(\vec{r}) \right] \psi'_i(\vec{r}) = \epsilon_i \psi'_i(\vec{r})$



4. construct  $n'(\vec{r}) = \sum_i |\psi'_i(\vec{r})|^2$



5. if  $|n'(\vec{r}) - n(\vec{r})| < \delta$ , then STOP.

else let  $\psi_i(\vec{r}) = \psi'_i(\vec{r})$ , GOTO 2



## Hartree-Fock approximation (1930):

- A brief review of variational principle (single particle version)

$$H\psi(\vec{r}) = \varepsilon\psi(\vec{r})$$

the ground state can be obtained by minimizing  $\langle \psi | H | \psi \rangle$ ,  
under the constraint  $\langle \psi | \psi \rangle = 1$

i.e. 
$$\frac{\delta}{\delta \psi^*(\vec{r})} \left( \langle \psi | H | \psi \rangle - \lambda (\langle \psi | \psi \rangle - 1) \right) = 0 \quad (\lambda \rightarrow \varepsilon)$$

- Hartree-Fock approximation

assume 
$$\Psi(\vec{r}_1, s_1, \vec{r}_2, s_2, \dots) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{r}_1, s_1) & \psi_1(\vec{r}_2, s_2) & \cdots & \psi_1(\vec{r}_N, s_N) \\ \psi_2(\vec{r}_1, s_1) & \psi_2(\vec{r}_2, s_2) & \cdots & \psi_2(\vec{r}_N, s_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(\vec{r}_1, s_1) & \psi_N(\vec{r}_2, s_2) & \cdots & \psi_N(\vec{r}_N, s_N) \end{vmatrix}$$

$$\Rightarrow \langle \Psi | H | \Psi \rangle = \sum_{i=1}^N \langle \psi_i | \frac{p^2}{2m} + U(\vec{r}) | \psi_i \rangle + \frac{1}{2} \sum_{i,j=1(i \neq j)}^N \langle \psi_i | \langle \psi_j | \frac{e^2}{|\vec{r} - \vec{r}'|} | \psi_i \rangle | \psi_j \rangle \quad \text{Hartree energy}$$

$$- \frac{1}{2} \sum_{i,j=1(i \neq j)}^N \langle \psi_i | \langle \psi_j | \frac{e^2}{|\vec{r} - \vec{r}'|} | \psi_j \rangle | \psi_i \rangle \quad \text{Fock energy}$$

## Variational principle

$$\frac{\delta}{\delta \psi_\ell^*(\vec{r}, s)} \left( \langle \Psi | H | \Psi \rangle - \sum_{i=1}^N \lambda_i (\langle \psi_i | \psi_i \rangle - 1) \right) = 0$$

See hand-written note

$$\Rightarrow \left[ -\frac{\hbar^2}{2m} \nabla^2 + U_{ion}(\vec{r}) + V_{ee}^H(\vec{r}) \right] \psi_\ell(\vec{r}, s) + \sum_{s'} \int d^3 r' v_{ee}^F(\vec{r}, s; \vec{r}', s') \psi_\ell(\vec{r}', s') = \varepsilon_\ell \psi_\ell(\vec{r}, s)$$

$$V_{ee}^H(\vec{r}) = e^2 \int d^3 r' \frac{\sum_i |\psi_i(\vec{r}', s')|^2}{|\vec{r} - \vec{r}'|} = e^2 \int d^3 r' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} \quad \text{Hartree (or direct) potential}$$

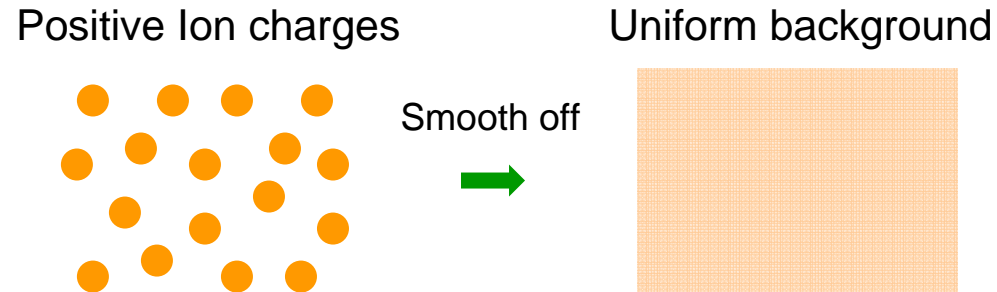
Sum over filled states only

$$v_{ee}^F(\vec{r}, s; \vec{r}', s') = -e^2 \frac{\sum_i \psi_i^*(\vec{r}', s') \psi_i(\vec{r}, s)}{|\vec{r} - \vec{r}'|} \delta_{s, s'} \quad \text{Fock (or exchange) potential}$$

- The exchange potential exists only between electrons with parallel spins.
- The exchange potential is non-local! This makes the HFA much harder to calculate!
- Still need self-consistency.
- Again, no guarantee on the correctness (even qualitatively) of the self-consistent result!

## Hartree-Fock theory of uniform electron gas

- The jellium approximation



- Below we show that plane waves are sol'n's of HFA

assume  $\psi_k(\vec{r}, s) = \frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt{V}} \chi_s \rightarrow V_{ee}^H = -e \int d^3 r' \frac{(-en_0)}{|\vec{r} - \vec{r}'|}$

