

# **Density Functional Theory**

## **The Basis of Most Modern Calculations**

**Richard M. Martin**

**University of Illinois at Urbana-Champaign**

### **Lecture II**

**Behind the functionals – limits and challenges**

**See also pdf file of lecture notes on  
Density Functional Theory**

**Lecture at Summer School**

**First Principles Calculations for Condensed Matter and Nanoscience**

**University of California at Santa Barbara – August, 2005**

# Density Functional Theory

## The Basis of Most Modern Calculations

**Hohenberg-Kohn; Kohn-Sham – 1965**

**Defined a new approach to the many-body interacting electron problem**

- **Yesterday**

- Brief statement of the Hohenberg-Kohn theorems and the Kohn-sham Ansatz
- Overview of the solution of the Kohn-Sham equations and the importance of pseudopotentials in modern methods

- **Today**

- Deeper insights into the Hohenberg-Kohn theorems and the Kohn-sham Ansatz
- The nature of the exchange-correlation functional
- Understanding the **limits** of present functionals and the **challenges** for the future

# The Fundamental Hamiltonian

## Interacting electrons in an external potential

$$\hat{H} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$- \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}$$

- Only one small term: The kinetic energy of the nuclei
- If we omit this term, the nuclei are a fixed external potential acting on the electrons
- The final term is essential for charge neutrality – but is a classical term that is added to the electronic part

## Many-Body Electron Problem

The many-electron wavefunction is a function in  $3N$  dimensional space

$$\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \quad (2)$$

The total energy is the expectation value

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \equiv \langle \hat{H} \rangle = \langle \hat{T} \rangle + \langle \hat{V}_{int} \rangle + \int d^3r V_{ext}(\mathbf{r}) n(\mathbf{r}). \quad (3)$$

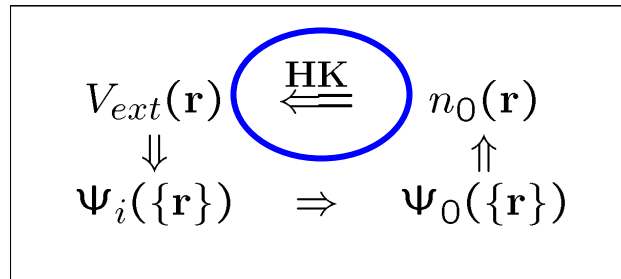
The ground state wavefunction  $\Psi_0$  is the state with lowest energy *that obeys the symmetries of the particles and conservation laws.*

$$E_0 = \min \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (4)$$

# The basis of most modern calculations

## Density Functional Theory (DFT)

- Hohenberg-Kohn (1964)



- All properties of the many-body system are determined by the ground state density  $n_0(\mathbf{r})$
- Each property is a functional of the ground state density  $n_0(\mathbf{r})$  which is written as  $f[n_0]$
- A functional  $f[n_0]$  maps a function to a result:  $n_0(\mathbf{r}) \rightarrow f$

# The Hohenberg-Kohn Theorems

- Theorem I: For any system of electrons in an external potential  $V_{ext}(\mathbf{r})$ , that potential is determined uniquely, except for a constant, by the ground state density  $n(\mathbf{r})$ .

Corollary I: Since the hamiltonian is thus fully determined, except for a constant shift of the energy, the full many-body wavefunction and all other properties of the system are also completely determined!

$$\begin{aligned} n_0(\mathbf{r}) &\longrightarrow V_{ext}(\mathbf{r}) \quad (\text{except for constant}) \\ &\longrightarrow \text{All properties} \end{aligned}$$

# The Hohenberg-Kohn Theorems

- Theorem II: A universal functional for the energy  $E[n]$  of the density  $n(\mathbf{r})$  can be defined for all electron systems. The exact ground state energy is the global minimum for a given  $V_{ext}(\mathbf{r})$ , and the density  $n(\mathbf{r})$  which minimizes this functional is the exact ground state density.

Corollary II: The functional  $E[n]$  alone is sufficient to determine the exact ground state energy and density.

Excited states of the electrons must be determined by other means.

Minimizing  $E[n]$  for a given  $V_{ext}(\mathbf{r}) \rightarrow n_0(\mathbf{r})$  and  $E$

In principle, one can find all other properties and they are functionals of  $n_0(\mathbf{r})$ .

