

Many electron ground state: E_G

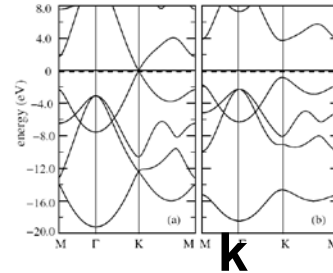
Density Functional Theory

HISTORY

1920's: Quantum Mechanics – electronic spectra

1930's: Thomas-Fermi model: $E[n(r)]$, $n(r) \sim$ homogeneous
Hartree, Hartree-Fock calculations

1940's: Band-structure calculations: ϵ
OPW (Herring), APW (Slater)



1950's: OPW-pseudopotentials (JC Phillips); **computers!**

1960's: Empirical pseudopotential method (EPM), plane waves
theory – experiments
Optical spectra problem of solids essentially solved

1964-5: Density Functional Theory (Hohenberg, **Kohn**, Sham)
(Nobel prize in Chemistry, 1999).

HISTORY (contd)

1970's: Applications of EPM-surfaces, crystals,
Self-consistent charge density-bonding
DFT with plane wave (Ihm, ML Cohen)

1980's: **Total energy Approach** – ab initio pseudopotentials
→ a variety of material properties
Payne et al, Rev. Mod. Phys. 64, pp 1045-1097 (1992).

Car-Parrinello Molecular Dynamics: thermodynamics
Phys. Rev. Lett. 55, 2471 (1985). > 4000 citations

1990's to present: Applications of total energy and **CPMD** to
a very wide range of materials and properties
nano-structures, bio-molecules
High-Performance [Parallel] Computing (HPC)

Computational Materials Science: independent approach

Density Functional Theory

Interacting Many Body Problem: $H_e \Psi_G = E_G \Psi_G$

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

$$H_e = T + V_{\text{ext}} + V_{\text{int}}$$

$\Psi_G(\{d_I, Z_I\}, \{\mathbf{r}_i\})$

3 N_e variables!

$$E_G = \underset{\Psi}{\text{Min}} \frac{\langle \Psi | H_e | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \langle T \rangle + \langle V_{\text{int}} \rangle + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) n(\mathbf{r})$$

Hellman-Feynman force theorem: $F_I = -\frac{\partial E}{\partial \mathbf{R}_I} = -\int d^3r n(\mathbf{r}) \frac{\partial V_{\text{ext}}(\mathbf{r})}{\partial \mathbf{R}_I} - \frac{\partial E_{\mathbf{c}}}{\partial \mathbf{R}_I}$
 (when Ψ is an eigenfunction)

Dependence on density alone!

Thomas Fermi model of electrons: $E = E[n(\mathbf{r})]$

Can E_G be related to density alone?

Function of only **3 variables!**

Density Functional Theory

Hohenberg and Kohn, Phys. Rev. (1964)

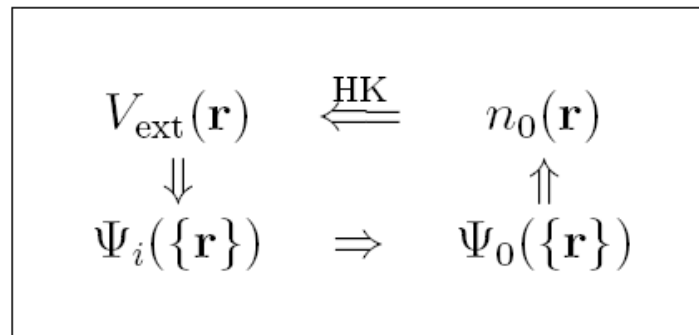
Theorem 1: For any system of electrons in an external potential $V_{\text{ext}}(\mathbf{r})$, that potential is determined uniquely (within an additive constant) by the ground state density $n(\mathbf{r})$.

As a result, the full many body wave function Ψ and derived properties are also determined uniquely by $n(\mathbf{r})$.

Theorem 1: A universal functional for the energy $E_G[n(\mathbf{r})]$ can be defined for all electronic systems. The global minimum of $E_G[n]$ for a given $V_{\text{ext}}(\mathbf{r})$ gives the exact ground state energy and density.