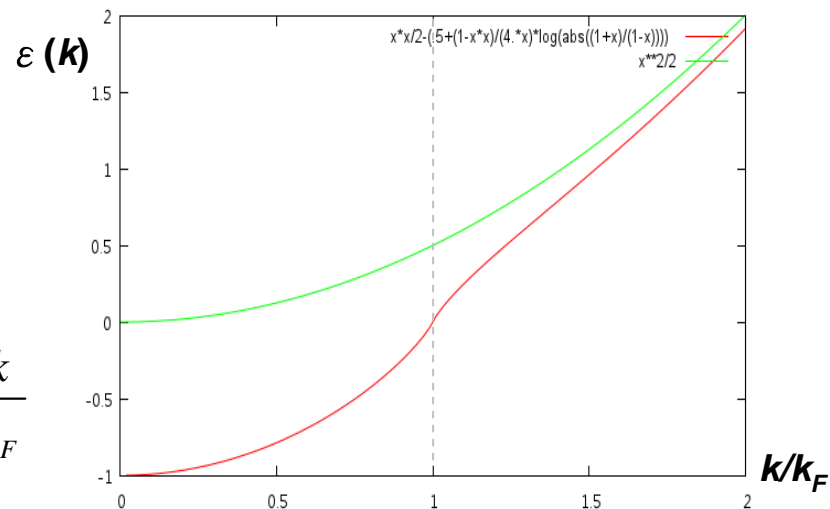
This cancels with  $U_{ion}(\vec{r}) = -e \int d^3 r' \frac{(+en_0)}{|\vec{r} - \vec{r}'|}$

$$\begin{aligned} \sum_{s'} \int d^3 r' v_{ee}^F(\vec{r}, s; \vec{r}', s') \psi_k(\vec{r}', s') &= -\frac{e^2}{V} \int d^3 r' \frac{\sum_{k', s'} e^{i\vec{k}'\cdot(\vec{r}-\vec{r}')} \delta_{s, s'}}{|\vec{r} - \vec{r}'|} \frac{e^{i\vec{k}\cdot\vec{r}'}}{\sqrt{V}} \chi_{s'} \\ &= -\frac{4\pi e^2}{V} \sum_{k'} \frac{1}{|\vec{k} - \vec{k}'|^2} \psi_k(\vec{r}, s) \end{aligned}$$

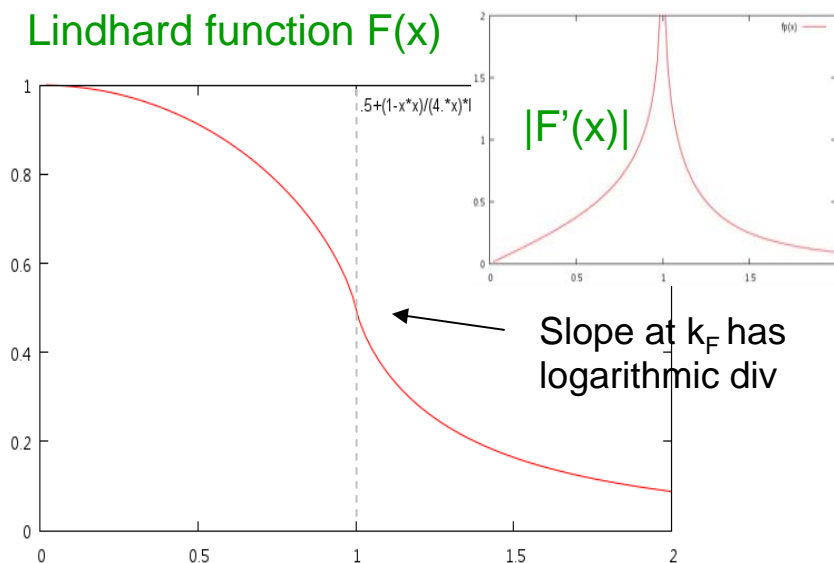
$$\Rightarrow \left( -\frac{\hbar^2}{2m} \nabla^2 - \frac{4\pi e^2}{V} \sum_{k' < k_F} \frac{1}{|\vec{k} - \vec{k}'|^2} \right) \psi_k(\vec{r}) = \varepsilon_k \psi_k(\vec{r})$$

∴ HF energy

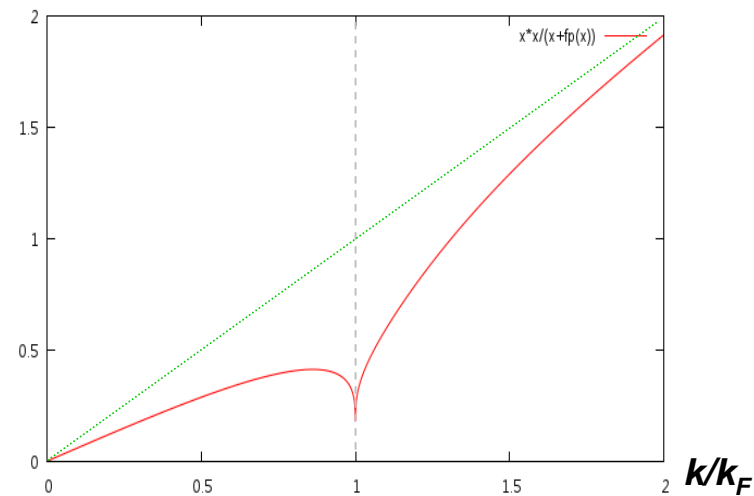
$$\begin{aligned} \varepsilon(\vec{k}) &= \frac{\hbar^2 k^2}{2m} - 4\pi e^2 \int_{k' < k_F} \frac{d^3 k'}{(2\pi)^3} \frac{1}{|\vec{k} - \vec{k}'|^2} \\ &= \frac{\hbar^2 k^2}{2m} - \frac{2e^2}{\pi} k_F \left[ \frac{1}{2} + \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right| \right], \quad x = \frac{k}{k_F} \end{aligned}$$



Lindhard function F(x)



“DOS” D(k(ε)) (arb. unit)





- If, when you remove one electron from an N-electron system, the other N-1 wave functions do not change, then  $|\varepsilon(k)|$  is the ionization energy (Koopman's theo. 1933).
- In reality, the other N-1 electrons would relax to screen the hole created by ionization. (called "final state effect", could be large.)
- Total energy of the electron gas (in the HFA)

