

Density Functional Theory

The Basis of Most Modern Calculations

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**Lecture at Summer School
Hands-on introduction to Electronic Structure
Materials Computation Center
University of Illinois – June, 2005**

Hohenberg-Kohn; Kohn-Sham – 1965

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

Reference:

**Electronic Structure: Basic Theory and Practical Methods,
Richard M. Martin (Cambridge University Press, 2004)**

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

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

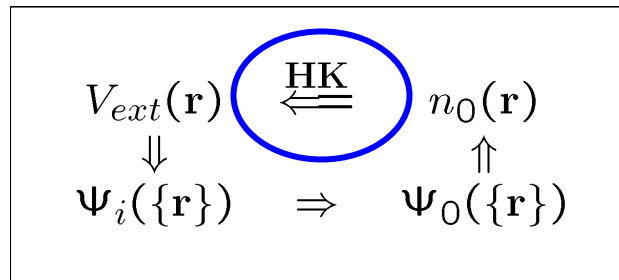
The ground state wavefunction Ψ_0 is the state with lowest energy *that obeys the symmetries of the particles and conservation laws.*

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

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!

$$n_0(\mathbf{r}) \longrightarrow V_{ext}(\mathbf{r}) \quad (\text{except for constant})$$

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!

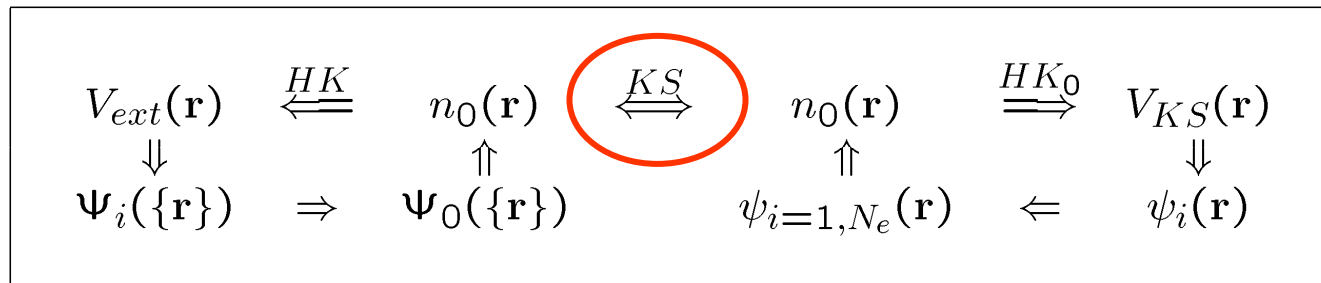
The Hohenberg-Kohn Theorems - Continued

- Generalization by Levy and Lieb
 - Recast as a two step process
 - Consider all many-body wavefunctions Ψ 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 varies in space

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

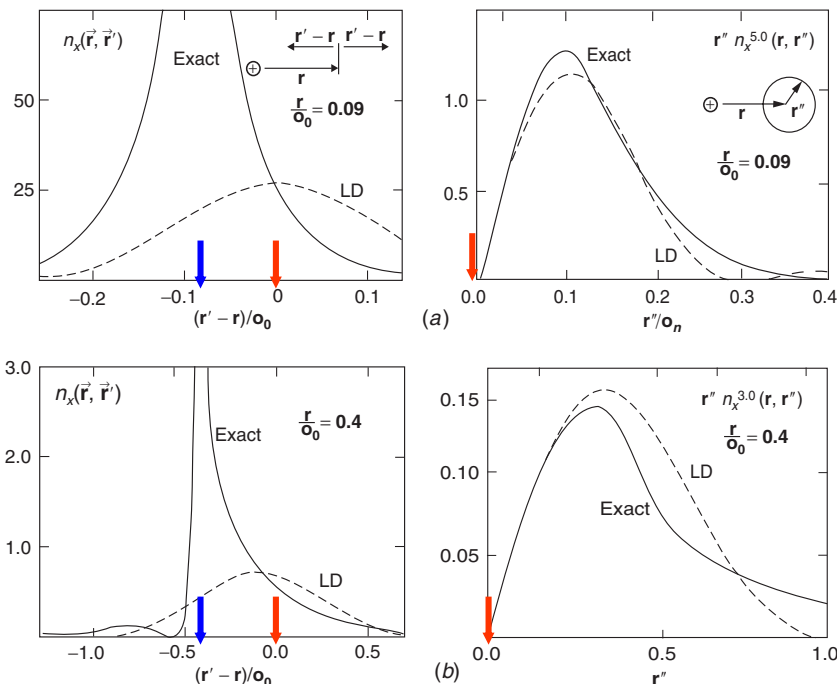
- Exchange and correlation \rightarrow around each electron, other electrons tend to be excluded – “x-c hole”
- E_{xc} is the interaction of the electron with the “hole” – spherical average – attractive – $E_{xc}[n] < 0$.

Exchange hole in Ne atom

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

Very non-spherical

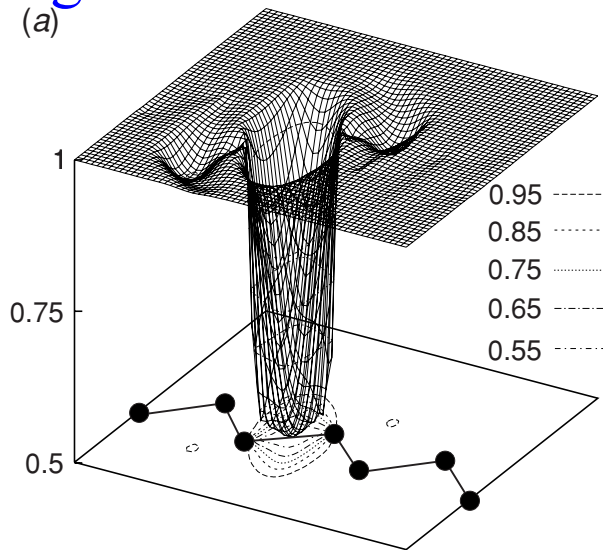
Spherical average very close to the hole in a homogeneous electron gas!