# The Hohenberg-Kohn Theorems - Proof

Proof of Theorem I:

Suppose that there were two different external potentials  $V_{ext}^{(1)}(\mathbf{r})$  and  $V_{ext}^{(2)}(\mathbf{r})$  with the same ground state density  $n(\mathbf{r})$ . The two external potentials lead to two different hamiltonians,  $\hat{H}^{(1)}$  and  $\hat{H}^{(2)}$ , which have different ground state wavefunctions,  $\Psi^{(1)}$  and  $\Psi^{(2)}$ , which are hypothesized to have the same density  $n(\mathbf{r})$ . Then:

$$E^{(1)} = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle. \quad (6)$$

which leads to

$$E^{(1)} < E^{(2)} + \int d^3r \{ V_{ext}^{(1)}(\mathbf{r}) - V_{ext}^{(2)}(\mathbf{r}) \} n(\mathbf{r}). \quad (7)$$

But changing the labels leads to

$$E^{(2)} < E^{(1)} + \int d^3r \{ V_{ext}^{(2)}(\mathbf{r}) - V_{ext}^{(1)}(\mathbf{r}) \} n(\mathbf{r}). \quad (8)$$

which is a contradiction!



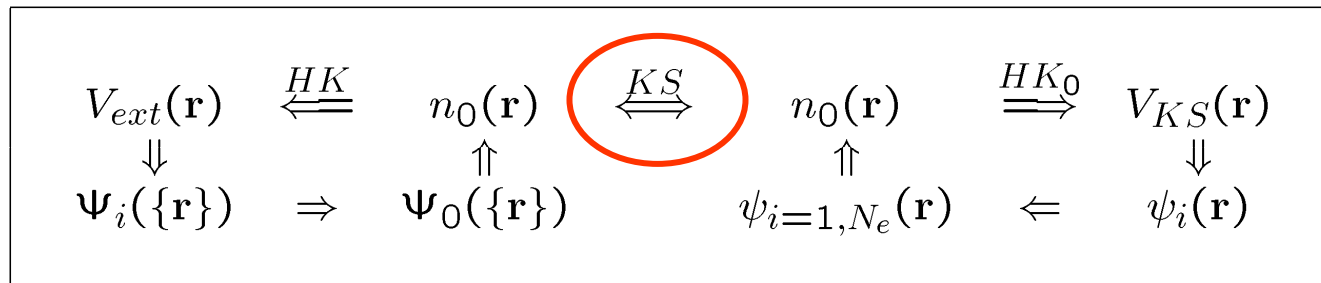
# The Hohenberg-Kohn Theorems - Continued

- Generalization by Levy and Lieb
  - Recast as a two step process
    - Consider all many-body wavefunctions  $\Psi$  with the same density
    - First, minimize for a given density  $\mathbf{n}$
    - Next, minimize  $\mathbf{n}$  to find density with lowest energy  $\mathbf{n}_0$
- What is accomplished by the Hohenberg-Kohn theorems?
- **Existence proofs**
- **A Nobel prize for this???**
- **The genius is the next step –  
to realize that this provides a new way to  
approach the many-body problem**

# The Kohn-Sham Ansatz

- **Kohn-Sham (1965) – Replace** original many-body problem with an **independent electron problem – that can be solved!**
- The ground state density is required to be the same as the exact density

$$n_0(\mathbf{r}) = \sum_{\sigma} \sum_{i=1} |\psi_i^{\sigma}(\mathbf{r})|^2,$$



- **Only the ground state density and energy** are required to be the same as in the original many-body system

# The Kohn-Sham Ansatz II

- From Hohenberg-Kohn the ground state energy is a functional of the density  $E_0[n]$ , minimum at  $n = n_0$
- From Kohn-Sham

$$n_0(\mathbf{r}) = \sum_{\sigma} \sum_{i=1} |\psi_i^{\sigma}(\mathbf{r})|^2,$$

$$E_{KS} = \frac{1}{2} \sum_{\sigma} \sum_{i=1} |\nabla \psi_i^{\sigma}|^2 + \int d\mathbf{r} V_{ext}(\mathbf{r}) n(\mathbf{r}) + E_{Hartree}[n] + E_{II} + \underline{E_{xc}[n]}.$$

Equations for independent particles - **soluble**

Exchange-Correlation Functional – Exact theory but **unknown** functional!