Substrat double counting  
between  $k$  and  $k'$

$$\begin{aligned}
 E_{HF} &= \sum_{k < k_F} \left[ \varepsilon(\vec{k}) - \frac{1}{2} V_F(\vec{k}) \right] \\
 &= N \left( \frac{3}{5} \frac{\hbar^2 k_F^2}{2m} - \frac{3}{4} \frac{e^2 k_F}{\pi} \right) = N \left[ \frac{3}{5} \frac{\hbar^2}{2ma_0^2} (k_F a_0)^2 - \frac{3}{2\pi} \frac{e^2}{2a_0} k_F a_0 \right] \\
 \Rightarrow \frac{E_{HF}}{N} &= \frac{2.21}{r_s^2} - \frac{0.916}{r_s}, \quad \text{in which } \frac{4}{3} \pi (r_s a_0)^3 = n \\
 \left( r_s \text{ in } a_0 = \frac{\hbar^2}{me^2}, E \text{ in Ry} = \frac{e^2}{2a_0} \text{ or } \frac{\hbar^2}{2ma_0^2} \right)
 \end{aligned}$$

- More on the HF energy

$$\begin{aligned}
 E_{HF} &= \frac{1}{2} \sum_{\ell,s} \int d^3r V_{ee}^H(\vec{r}) |\psi_\ell(\vec{r},s)|^2 + \frac{1}{2} \sum_{\ell,s,s'} \int d^3r \int d^3r' v_{ee}^F(\vec{r},s;\vec{r}',s') \psi_\ell^*(\vec{r},s) \psi_\ell(\vec{r}',s') \\
 &= \frac{1}{2} \sum_{s,s'} e^2 \int d^3r d^3r' \frac{n_{s'}(\vec{r}') n_s(\vec{r})}{|\vec{r}-\vec{r}'|} - \frac{1}{2} \sum_{s,s'} e^2 \int d^3r \int d^3r' \frac{\sum_{i,\ell} \psi_i^*(\vec{r}',s') \psi_i(\vec{r},s) \psi_\ell^*(\vec{r},s) \psi_\ell(\vec{r}',s')}{|\vec{r}-\vec{r}'|} \delta_{ss'} \\
 &= \frac{1}{2} e^2 \int d^3r d^3r' \sum_{s,s'} \frac{n_{s'}(\vec{r}') n_s(\vec{r})}{|\vec{r}-\vec{r}'|} g_{ss'}^{HF}(\vec{r},\vec{r}')
 \end{aligned}$$

- Pair correlation function

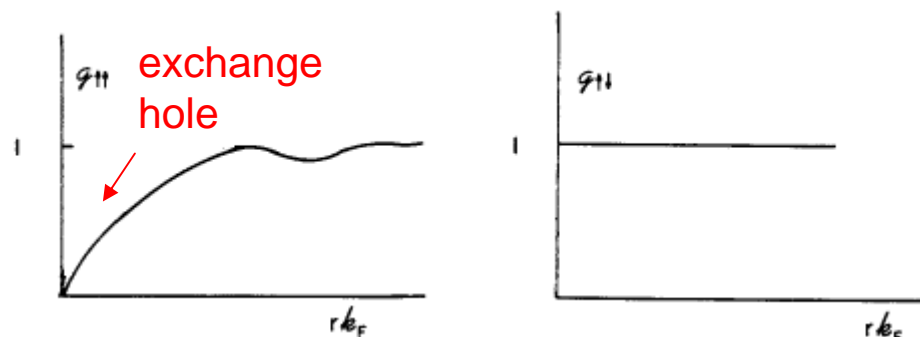
$$g_{ss'}^{HF}(\vec{r},\vec{r}') \equiv 1 - \frac{\left| \sum_i \psi_i^*(\vec{r}',s') \psi_i(\vec{r},s) \right|^2}{n_{s'}(\vec{r}') n_s(\vec{r})} \delta_{ss'}$$

The conditional probability to find a spin- $s'$  electron at  $r'$ ,  
when there is already a spin- $s$  electron at  $r$ .

- In the jellium model ( $n_s = N/2V$ ),

$$\begin{aligned}
 g_{ss'}^{HF}(\vec{r},\vec{r}') &\equiv 1 - \left| \frac{2}{N} \sum_{k < k_F} e^{i\vec{k} \cdot (\vec{r}-\vec{r}')} \right|^2 \delta_{ss'} \\
 \tilde{r} \equiv |\vec{r}-\vec{r}'|, \quad &= 1 - \left( 3 \frac{\sin k_F \tilde{r} - k_F \tilde{r} \cos k_F \tilde{r}}{k_F^3 \tilde{r}^3} \right)^2 \delta_{ss'}, \quad \text{or } 1 - \left( \frac{3}{k_F \tilde{r}} j_1(k_F \tilde{r}) \right)^2 \delta_{ss'}
 \end{aligned}$$

- Fock (exchange) potential keeps electrons **with the same spin** apart  
(This is purely a quantum statistical effect)



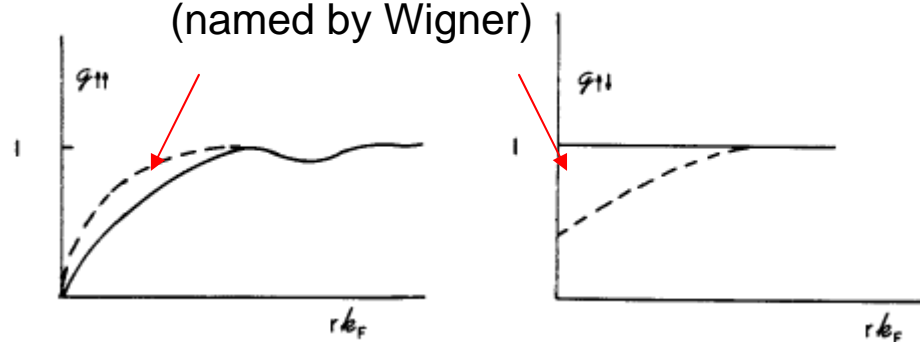
interaction of the electron with the “hole”:

$$\varepsilon_{X\ hole} = (-e) \int d^3r \frac{en_0 (1 - g_{\uparrow\uparrow}^{HF}(r))}{r} \times \frac{1}{2} = -\frac{3}{4} \frac{e^2 k_F}{\pi}$$