Exact form of the functional $E_G[n]$ is unknown and must be very complicated!

$E_G [n]$ can give only the ground state, the excited states need more work.



How to construct the Density Functional?

Given by Levy and Lieb

$$E_G[n] = \underset{\Psi}{\text{Min}} \langle \Psi | H_e | \Psi \rangle, \text{ such that } \Psi \text{ gives the given density } n(\mathbf{r}).$$
$$= \int d^3r V_{ext}(\mathbf{r})n(\mathbf{r}) + \underset{\Psi}{\text{Min}} \langle \Psi | T + V_{int} | \Psi \rangle$$

Clearly,

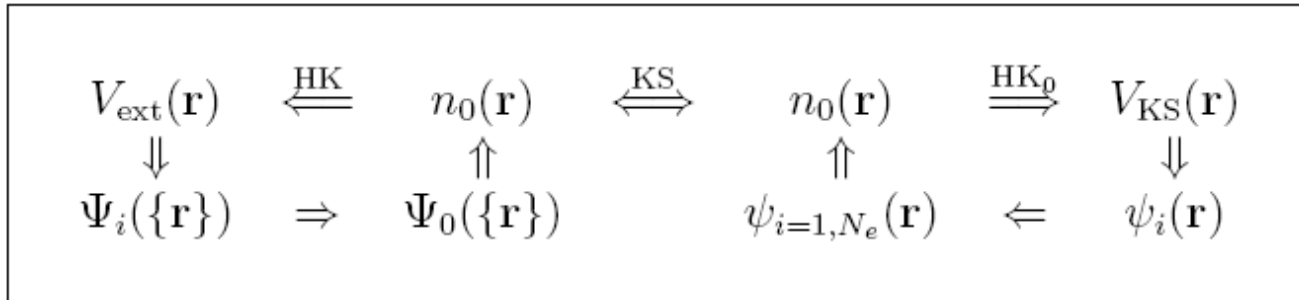
$F[n]$ is a universal functional of $n(\mathbf{r})$, not depending on V_{ext} .

Kohn-Sham Ansatz: $n(\mathbf{r}) = \sum |\psi_i(\mathbf{r})|^2$

Map an interacting electron H_e problem onto an effective non-interacting problem $H_{eff} = -\frac{1}{2} \partial^2 / \partial x^2 + V_{eff}(\mathbf{r})$

$$T_s = -\frac{\hbar^2}{2m} \sum_{i=1}^N \langle \psi_i | \nabla^2 | \psi_i \rangle$$

Kohn-Sham scheme:



$$V_{\text{KS}}(\mathbf{r}) - V_{\text{ext}}(\mathbf{r}) = V_{\text{int}}^{\text{eff}}(\mathbf{r}, [n(\mathbf{r})])$$

Kohn-Sham energy functional:

$$\tilde{E} = \mathbf{T}_s + \int V_{\text{ext}}(\mathbf{r}) n_{\text{eff}}(\mathbf{r}) d\mathbf{r} + E_{\text{Hartree}}[n_{\text{eff}}] + E_{\text{xc}}[n_{\text{eff}}]$$

$$\begin{aligned} E_{\text{xc}}[n(\mathbf{r})] &= F[n(\mathbf{r})] - (\mathbf{T}_s + E_{\text{Hartree}}) \\ &= (\mathbf{T}_{\text{exact}} - \mathbf{T}_s) + (E_{\text{int}} - E_{\text{Hartree}}) \end{aligned}$$

E_{xc} is the functional where the most crucial approximations are absorbed in:
(\mathbf{T} and E_{int}) in exact form are unknown.

Variation of E_{KS} with respect to ψ 's gives **Kohn Sham equations:**

$$\left(-\frac{1}{2} \partial^2 / \partial \mathbf{x}^2 + V_{\text{eff}}[n(\mathbf{r})] \right) \psi_i = \epsilon_i \psi_i$$

Local Density of Approximation (LDA) to E_{xc}

Assume that $E_{xc}[n]$ is a sum of contributions from each point in real-space depending **only on the density each point**, independent of other points:

$$E_{xc}[n] = \int d^3r n(\mathbf{r}) \epsilon_{xc}(n(\mathbf{r}))$$

Since ϵ_{xc} is assumed to be universal, it could be taken as the same as that of the homogeneous electron gas of a given density.