- The new paradigm – find **useful, approximate functionals**

# The Kohn-Sham Ansatz III

- **Approximations to the functional  $E_{xc}[n]$**
- Requires information on the many-body system of interacting electrons
- **Local Density Approximation - LDA**
  - Assume the functional is the same as a model problem – the homogeneous electron gas
  - $E_{xc}$  has been calculated as a function of density using quantum Monte Carlo methods (Ceperley & Alder)
- **Gradient approximations - GGA**
  - Various theoretical improvements for electron density that is varies in space

# What is $E_{xc}[n]$ ?

- Exchange and correlation  $\rightarrow$  around each electron, other electrons tend to be excluded – “x-c hole”
- $E_{xc}$  is the interaction of the electron with the “hole” – spherical average – attractive –  $E_{xc}[n] < 0$ .

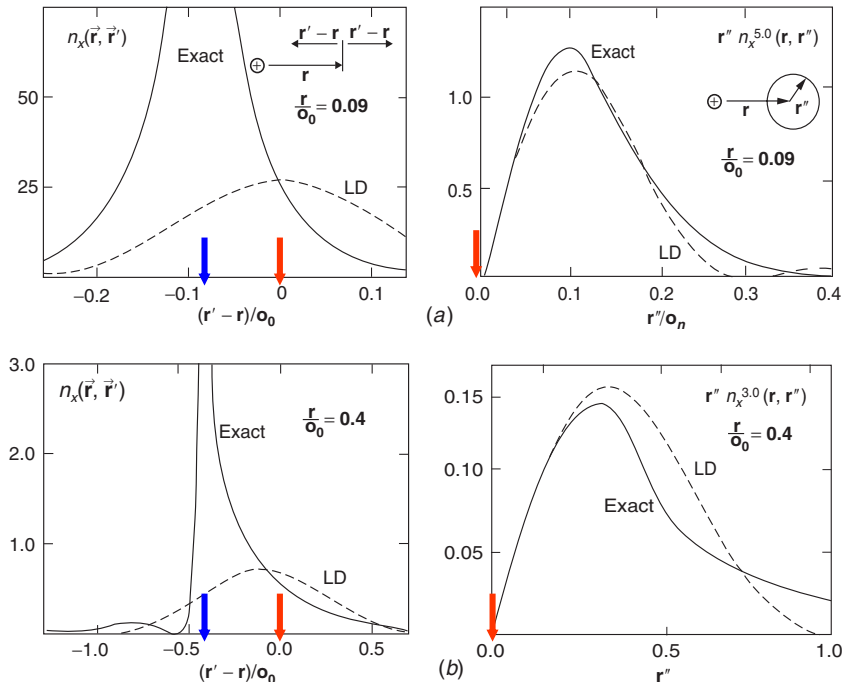
## Exchange hole in Ne atom

Fig. 7.2 Gunnarsson, et. al. [348]

● nucleus ● electron

Very non-spherical

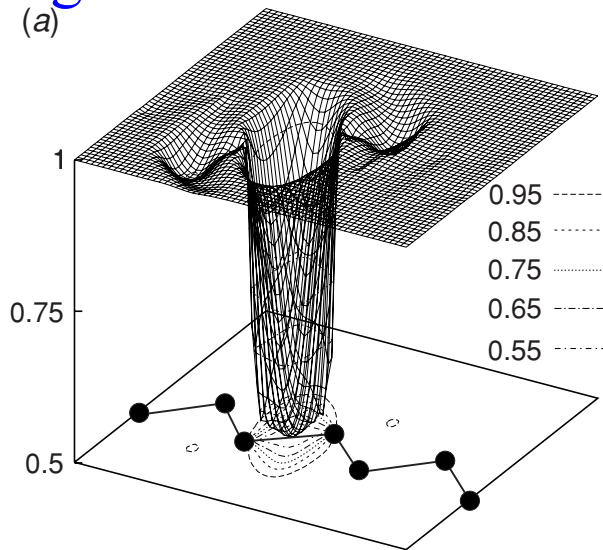
Spherical average very close to the hole in a homogeneous electron gas!