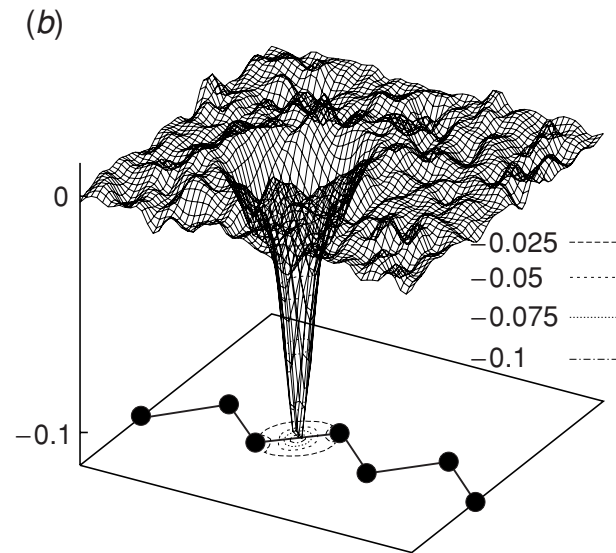
Exchange-correlation (x-c) hole in silicon

- Calculated by Monte Carlo methods

Exchange



Correlation



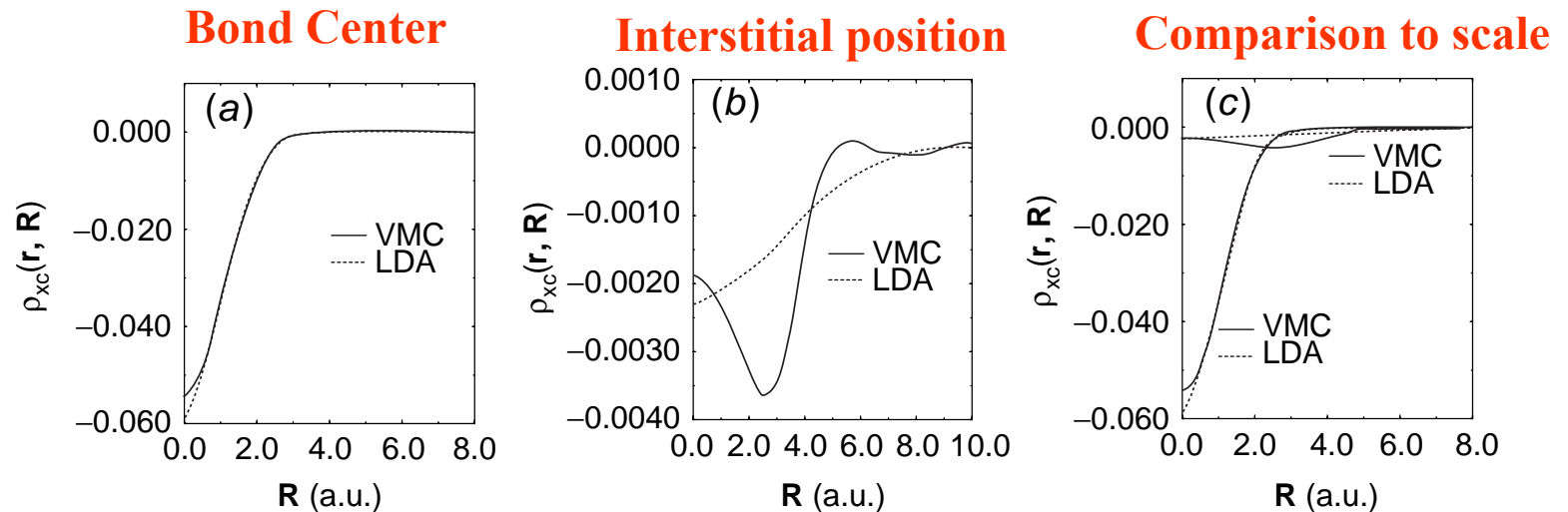
Hole is reasonably well localized near the electron
Supports a local approximation

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.

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

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

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

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

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

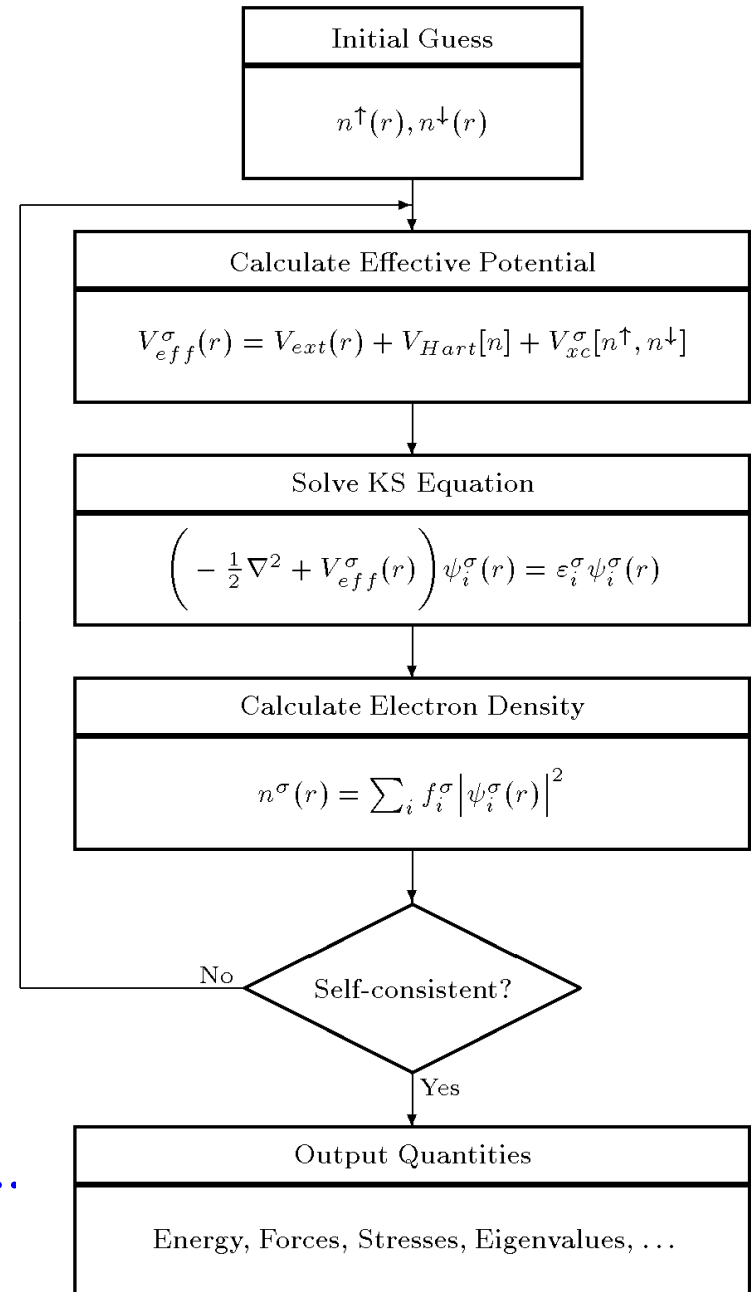
$$\begin{aligned} V_{KS}^{\sigma}(\mathbf{r}) &= V_{ext}(\mathbf{r}) + \frac{\delta E_{Hartree}}{\delta n(\mathbf{r}, \sigma)} + \frac{\delta E_{xc}}{\delta n(\mathbf{r}, \sigma)} \\ &= V_{ext}(\mathbf{r}) + V_{Hartree}(\mathbf{r}) + \underline{V_{xc}^{\sigma}(\mathbf{r})} \end{aligned} \quad (4)$$