Exchange energy $\epsilon_x(n) = -0.458/r_s$ (Hartree),
 r_s being the Wigner Seitz radius.

Correlation energy $\epsilon_c(n)$:

- RPA result: good at high density
- Essentially exact Monte Carlo (Ceperly and Alder, 1980)
- Interpolation between high and low densities: Wigner (1934)

Generalized Gradient Approximation (GGA) to E_{xc}

Assume that $E_{xc}[n]$ is a sum of contributions from each point in real-space depending **only on the density and its gradient each point**, independent of other points:

$$E_{xc} = \int d^3r n(\mathbf{r}) \epsilon_{xc}(n(\mathbf{r}), \nabla n)$$

Many forms of GGA available (eg. PBE, PW91, etc):

Increase the magnitude of exchange energy – lower the total energy.

Decrease the magnitude of correlation energy – increases total energy (smaller in size relative to the change in exchange energy).

GGA led to improvements in estimation of cohesive, dissociation energies, and the DFT becoming more widely used in chemistry.

W. Kohn gets Nobel prize in Chemistry (1999).

Kohn-Sham equations:

Minimize $E_G[\{\psi_i\}]$ with respect to ψ_i with constraint of orthonormalization of ψ_i 's.

$$\left(-\frac{1}{2} \frac{\partial^2}{\partial x^2} + V_{\text{eff}}[n(r)] \right) \psi_i = \epsilon_i \psi_i$$

One is tempted to interpret ϵ_i 's as electronic energy eigenvalues, but indeed they are simply Lagrange's multipliers associated with the ort. Constraint!

Thus, band-gaps given by the difference between HOMO and LUMO or conduction and valence band energies are not expected to be right.

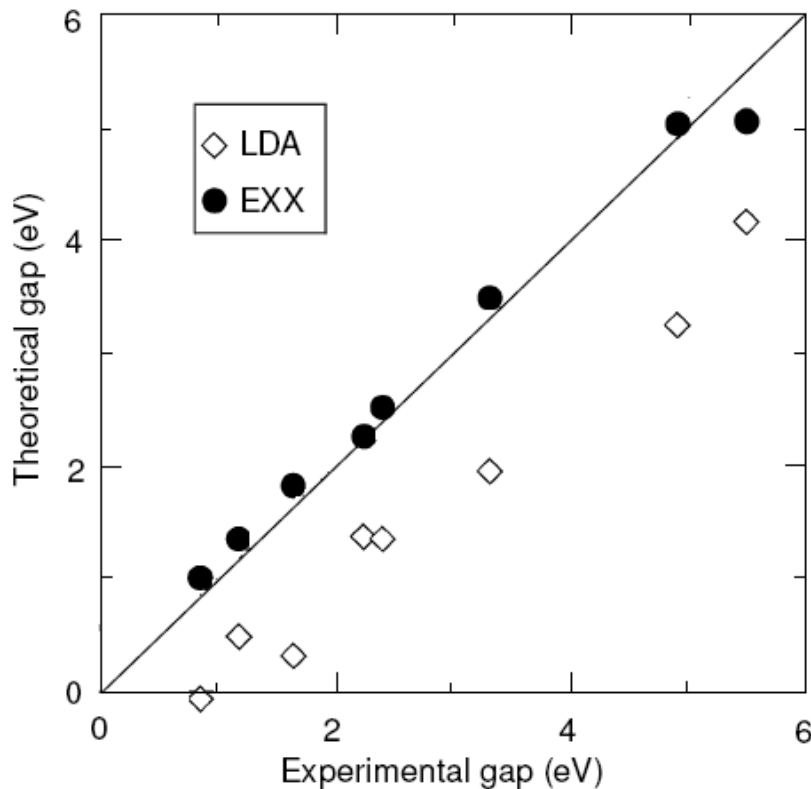
It is much easier to get the band structure qualitatively right, hence DFT also gives is reasonably well.

The main accomplishment of DFT is to get total energy Correctly.

Note that DFT is not the same as band-structure!