- Beyond HFA

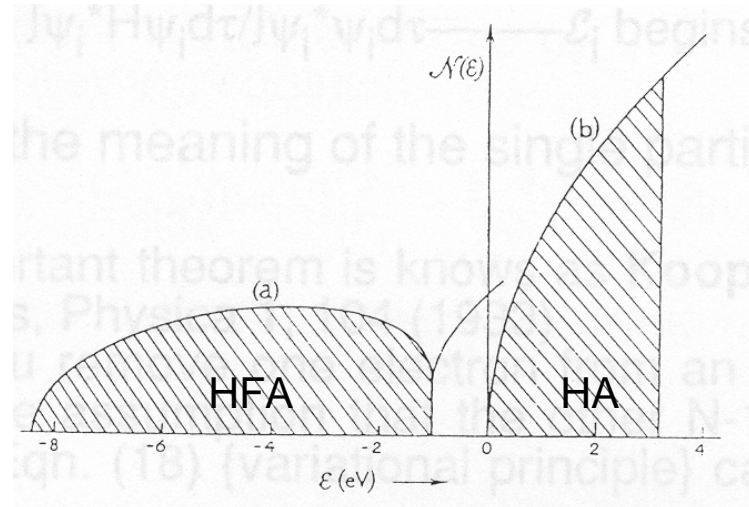
Now there is a hole even if the electrons have different spins!

**exchange-correlation (xc) hole**  
(named by Wigner)



could be non-spherical  
in real material

## DOS for an electron gas in HA and HFA



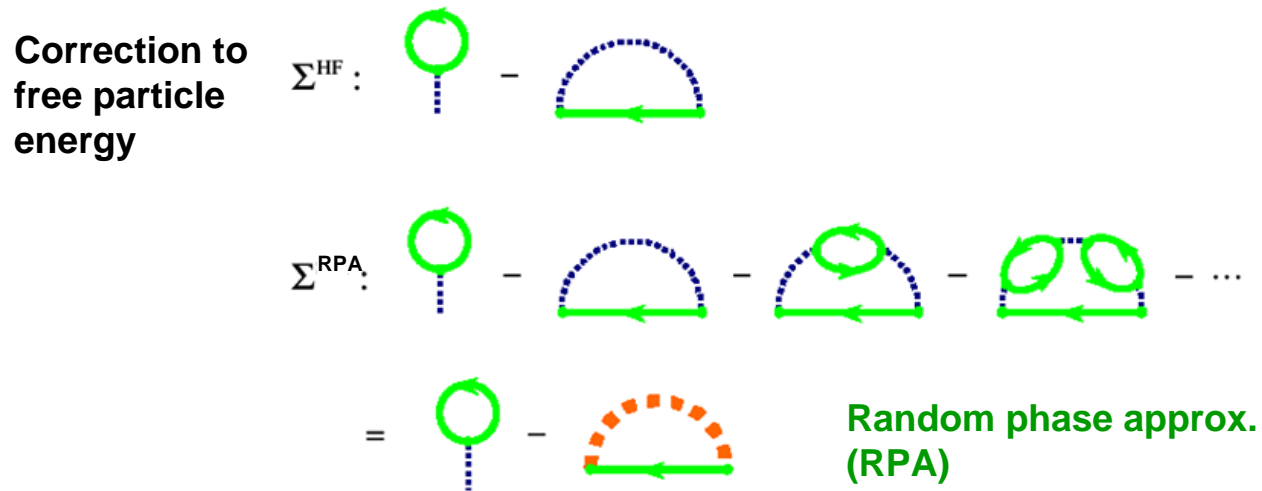
What's wrong with HFA?

- In the HFA, the DOS goes to zero at the Fermi energy. HFA gets the specific heat and the conductivity seriously wrong.
- The band width is 2.4 times too wide (compared to free e)
- The manybody wave function is not necessarily a single Slater determinant.

Beyond HFA:

- Green function method: diagrammatic perturbation expansion
- Density functional theory: inhomogeneous electron gas, beyond jellium
- Quantum Monte Carlo
- ...

## Green function method (diagrammatic perturbation expansion)



- The energy correction beyond HFA is called **correlation energy** (or **stupidity energy**).

$$E_C = E_{\text{EXACT}} - E_{\text{HF}}$$

- Gell-Mann+Bruckner's result (1957, for **high density** electron gas)

$$E/N = 2.21/r_S^2 + 0 - 0.916/r_S + 0.0622 \ln(r_S) - 0.096 + O(r_S)$$

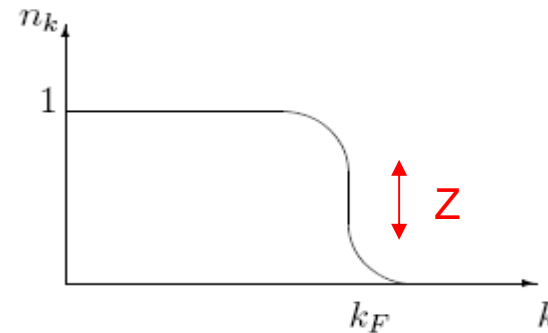
$$= E_K + E_H - E_F + E_C \quad (E \text{ in Ry, } r_S \text{ in } a_0)$$

- This is still under the jellium approximation.
- Good for  $r_S < 1$ , less accurate for electrons with low density (Usual metals,  $2 < r_S < 5$ )
- E. Wigner predicted that very low-density electron gas ( $r_S > 10?$ ) would spontaneously form a non-uniform phase (Wigner crystal)

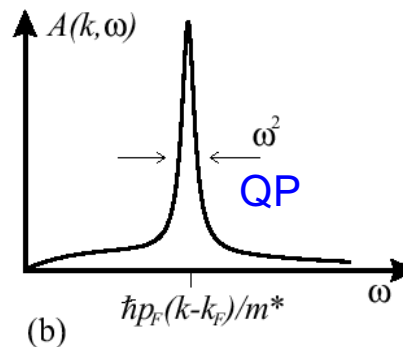
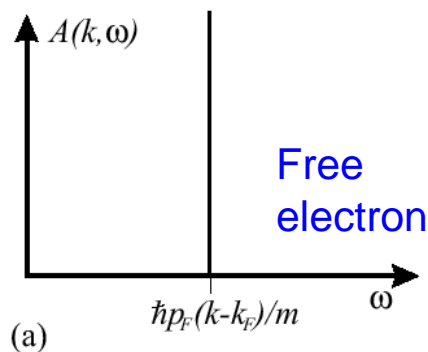
## Luttinger, Landau, and quasiparticles