Constraint – required
Exclusion principle for
independent particles

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

Solving Kohn-Sham Equations

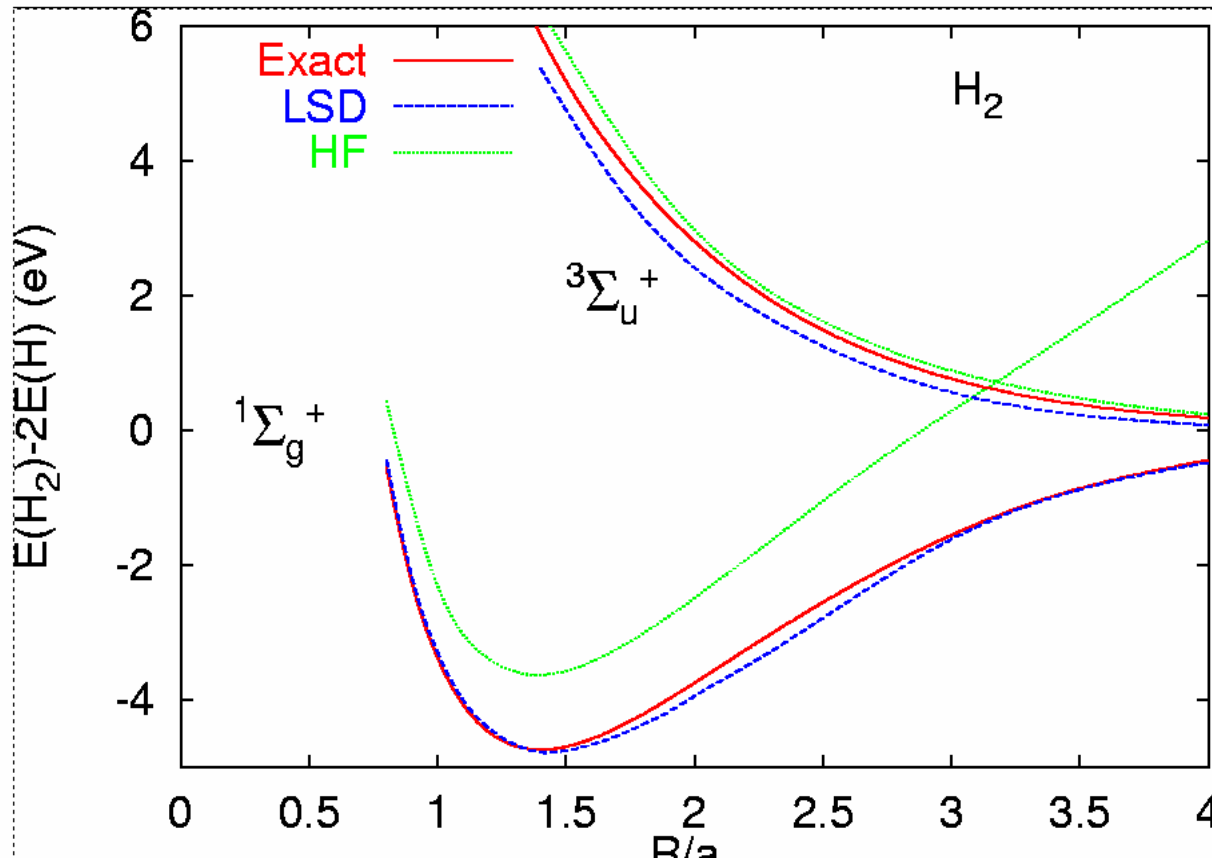
- Structure, types of atoms
- Guess for input
- Solve KS Eqs.
- New Density and Potential
- Self-consistent?
- Output:
 - Total energy, force, stress, ...
 - Eigenvalues



Example of Results – Test Case

- Hydrogen molecules - using the LSDA

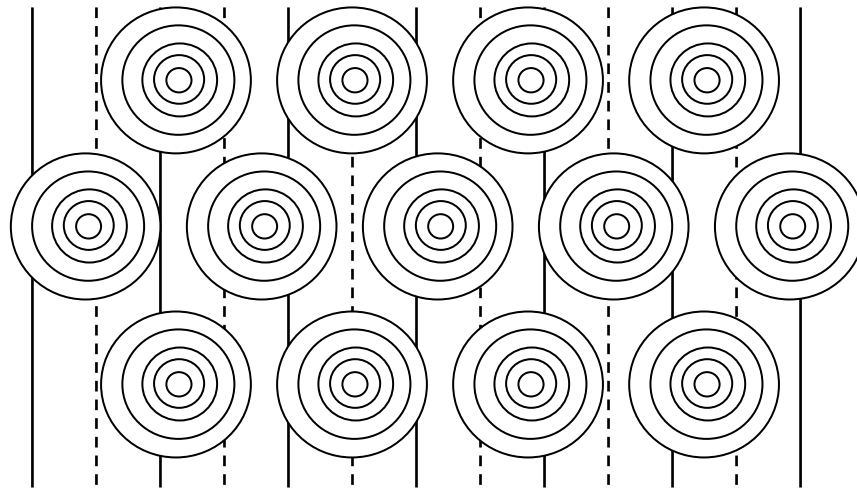
(from O. Gunnarsson)



Calculations on Materials

Molecules, Clusters, Solids,

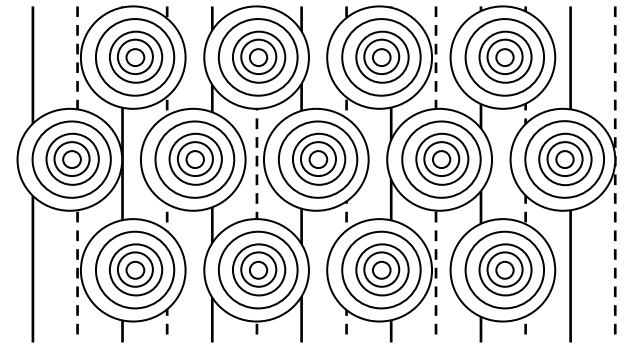
- Basic problem - many electrons in the presence of the nuclei