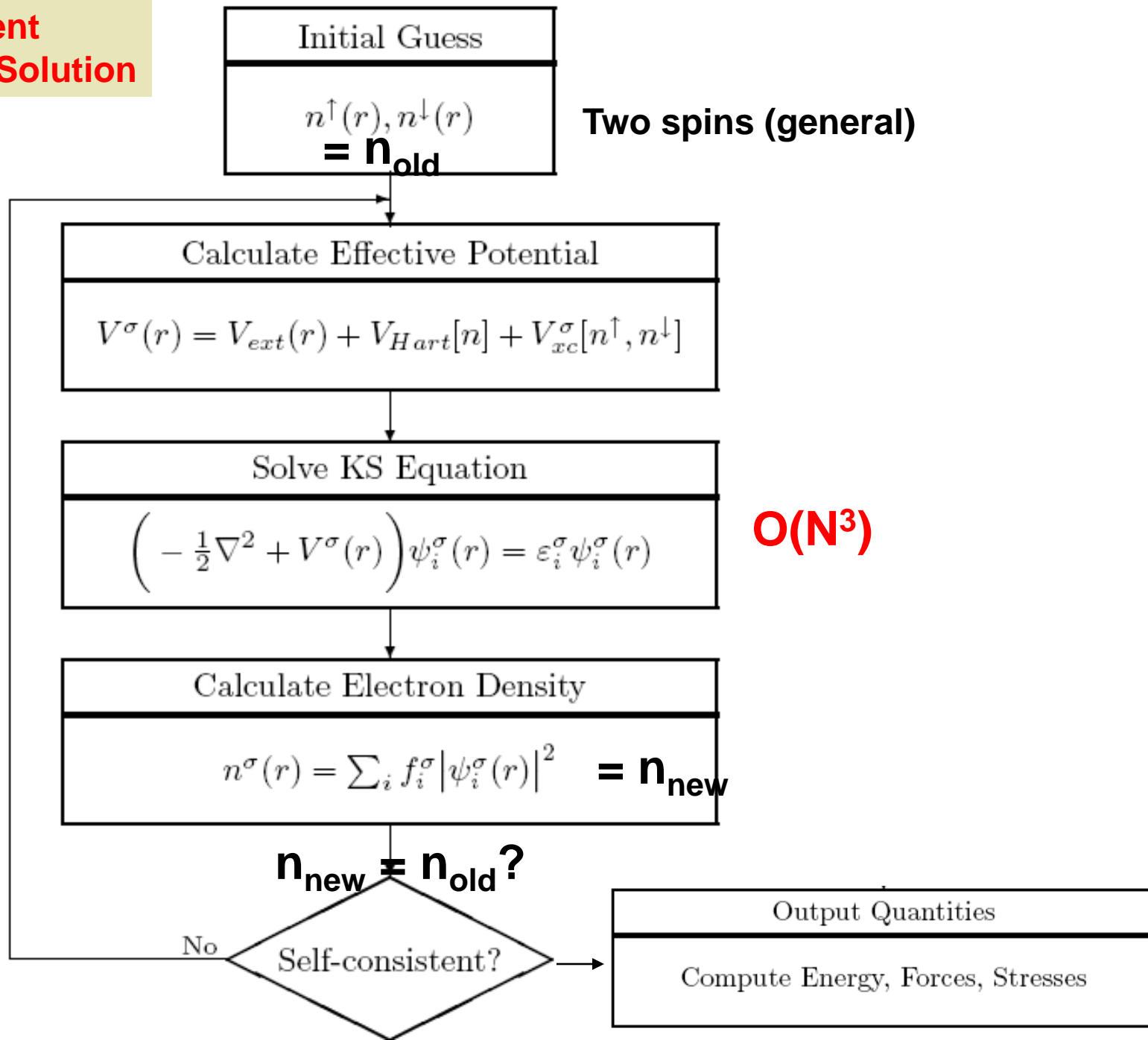
In fact, ϵ_i 's arising in the Kohn-Sham scheme do not have a physical meaning, except for the highest occupied state i .

Hence, accurate estimation of band-gaps is not expected. You need other techniques (like self-interaction correction or the time-dependent DFT).



Including exact exchange
Is found to have improved
the estimation of band-gaps.
(Staedele, et al).