- Modification of the Fermi sea due to e-e interaction ( $T=0$ )

Perturbation to all orders  
(if perturbation is valid)



- There is still a jump that defines the FS (Luttinger, 1960). Its magnitude  $Z (<1)$  is related to the effective mass of a QP.
- A quasiparticle (QP) = an electron “dressed” by other electrons.  
A strongly interacting electron gas = a weakly interacting gas of QPs. (Landau, 1956)
- It is a quasi-particle because, it has a finite life-time. Therefore, its spectral function has a finite width:



This peak sharpens as we get closer to the FS (longer lifetime)

**Inhomogeneous Electron Gas\***

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(Received 18 June 1964)

This paper deals with the ground state of an interacting electron gas in an external potential  $v(\mathbf{r})$ . It is proved that there exists a universal functional of the density,  $F[n(\mathbf{r})]$ , independent of  $v(\mathbf{r})$ , such that the expression  $E \equiv \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})]$  has as its minimum value the correct ground-state energy associated with  $v(\mathbf{r})$ . The functional  $F[n(\mathbf{r})]$  is then discussed for two situations: (1)  $n(\mathbf{r}) = n_0 + \tilde{n}(\mathbf{r})$ ,  $\tilde{n}/n_0 \ll 1$ , and (2)  $n(\mathbf{r}) = \varphi(\mathbf{r}/r_0)$  with  $\varphi$  arbitrary and  $r_0 \rightarrow \infty$ . In both cases  $F$  can be expressed entirely in terms of the correlation energy and linear and higher order electronic polarizabilities of a uniform electron gas. This approach also sheds some light on generalized Thomas-Fermi methods and their limitations. Some new extensions of these methods are presented.

Cited 8578 times (by 11/26/2011)

**Self-Consistent Equations Including Exchange and Correlation Effects\***

W. KOHN AND L. J. SHAM 沈吕九

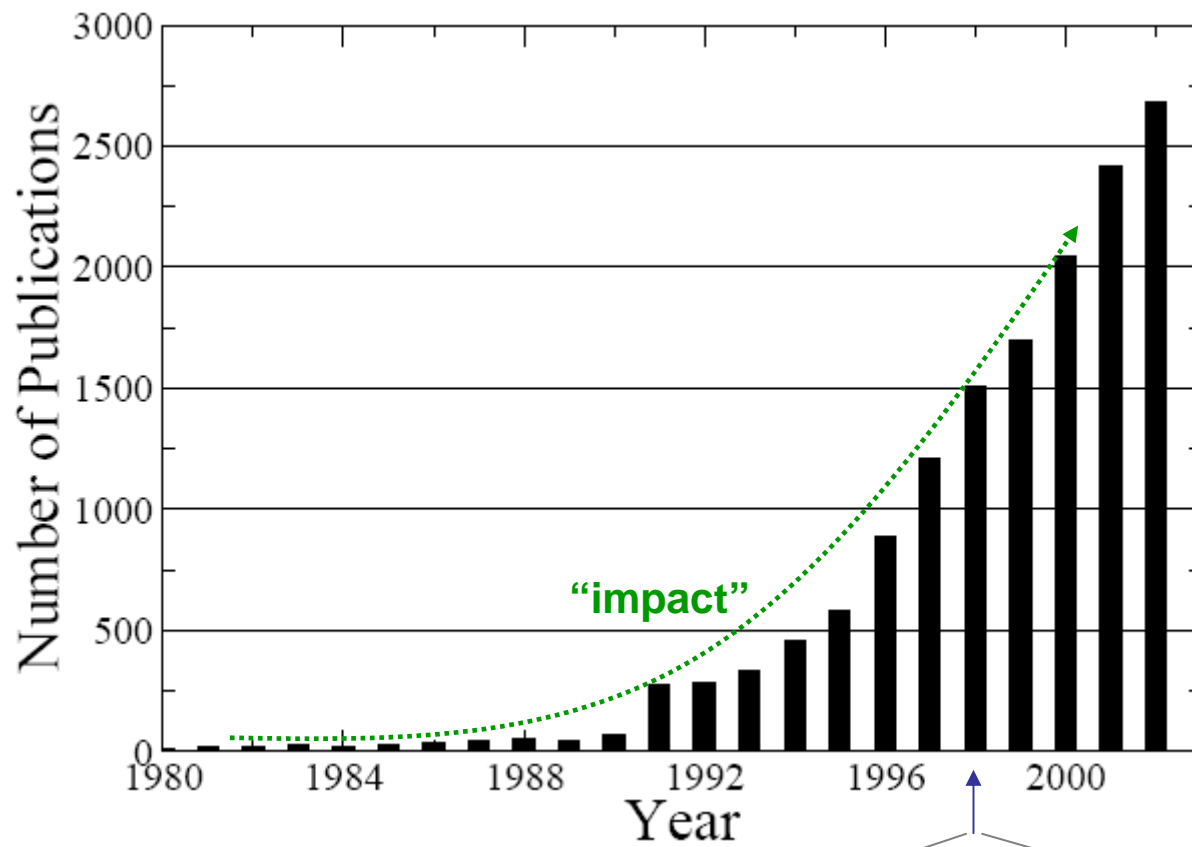
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(Received 21 June 1965)

From a theory of Hohenberg and Kohn, approximation methods for treating an inhomogeneous system of interacting electrons are developed. These methods are exact for systems of slowly varying or high density. For the ground state, they lead to self-consistent equations analogous to the Hartree and Hartree-Fock equations, respectively. In these equations the exchange and correlation portions of the chemical potential of a uniform electron gas appear as additional effective potentials. (The exchange portion of our effective potential differs from that due to Slater by a factor of  $\frac{2}{3}$ .) Electronic systems at finite temperatures and in magnetic fields are also treated by similar methods. An appendix deals with a further correction for systems with short-wavelength density oscillations.