- Core states – strongly bound to nuclei – atomic-like
- Valence states – change in the material – determine the bonding, electronic and optical properties, magnetism,

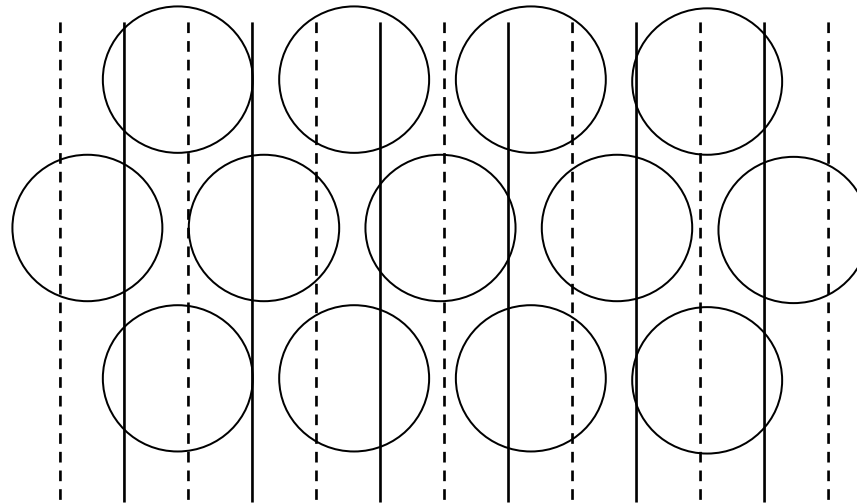
The Three Basic Methods for Modern Electronic Structure Calculations

- **Plane waves**
 - The simplicity of Fourier Expansions
 - The speed of Fast Fourier Transforms
 - Requires smooth pseudopotentials
- **Localized orbitals**
 - The intuitive appeal of atomic-like states
 - Simplest interpretation in tight-binding form
 - Gaussian basis widely used in chemistry
 - Numerical orbitals used in SIESTA
- **Augmented methods**
 - “Best of both worlds” – also most demanding
 - Requires matching inside and outside functions
 - Most general form – (L)APW



Plane Waves

- The most general approach



$$\psi_{i,\mathbf{k}}(\mathbf{r}) \propto \sum_m c_{i,m}(\mathbf{k}) \times \exp(i(\mathbf{k} + \mathbf{G}_m) \cdot \mathbf{r}) \quad (1)$$

- Kohn-Sham Equations in a crystal

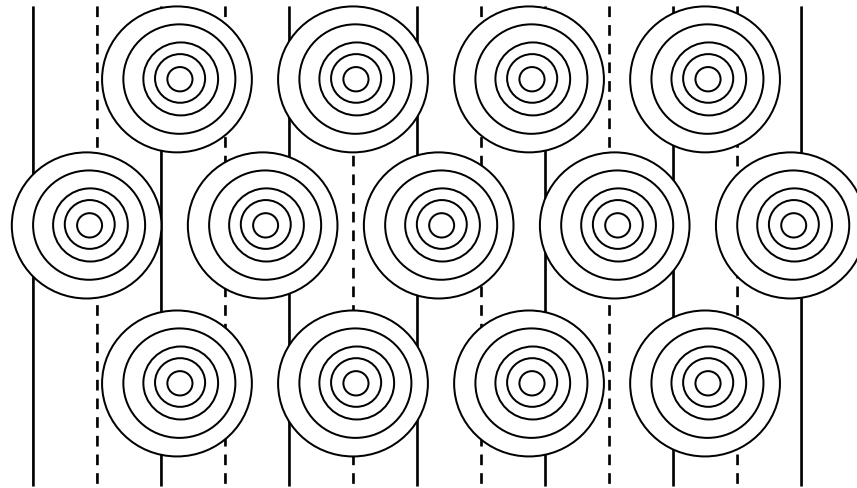
$$\sum_{m'} H_{m,m'}(\mathbf{k}) c_{i,m'}(\mathbf{k}) = \varepsilon_i(\mathbf{k}) c_{i,m}(\mathbf{k}) \quad (2)$$

$$H_{m,m'}(\mathbf{k}) = \frac{\hbar^2}{2m_e} |\mathbf{k} + \mathbf{G}_m|^2 \delta_{m,m'} + V_{eff}(\mathbf{G}_m - \mathbf{G}_{m'}). \quad (3)$$

- The problem is the atoms! High Fourier components!