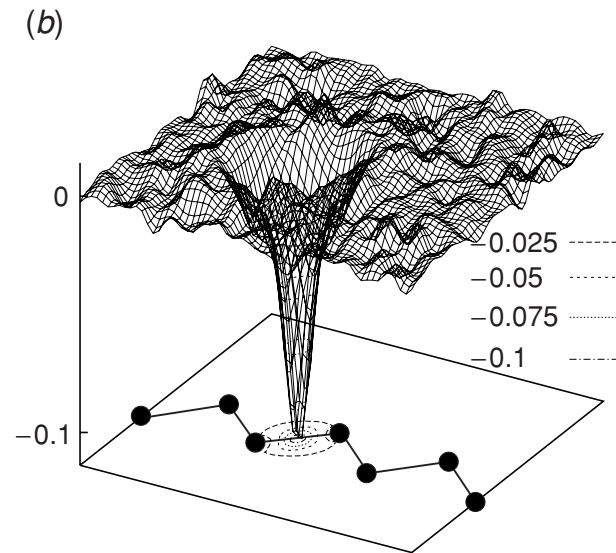
# Exchange-correlation (x-c) hole in silicon

- Calculated by Monte Carlo methods

Exchange



Correlation



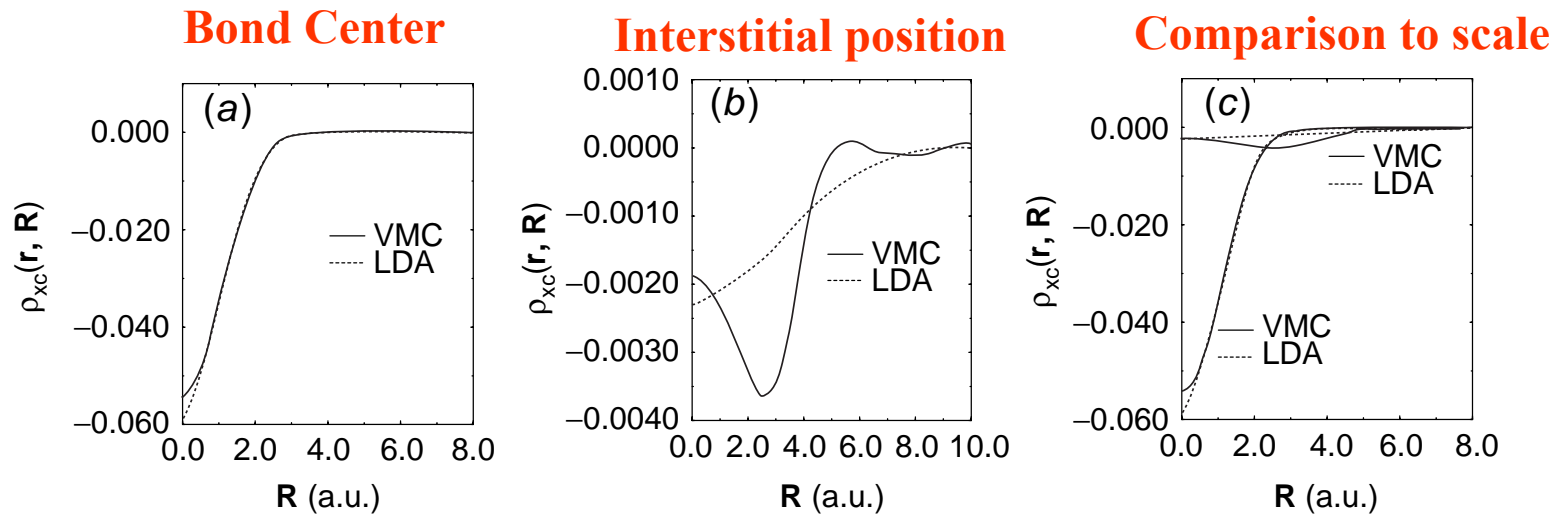
Hole is reasonably well localized near the electron  
Supports a local approximation

Fig. 7.3 - Hood, et. al. [349]

# Exchange-correlation (x-c) hole in silicon

- Calculated by Monte Carlo methods

Exchange-correlation hole – spherical average



x-c hole close to that in the homogeneous gas in the most relevant regions of space

Supports local density approximation ! Fig. 7.4 - Hood, et. al. [349]

# The Kohn-Sham Equations

- Assuming a form for  $E_{xc}[n]$
- Minimizing energy (with constraints)  $\rightarrow$  Kohn-Sham Eqs.