Cited 18298 times (by 11/26/2011)

“density functional theory” appears in title or abstract



1964

“availability of computing power”





$$\left[ \sum_{i=1}^N \left( \frac{p_i^2}{2m} + U_{ion}(\vec{r}_i) \right) + \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} V_{ee}(\vec{r}_i - \vec{r}_j) \right] \Psi(\vec{r}_1, \vec{r}_2, \dots) = E \Psi(\vec{r}_1, \vec{r}_2, \dots)$$

Particle density  $n(\vec{r}) = N \int d^3 r_2 \int d^3 r_3 \dots \int d^3 r_N \Psi^*(\vec{r}, \vec{r}_2, \dots) \Psi(\vec{r}, \vec{r}_2, \dots)$

Usually:  $U_{ion} \rightarrow \Psi \rightarrow n$

DFT:  $n \rightarrow \Psi \rightarrow U_{ion}$

### The 1<sup>st</sup> Hohenberg-Kohn theorem

The potential  $U_{ion}$  is a unique functional of the **ground state** density  $n$ .

Pf: suppose  $U, U'$  give the same ground state density,  $n=n'$

$$E_G = \langle \Psi_G | H | \Psi_G \rangle; \quad E_G' = \langle \Psi_G' | H' | \Psi_G' \rangle$$

$$E_G' < \langle \Psi_G | H' | \Psi_G \rangle = \langle \Psi_G | H + U' - U | \Psi_G \rangle = E_G + \langle \Psi_G | U' - U | \Psi_G \rangle$$

$$\rightarrow E_G' < E_G + \int d^3 r n(\vec{r}) [U(\vec{r})' - U(\vec{r})]$$

same argument also gives

$$E_G < E_G' + \int d^3 r n(\vec{r}) [U(\vec{r}) - U'(\vec{r})]$$

$$\Rightarrow E_G' + E_G < E_G + E_G' \quad \rightarrow \leftarrow$$

**In principle**, given  $n(r)$ , one can uniquely determine  $U(r)$ .

Since  $n(\mathbf{r})$  determines  $U_{\text{ion}}(\mathbf{r})$ , which determines everything else ( $E_G$ ,  $|\Psi_G\rangle$ ... etc), one can say that,  $E_G$  is a functional of  $n(\mathbf{r})$ :

$$E_G[n] = T[n] + U[n] + V_{ee}[n]$$

### The 2nd Hohenberg-Kohn theorem

The true ground state density  $n$  minimizes the energy functional  $E_G[n]$ , with the following constraint,  $\int d^3r n(\vec{r}) = N$ .

Pf:

If  $n'$  is a density different from the ground-state density  $n$  in potential  $U(\mathbf{r})$ , then the  $U'(\mathbf{r})$  (and  $\Psi'$ ), that produce this  $n'$  are different from the  $\Psi_G$  in  $U(\mathbf{r})$ . According to the variational principle,

$$E[n'] = \langle \Psi' | H | \Psi' \rangle \geq \langle \Psi_G | H | \Psi_G \rangle = E_G[n]$$

Thus, for potential  $U(\mathbf{r})$ ,  $E[n']$  is minimized by the ground-state density  $n$ .

- The energy functional

$$\begin{aligned} E_G[n] &= T[n] + V_{ee}[n] + U[n] \\ &= F[n] + U[n] \end{aligned} \quad U[n] = \int d^3r n(\vec{r}) U(\vec{r})$$

The  $F[n]$  functional is the same for all electronic systems.

In principle, what has been accomplished here is **enormous**. In principle, there exists a universal functional  $F[n]$  that needs to be found once and for all. One adds to it any particular set of nuclei, in the form of the potential  $U(\vec{r})$ , and then has only to find the function  $n(\vec{r})$  that minimizes it in order to solve ~~the~~ full complexities of Schrödinger's equation.

“No one knows the true  $F[n]$ , and no one will, so it is replaced by various **uncontrollable** approximations.”

(Marder, p.247)

$$F[n] = T[n] + V_H[n] + V_{xc}[n]$$

- Kinetic energy functional

For free electron gas

$$T[n] = V \int \frac{d^3k}{(2\pi)^3} \frac{\hbar^2 k^2}{2m} = V \frac{\hbar^2 k_F^5}{10\pi^2 m}$$

**Thomas-Fermi approx.**  $k_F = (3\pi^2 n(\vec{r}))^{1/3}$

(good for slow density variation)

$$\therefore T^{TF}[n] \approx V \frac{3\hbar^2 (3\pi^2)^{2/3}}{10\pi^2 m} n(\vec{r})^{5/3}$$

- Hartree energy functional

(exact)

$$V_H[n] = \frac{e^2}{2} \iint d^3r d^3r' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

- Exchange-correlation functional

**Local density approx.**  
(LDA)

$$V_{xc}^{LDA}[n] \approx \int d^3r n(\vec{r}) \varepsilon_{xc}(n(\vec{r}))$$



Vxc[n] calculated  
with QMC methods  
(Ceperley & Alder)

where  $\varepsilon_{xc}[n]$  is the xc-energy (per particle) for free electron gas with **local density**  $n(\vec{r})$ .