Plane Waves

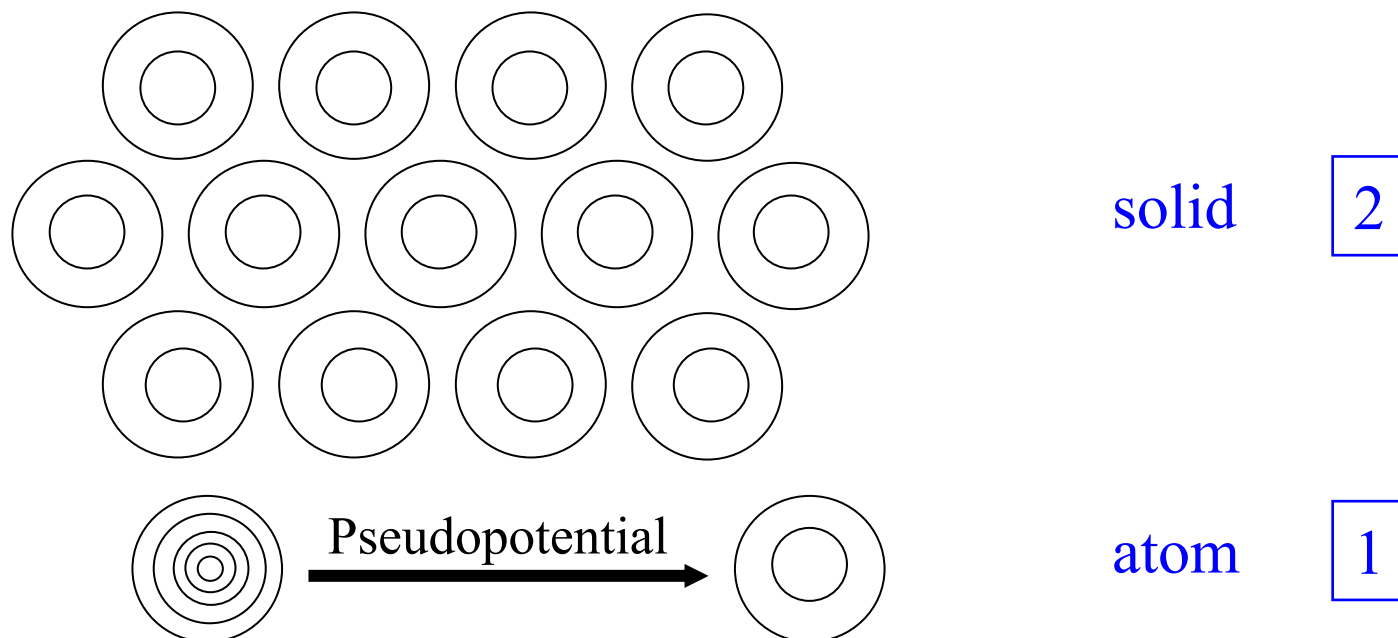
- (L)APW method



- **Augmentation:** represent the wave function inside each sphere in spherical harmonics
 - “Best of both worlds”
 - But requires matching inside and outside functions
 - Most general form – can approach arbitrarily precision

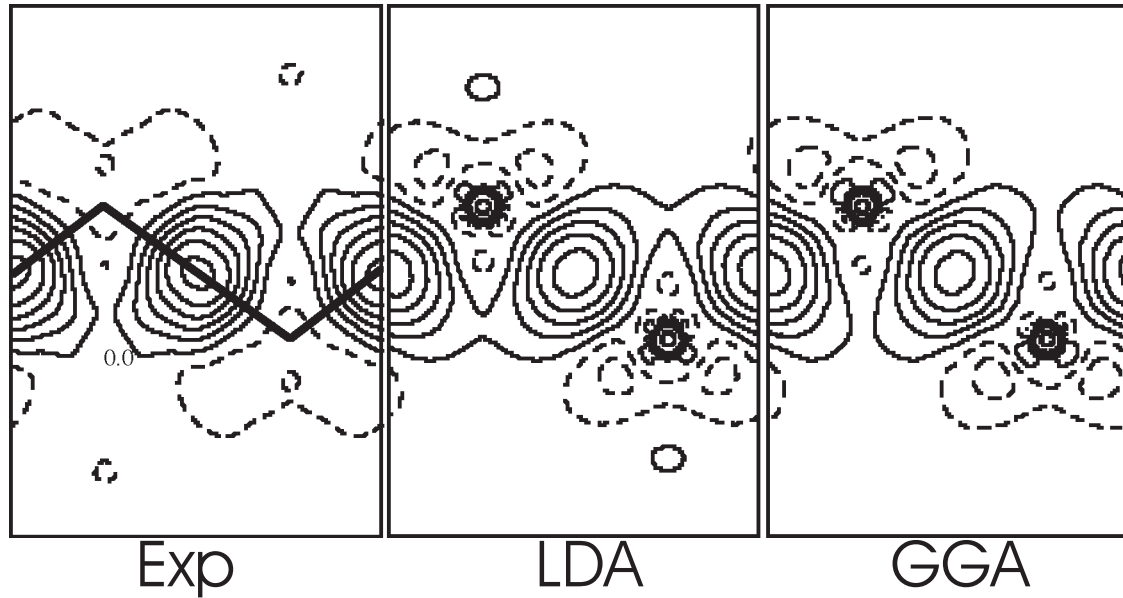
Plane Waves

- **Pseudopotential Method** – replace each potential



- **1** Generate **Pseudopotential** in atom (spherical) – **2** use in solid
- **Pseudopotential** can be constructed to be weak
 - Can be chosen to be smooth
 - Solve Kohn-Sham equations in solid directly in Fourier space

Charge Density of Si – Experiment - LAPW calculations with LDA, GGA



- Electron density difference from sum of atoms
 - Experimental density from electron scattering
 - Calculations with two different functionals
 - J. M. Zuo, P. Blaha, and K. Schwarz, J. Phys. Cond. Mat. 9, 7541 (1997).
 - Very similar results with pseudopotentials
 - O. H. Nielsen and R. M. Martin (1995)

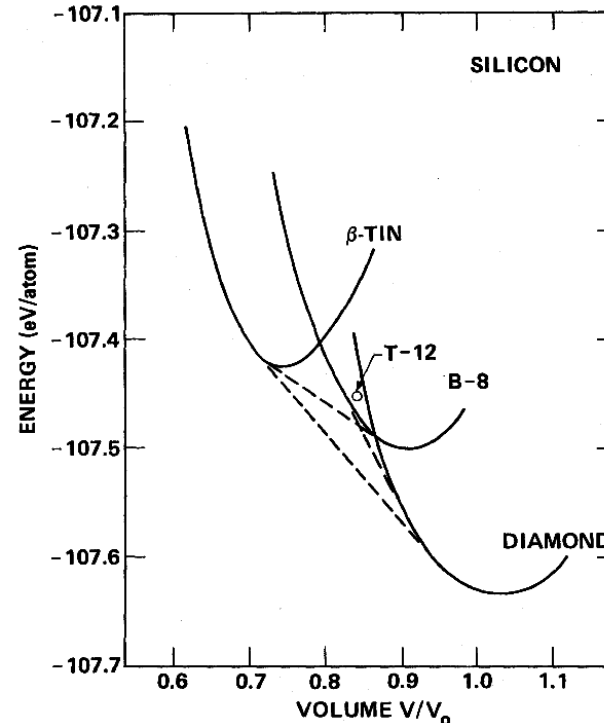
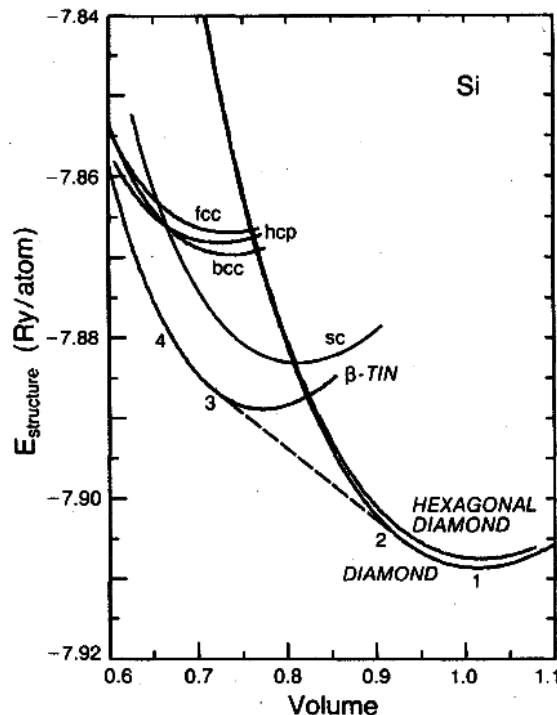
Comparisons – LAPW – PAW - - Pseudopotentials (VASP code)