$$n_0(\mathbf{r}) = \sum_{\sigma} \sum_{i=1} |\psi_i^{\sigma}(\mathbf{r})|^2,$$

$$E_{KS} = \frac{1}{2} \sum_{\sigma} \sum_{i=1} |\nabla \psi_i^{\sigma}|^2 + \int d\mathbf{r} V_{ext}(\mathbf{r}) n(\mathbf{r}) + E_{Hartree}[n] + E_{II} + E_{xc}[n].$$

$$\frac{\delta E_{KS}}{\delta \psi_i^{\sigma*}(\mathbf{r})} = 0, \quad (1)$$

$$\langle \psi_i^{\sigma} | \psi_j^{\sigma'} \rangle = \delta_{i,j} \delta_{\sigma,\sigma'}. \quad (2)$$

$$\left(-\frac{1}{2}\nabla^2 + V_{KS}^{\sigma}(\mathbf{r}), -\epsilon_i^{\sigma}\right) \psi_i^{\sigma}(\mathbf{r}) = 0 \quad (3)$$

$$\begin{aligned} V_{KS}^{\sigma}(\mathbf{r}) &= V_{ext}(\mathbf{r}) + \frac{\delta E_{Hartree}}{\delta n(\mathbf{r}, \sigma)} + \frac{\delta E_{xc}}{\delta n(\mathbf{r}, \sigma)} \\ &= V_{ext}(\mathbf{r}) + V_{Hartree}(\mathbf{r}) + \underline{V_{xc}^{\sigma}(\mathbf{r})} \end{aligned} \quad (4)$$

Constraint – required  
Exclusion principle for  
independent particles

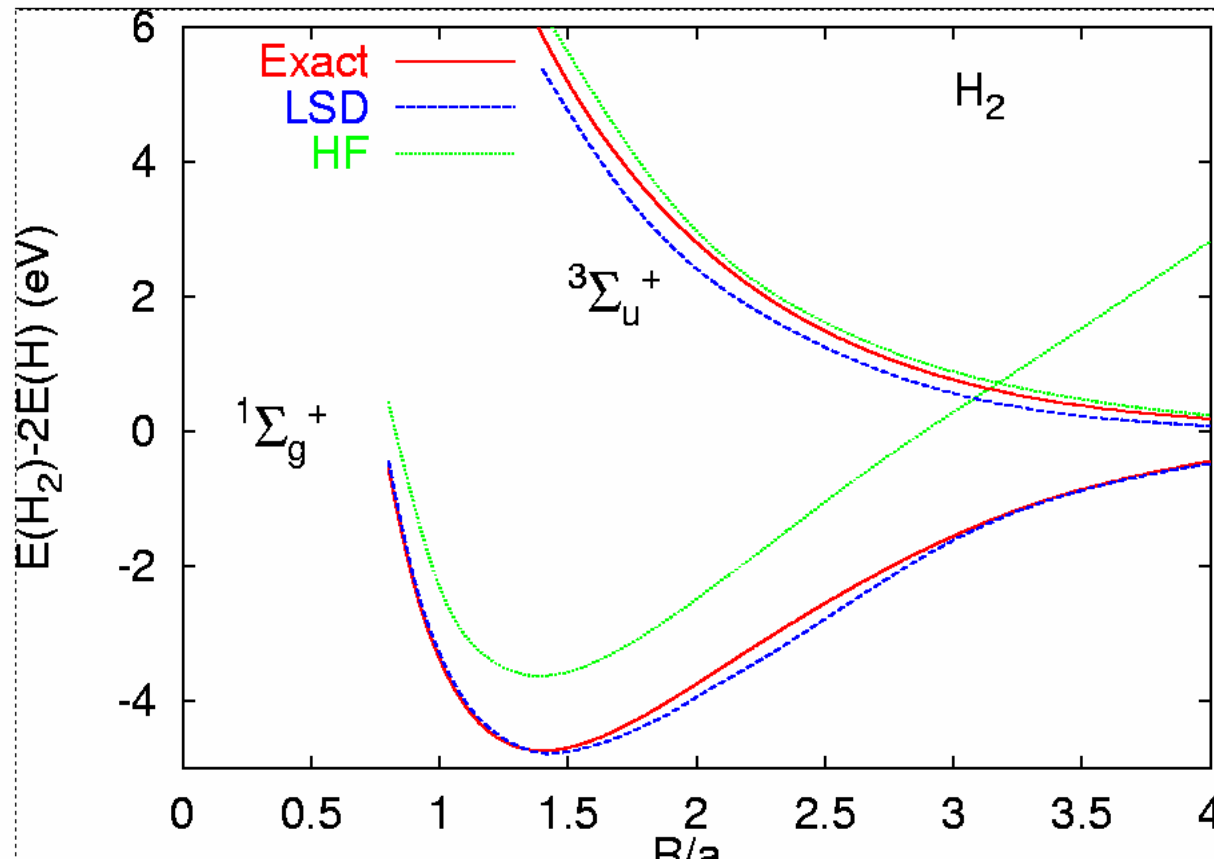
**Eigenvalues are  
approximation  
to the energies to  
add or subtract  
electrons  
–electron bands  
More later**