For example,

$$\varepsilon_x(n) = -\frac{3}{4} \frac{e^2 k_F}{\pi} = -\frac{3}{4} \frac{e^2}{\pi} (3\pi^2 n(\vec{r}))^{1/3}$$

**Generalized  
gradient approx.**  
(GGA)

$$V_{xc}^{LDA}[n] \approx \int d^3r n(\vec{r}) \varepsilon_{xc}[n(\vec{r}), \nabla n(\vec{r})]$$

## Kohn-Sham theory

No approx. yet

$$E[n] = T[n] + \int d^3r n(\vec{r})U(\vec{r}) + \frac{e^2}{2} \iint d^3r d^3r' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} + V_{xc}[n]$$

1. KS ansatz: **Parametrize** the particle density in terms of a set of one-electron orbitals representing a non-interacting reference system

$$n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2$$

2. Calculate non-interacting kinetic energy in terms of the  $\phi_i$ 's

$$T[n] \rightarrow T_0[n] = \sum_i \int d^3r \phi_i^*(\vec{r}) \left( -\frac{\hbar^2}{2m} \nabla^2 \right) \phi_i(\vec{r})$$

if you don't like this approximation, then keep

$$T[n] = T_0[n] + (T[n] - T_0[n])$$

3. Determine the optimal one-electron orbitals using the variational method under the constraint  $\langle \phi_i | \phi_j \rangle = \delta_{ij}$

$$\delta \left\{ E[n] - \sum_i \lambda_i (\langle \phi_i | \phi_i \rangle - 1) \right\} = 0$$

## Kohn-Sham equation

not valid for  
excited states

$$\rightarrow \left\{ -\frac{\hbar^2}{2m} \nabla^2 + U(\vec{r}) + e^2 \int d^3 r' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} + \frac{\delta V_{txc}[n]}{\delta n(\vec{r})} \right\} \phi_i(\vec{r}) = \lambda_i \phi_i(\vec{r})$$

$$\text{where } V_{txc}[n] = V_{xc}[n] + T[n] - T_0[n]$$

- Similar in form to the Hartree equation, and much simpler than HF eq.

However, here everything is exact, except the  $V_{txc}$  term. (exact but unknown)

- Neither KS eigenvalues  $\lambda_i$ , nor eigenstates, have accurate physical meaning.

- However,  $n(\vec{r}) = \sum_{i=1}^N |\phi_i(\vec{r})|^2$  ← the density is physical

Also, the highest occupied  $\lambda_i$  relative the vacuum is the ionization energy.

- If one approximates  $T \sim T_0$ , and use LDA,

then 
$$\frac{\delta V_{txc}[n(\vec{r})]}{\delta n(\vec{r})} = \varepsilon_{xc}[n(\vec{r})]$$

$$V_{xc}^{LDA}[n] \approx \int d^3 r n(\vec{r}) \varepsilon_{xc}[n(\vec{r})]$$

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + U(\vec{r}) + e^2 \int d^3 r' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} + \varepsilon_{xc}[n(\vec{r})] \right\} \phi_i(\vec{r}) = \lambda_i \phi_i(\vec{r})$$

## Self-consistent Kohn-Sham equation, an *ab initio* theory

1. choose initial  $\{\phi_i\}$

↓

2. construct  $n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2 \rightarrow V_{KS}(\vec{r}) = e^2 \int d^3r' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} + \varepsilon_{xc}[n(\vec{r})]$  ←  
(for LDA)

↓

3. solve  $\left[ -\frac{\hbar^2}{2m} \nabla^2 + U(\vec{r}) + V_{KS}(\vec{r}) \right] \phi'_i(\vec{r}) = \lambda_i \phi'_i(\vec{r})$

↓

4. construct  $n'(\vec{r}) = \sum_i |\phi'_i(\vec{r})|^2$

↓

5. if  $|n'(\vec{r}) - n(\vec{r})| < \delta$ , then STOP.

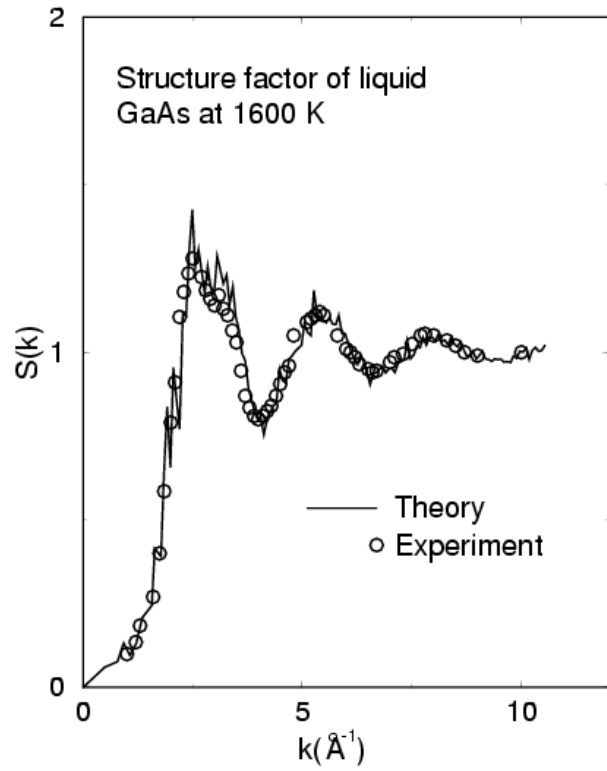
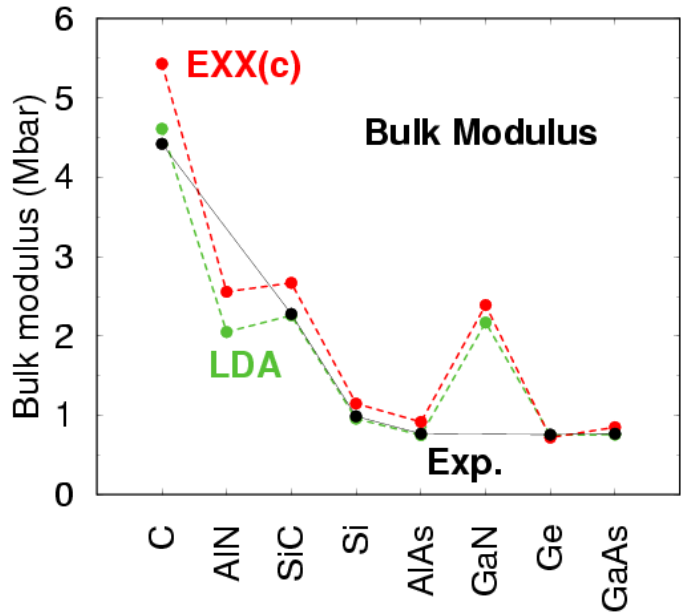
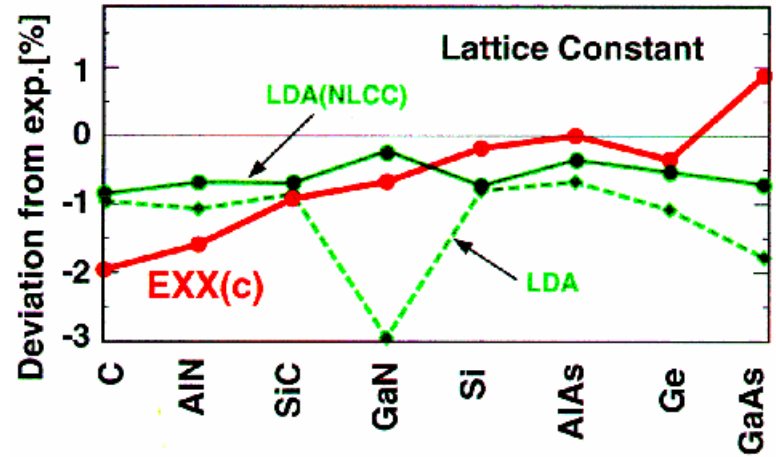
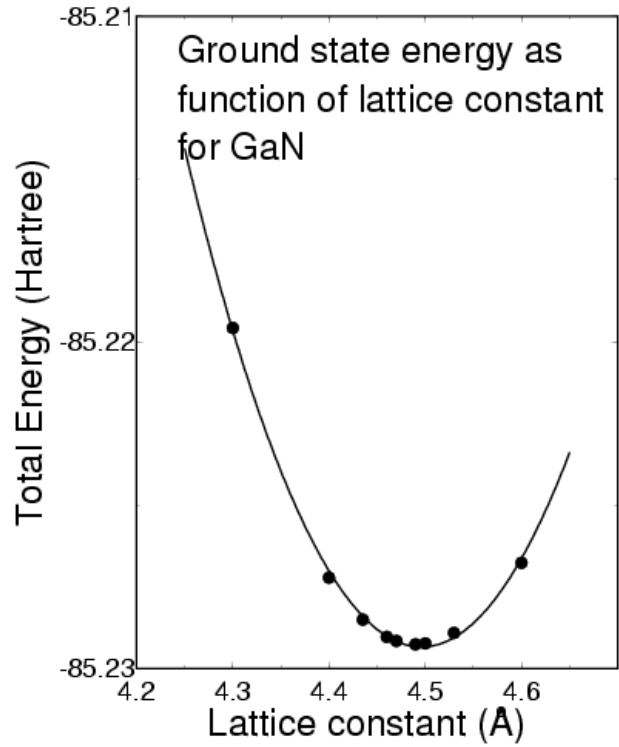
else let  $\phi_i(\vec{r}) = \phi'_i(\vec{r})$ , GOTO 2