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

- *a* – lattice constant; *B* – bulk modulus; *m* – magnetization
- ^aHolzwarth, *et al.*; ^bKresse & Joubert; ^cCho & Scheffler; ^dStizrude, *et al.*

Phase Transitions under Pressure

Silicon is a Metal for $P > 110$ GPa



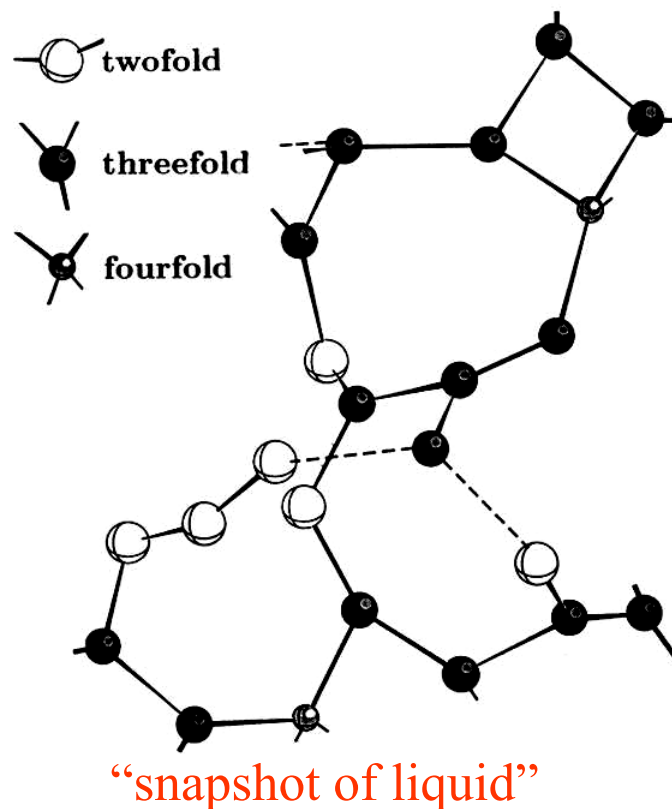
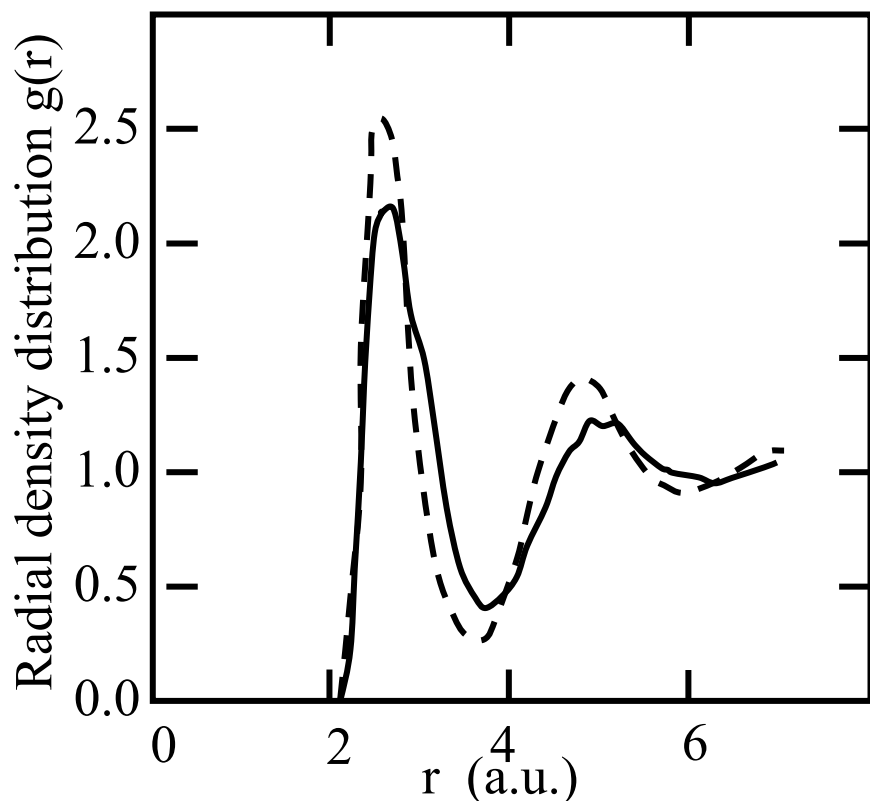
- Demonstration that pseudopotentials are an accurate “ab initio” method for calculations of materials
- Results are close to experiment!
 - M. T. Yin and M. L. Cohen, Phys. Rev. B 26, 5668 (1982).
 - R. Biswas, R. M. Martin, R. J. Needs and O. H. Nielsen, Phys. Rev. B 30, 3210 (1982).

The Car-Parrinello Advance

- **Car-Parrinello Method – 1985**
 - Simultaneous solution of Kohn-Sham equations for electrons and Newton's equations for nuclei
 - Iterative update of wavefunctions - instead of diagonalization
 - FFTs instead of matrix operations – $N \ln N$ instead of N^2 or N^3
 - Trace over occupied subspace to get total quantities (energy, forces, density, ...) instead of eigenfunction calculations
 - Feasible due to simplicity of the plane wave pseudopotential method
- **A revolution in the power of the methods**
 - Relaxation of positions of nuclei to find structures
 - Simulations of solids and liquids with nuclei moving thermally
 - Reactions, . . .
- **Stimulated further developments - VASP, ABINIT, SIESTA, . . .**