# Example of Results – Test Case

- Hydrogen molecules - using the LSDA

(from O. Gunnarsson)



# Comparisons – LAPW – PAW - - Pseudopotentials (VASP code)

Method	C		Si		CaF <sub>2</sub>		bcc Fe		
	<i>a</i>	<i>B</i>	<i>a</i>	<i>B</i>	<i>a</i>	<i>B</i>	<i>a</i>	<i>B</i>	<i>m</i>
NCPW <sup>a</sup>	3.54	460	5.39	98	5.21	90	2.75 <sup>c</sup>	226 <sup>c</sup>	
PAW <sup>a</sup>	3.54	460	5.38	98	5.34	100			
PAW <sup>b</sup>	3.54	460	5.40	95	5.34	101	2.75	247	2.00
USPW <sup>b</sup>	3.54	461	5.40	95	5.34	101	2.72	237	2.08
LAPW <sup>a</sup>	3.54	470	5.41	98	5.33	110	2.72 <sup>d</sup>	245 <sup>d</sup>	2.04 <sup>d</sup>
EXP <sup>a</sup>	3.56	443	5.43	99	5.45	85-90	2.87 <sup>d</sup>	172 <sup>d</sup>	2.12 <sup>d</sup>

- *a* – lattice constant; *B* – bulk modulus; *m* – magnetization
- <sup>a</sup>Holzwarth, *et al.*; <sup>b</sup>Kresse & Joubert; <sup>c</sup>Cho & Scheffler; <sup>d</sup>Stizrude, *et al.*

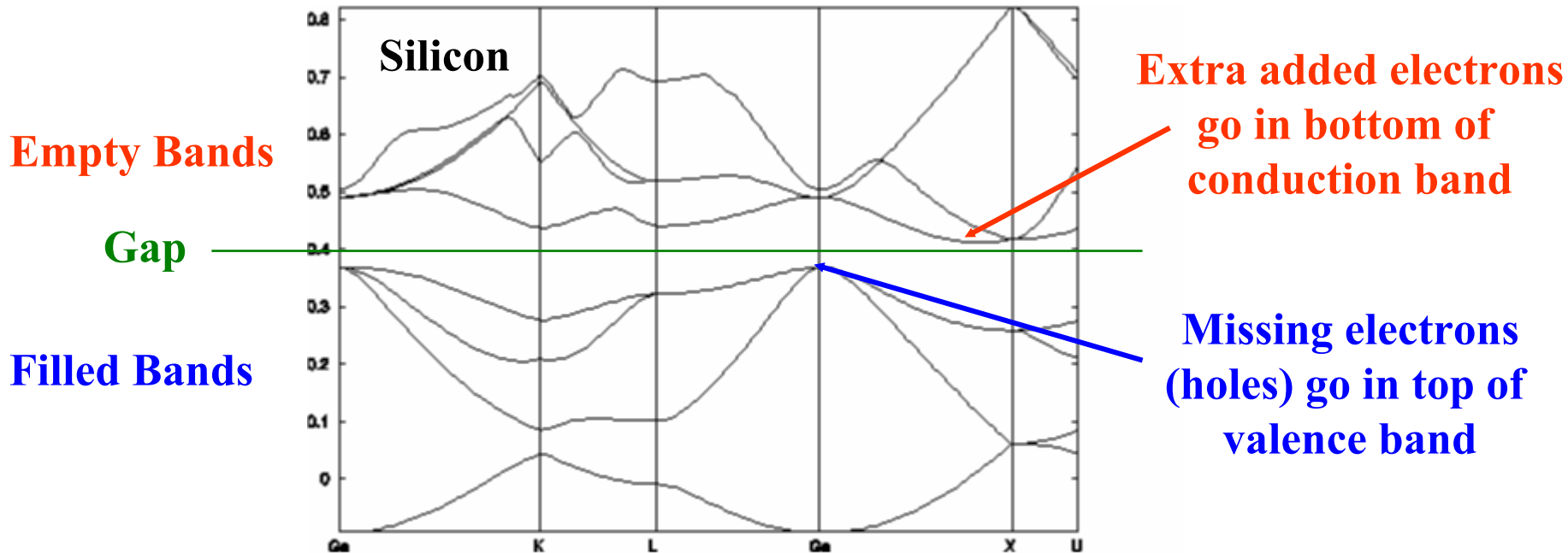
# What about eigenvalues?