Parameter  
free

• Total energy 
$$E = \sum_i \lambda_i - \frac{e^2}{2} \iint d^3r d^3r' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

**Double-counting correction.**  
Recall similar correction in HFA.

# Strength of DFT





## Weakness of DFT

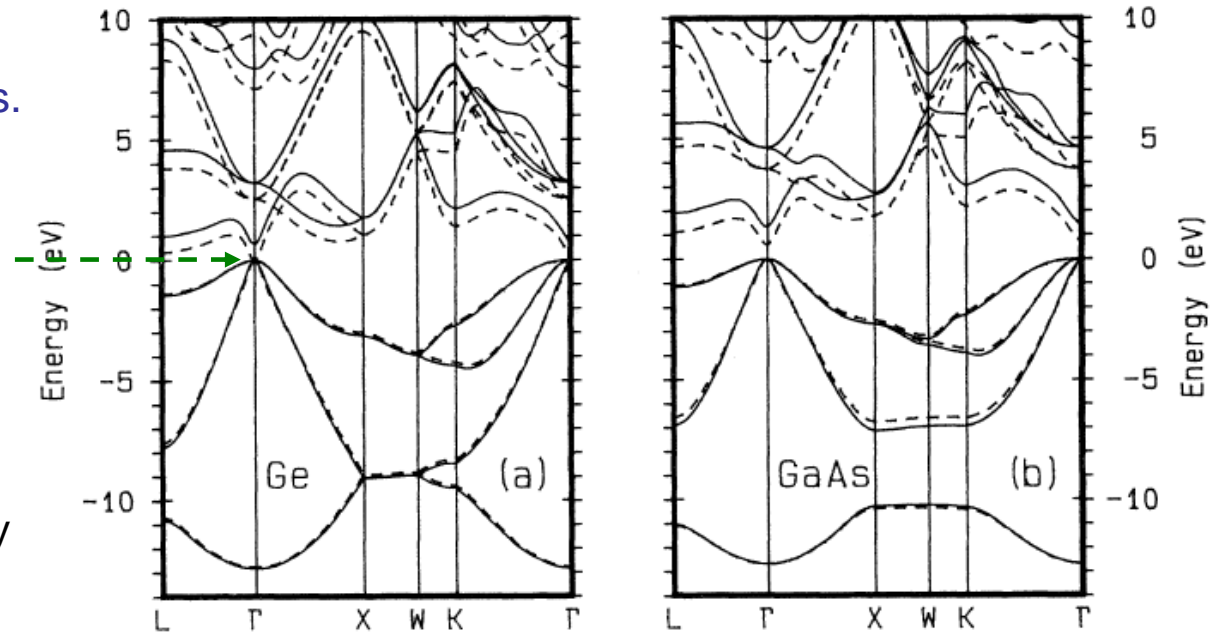
- **Band-gap problem:** HKS theorem not valid for excited states.

Band-gaps in semiconductors and insulators are usually underestimated.

LDA DFT Calcs.  
(dashed lines)

Metal in “LDA”  
calculations

Can be fixed by  
GWA...etc



Rohlfing and Louie PRB 1993

- **Neglect of strong correlations**

- Exchange-splitting underestimated for narrow *d*- and *f*-bands.
- Many transition-metal compounds are Mott-Hubbard or charge-transfer insulators, but DFT predicts metallic state.

LDA, GGAs, etc. fail in many cases with strong correlations.