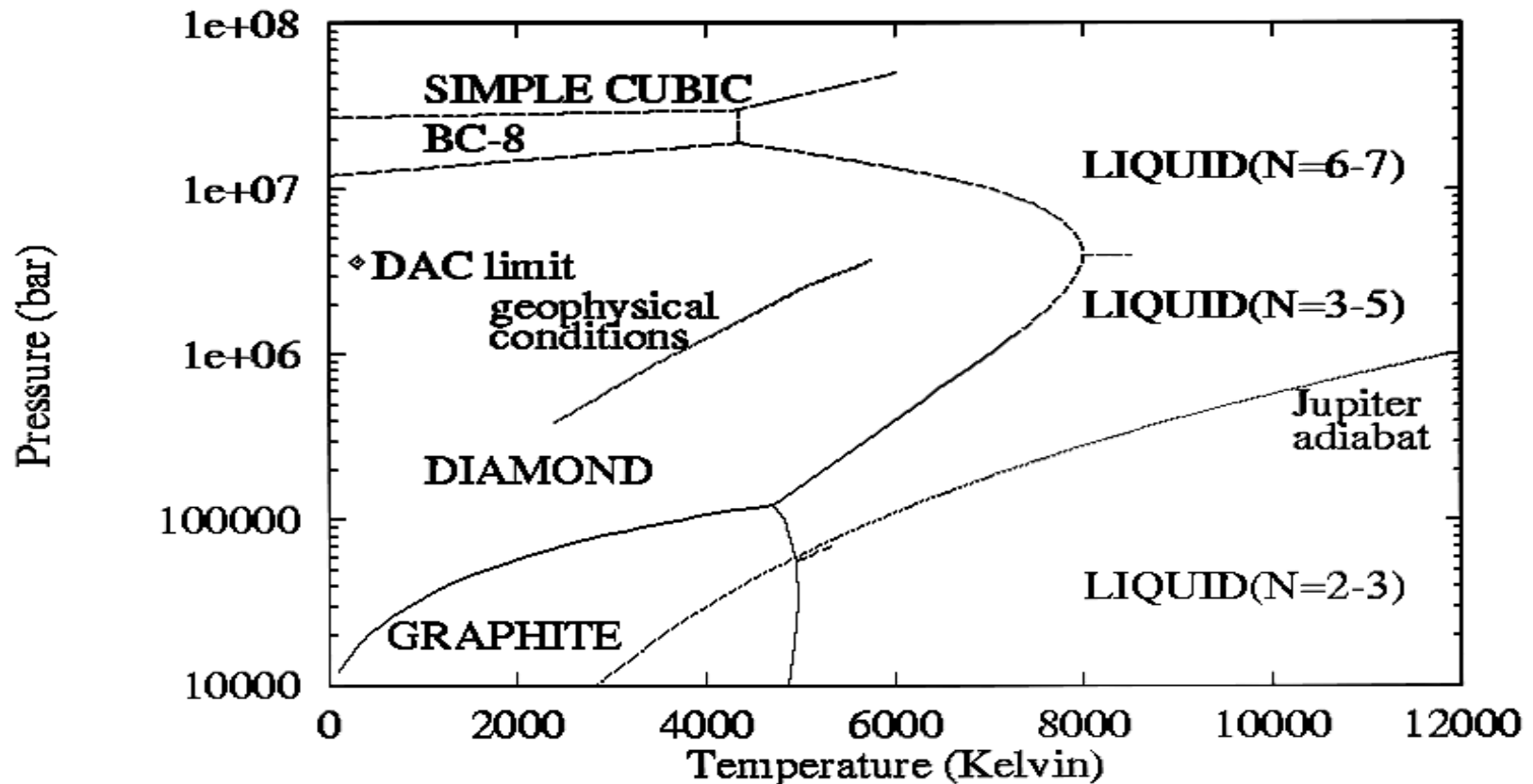
Simulation of Liquid Carbon

- Solid Line: Car-Parrinello plane wave pseudopotential method (Galli, et al, 1989-90)
- Dashed Line: TB potential of Xu, et al (1992)



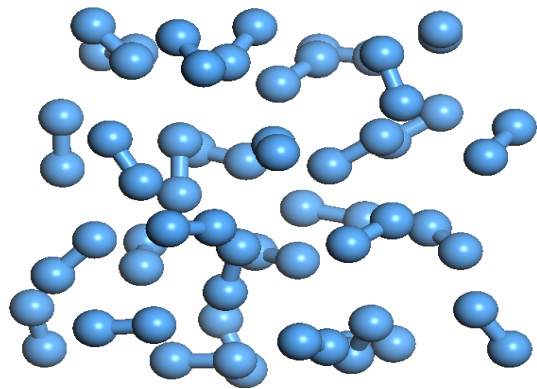
Example of Thermal Simulation

- Phase diagram of carbon
- Full Density Functional “Car-Parrinello” simulation
- G. Galli, et al (1989); M. Grumbach, et al. (1994)



Nitrogen under pressure – Recent discoveries

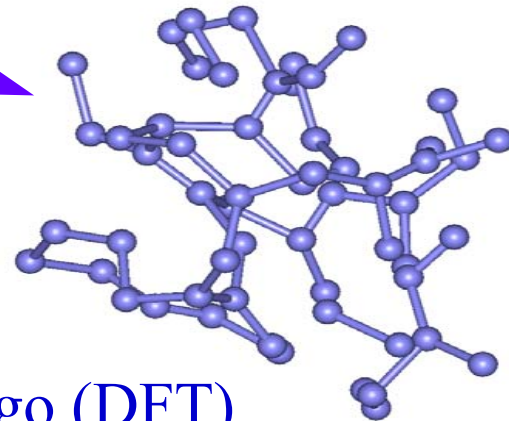
- Used SIESTA code for MD simulation
- Sample structures tested using ABINIT



- Hot Molecular Liquid
- 58 Gpa 7600 K
- Nitrogen Molecules Disassociate and Reform

Squeezed
&

Cooled



- $P > 100$ Gpa and 0K
- Network solid
- Predicted > 15 years ago (DFT)
- Found experimentally in 2000
- **New Prediction of Metallic N**