- The **only** quantities that are supposed to be correct in the Kohn-Sham approach are the **density, energy, forces, ....**
- These are **integrated quantities**
  - Density  $n(\mathbf{r}) = \sum_i |\Psi_i(\mathbf{r})|^2$
  - Energy  $E_{\text{tot}} = \sum_i \varepsilon_i + F[n]$
  - Force  $F_I = -dE_{\text{tot}} / dR_I$  where  $R_I$  = position of nucleus I
- **What about the individual  $\Psi_i(\mathbf{r})$  and  $\varepsilon_i$  ?**
  - In a non-interacting system,  $\varepsilon_i$  are the energies to add and subtract “Kohn-Sham-ons” – non-interacting “electrons”
  - In the real interacting many-electron system, energies to add and subtract electrons are well-defined **only** at the Fermi energy

- **The Kohn-Sham  $\Psi_i(\mathbf{r})$  and  $\varepsilon_i$  are approximate functions - a starting point for meaningful many-body calculations**

# Electron Bands

- Understood since the 1920's - independent electron theories predict that electrons form **bands of allowed eigenvalues**, **with forbidden gaps**
- **Established by experimentally for states near the Fermi energy**



# Bands and the “Band Gap Problem”

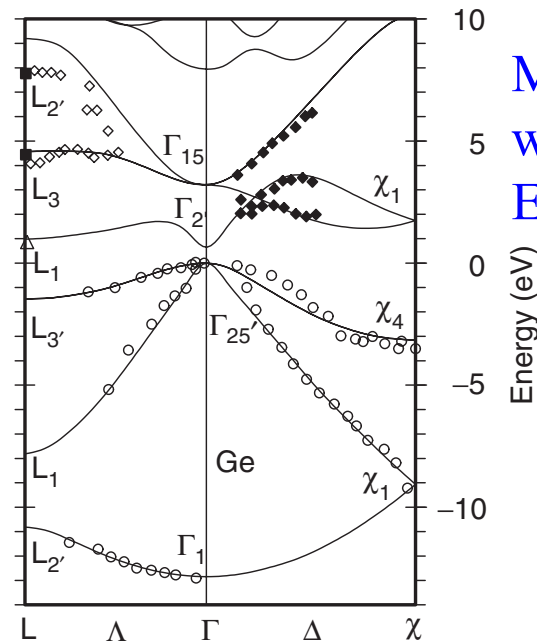
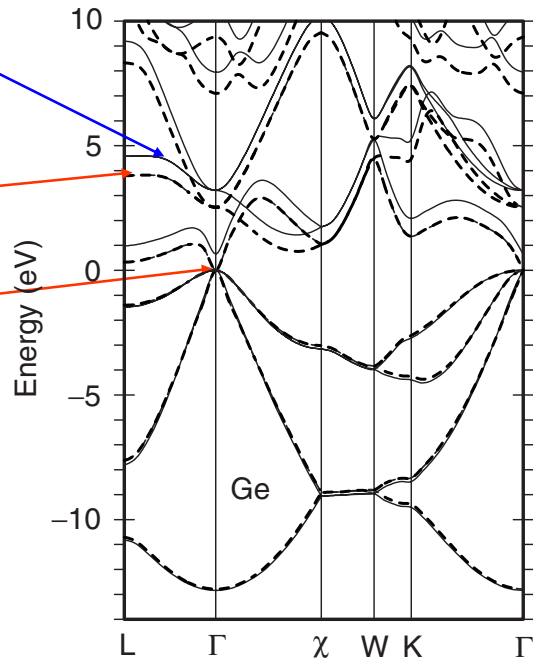
- Excitations are NOT well-predicted by the “standard” LDA, GGA forms of DFT

## Example of Germanium

Many-body bands

LDA bands

Ge is a metal in LDA!



Many-body theory with experimental points

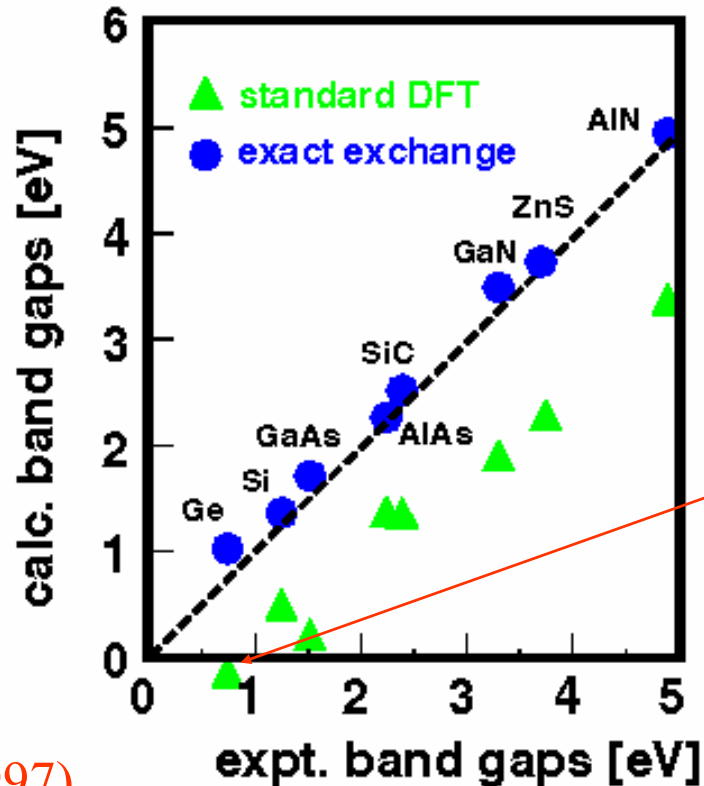
M. Rohlfing, et al

# The “Band Gap Problem”

- Excitations are NOT well-predicted by the “standard” LDA, GGA forms of DFT

The “Band Gap Problem”

Orbital dependent DFT is more complicated but gives improvements - treat exchange better, e.g, “Exact Exchange”



Ge is a metal in LDA!

M. Staedele et al, PRL 79, 2089 (1997)

# Failures!

- **All approximate functionals fail at some point!**
- **Most difficult cases**
  - **Mott Insulators – often predicted to be metals**
  - **Metal-insulator Transitions**
  - **Strongly correlated magnetic systems**
  - **Transition metal oxides**
  - **Hi-Tc materials**
  - ...

# Conclusions I

- Density functional theory is by far the most widely applied “*ab initio*” method used in for “real materials” in physics, chemistry, materials science
- Approximate forms have proved to be very successful
- **BUT there are failures**
- No one knows a feasible approximation valid for **all** problems – especially for cases with strong electron-electron correlations



# Conclusions II

- **Exciting arenas for theoretical predictions**
  - Working together with Experiments
  - Realistic simulations under real conditions
  - Molecules and clusters in solvents, . . .
  - Catalysis in real situations
  - Nanoscience and Nanotechnology
  - Biological problems
- **Beware -- understand what you are doing!**
  - Limitations of present DFT functionals
  - Use codes properly and carefully

# Conclusions III

- **Basis for further theoretical developments**
  - “GW” many-body calculations starting from DFT wavefunctions
  - Quantum Monte Carlo many-body calculations with trial functions generated from from DFT wavefunctions
  - Dynamical Mean Field Theory – done for models now with information taken from DFT calculations
  - Functional of Green’s functions and dynamical spectral functions – generalizations of DFT
- **Exciting time for developments in the theory of interacting electrons**