W. D. Mattson, S. Chiesa,
R. M. Martin, PRL, 2004.

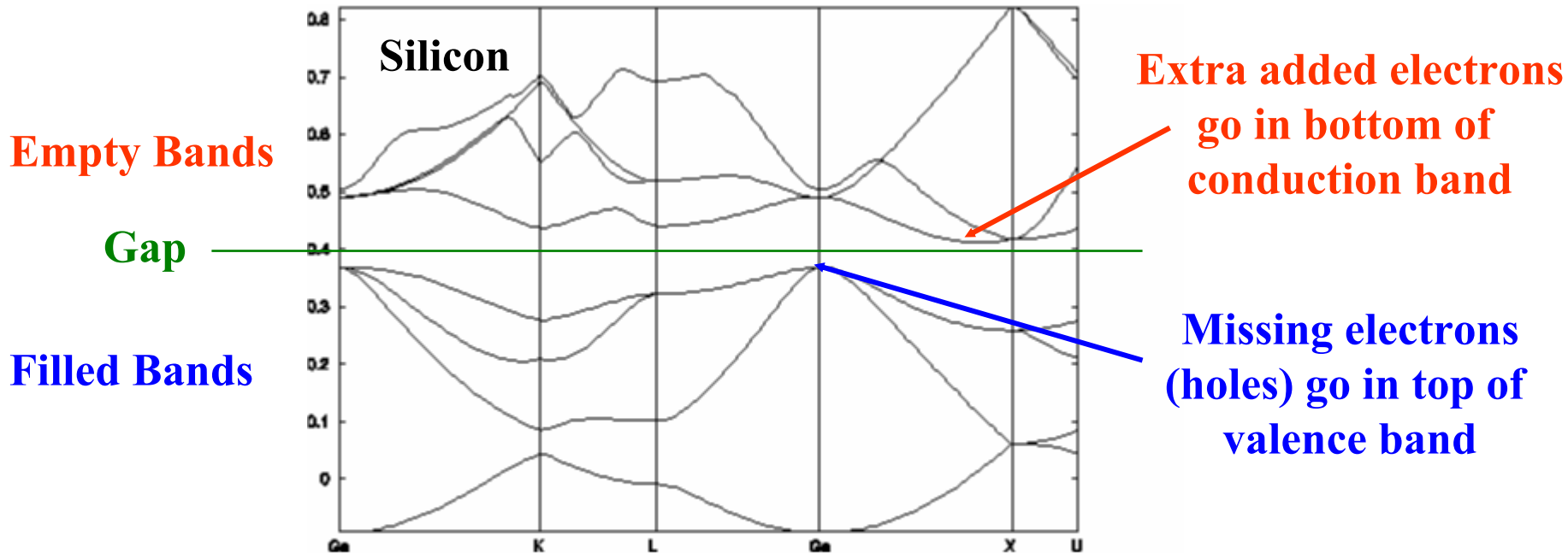
What about eigenvalues?

- 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 ε_i ?**
 - In a non-interacting system, ε_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 ε_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”

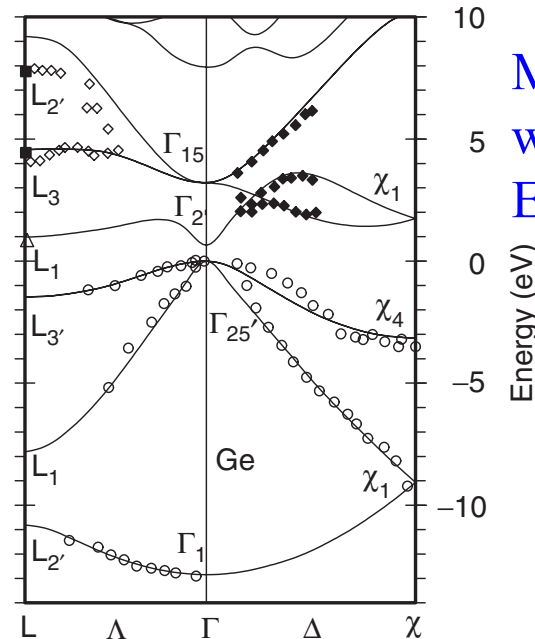
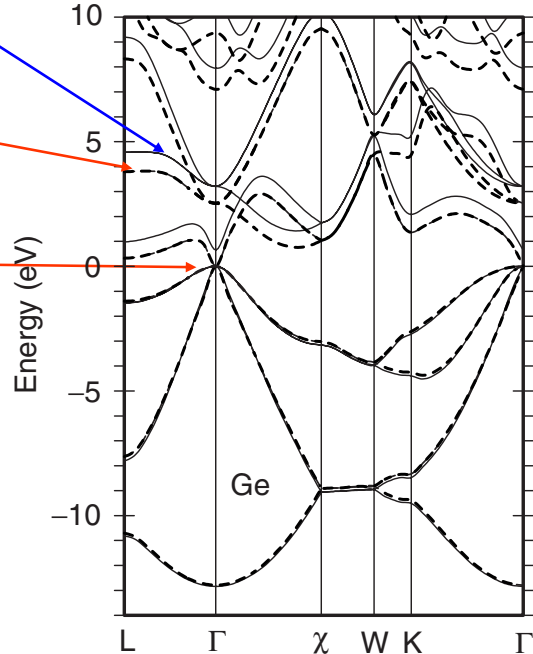
- Excitations are NOT well-predicted by the “standard” LDA, GGA forms of DFT

Example of Germanium

Many-body bands

LDA bands

Ge is a metal in LDA!



Many-body theory with experimental points

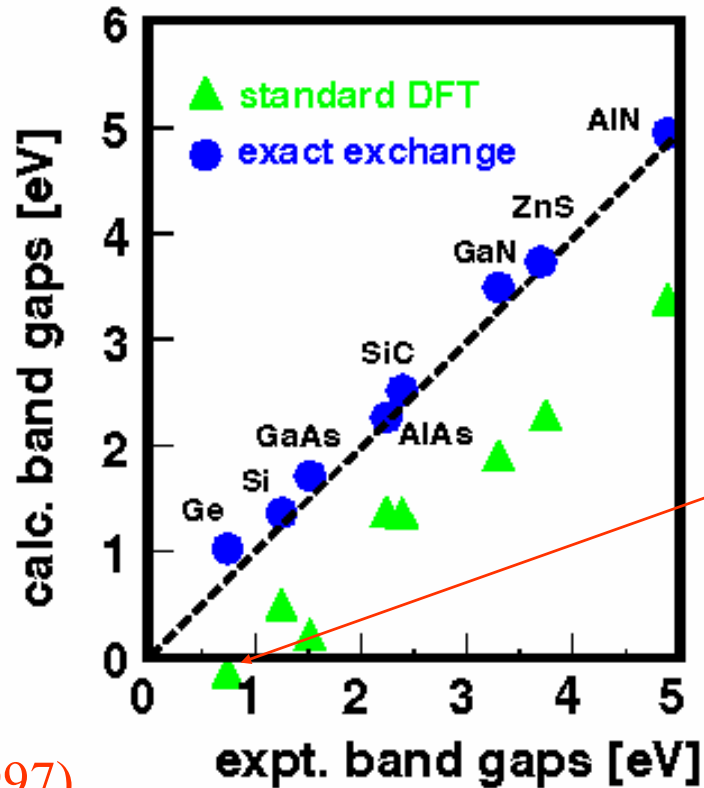
M. Rohlfing, et al

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 to understand what you are doing**
 - Limitations of present DFT functionals
 - Care to use codes properly