**Self-consistent
Kohn-Sham Solution**



Kinetic Energy Functionals:

There have been efforts in taking the Hohenberg-Kohn theorem further in practical applications.

Note that in the Kohn-Sham functional,

$$\tilde{E} = \mathbf{T}_s + \int V_{ext}(\mathbf{r})n_{eff}(\mathbf{r})dr + E_{Hartree}[n_{eff}] + E_{xc}[n_{eff}]$$

Only \mathbf{T}_s is not known as a functional of density!

Many schemes of approximation of $\mathbf{T}_s[n]$ are available.
(Burke et al; Carter et al; von Witzsacker et al, etc).

Advantages of this KEF-based approach:

Orbital-free

Linear (O(N)) scaling both in memory and cpu time

Unfortunately,

The approximation of the KEF is not as generally good as one would like...
It is also coupled with a problem of having a good representation of core and valence electrons.

Limitations of Available Density Functionals

LDA/GGA do not capture vdW interactions and forces

Strongly correlated systems, such as Mott insulators, High T_c s/c, etc
Width of bands of d-states are over-estimated

Lattice constants (LDA) underestimated by 2 %

Cohesive energies (LDA) overestimated by 20-40 % (better with GGA)

Magnetic couplings are overestimated

Electronic dielectric constant is overestimated by 20 %

Caution!

Band gaps are *not* supposed to be correct in DFT band structure

(2n+1) Theorem (Gonze and Vigneron, 1989):

For a given change small change in potential parameterized by λ , Kohn-Sham solution (both wave-functions and energy) can be expanded in

powers of λ : $(\dots) \lambda + (\dots) \lambda^2 + (\dots) \lambda^3 + \dots$

Knowledge of Kohn-Sham wavefunctions up to order n is adequate to yield Kohn-Sham energy up to order $(2n + 1)$.

n^{th} order contribution $(\psi, E) = n^{\text{th}}$ derivative of (ψ, E) with respect to λ

- **2n + 1 Theorem(Gonze and Vigneron, 89)**

$$V_{ext} \rightarrow V_{ext}^{(0)} + \lambda V_{ext}^{(1)} + \lambda^2 V_{ext}^{(2)} + \dots$$

$$\psi_i \rightarrow \psi_i^{(0)} + \lambda \psi_i^{(1)} + \lambda^2 \psi_i^{(2)} + \dots$$

$$E_G \rightarrow E_G^{(0)} + \lambda E_G^{(1)} + \lambda^2 E_G^{(2)} + \dots$$

$$\{ \psi_i^{(1, \dots, n)} \} \Rightarrow E_G^{(2n+1)}$$

n=0: Ground state Kohn-Sham solution

2 n +1 = 1: All first derivatives of EG can be obtained from the ground state ψ 's.

Example:

- 1. Hellman-Feynman forces on atoms (deriv. wrt atomic position)**
- 2. Stress on the crystal (deriv. wrt strain)**
- 3. Magnetization (deriv. wrt magnetic field)**
- 4. Electric polarization (deriv. wrt electric field)**

n=1: Kohn-Sham DFT Linear Response

2 n +1 = 3: All second and third derivatives can be obtained from the first order (linear response) ψ 's.

Examples:

- 1. Force constant matrices**
- 2. Elastic constants**
- 3. Dielectric constant**
- 4. All the mixed second derivatives like piezoelectric const.**
- 5. Raman tensor (third deriv. wrt atomic position, E, E).**

$$(H_{KS}^0 - \epsilon_i^0) \psi_i^1 = (H_{KS}^1 - \epsilon_i^1) \psi_i^0$$

A note on electric polarization

Dipole moment: $\mu = \int r \rho(r) dr$,

Polarization P defined as dipole moment per unit volume can **not** be determined from charge density of a periodic crystal.

One has to use the geometric phase based theory of polarization, which determines P through Kohn-Sham Bloch functions.

$$\gamma_{\mathbf{n}} = i \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} dk \langle u_{k\mathbf{n}} | \frac{d}{dk} | u_{k\mathbf{n}} \rangle$$

$$P = = i e / (2\pi)^3 \sum_{\mathbf{n}} \int \langle u_{k\mathbf{n}} | d/dk | u_{k\mathbf{n}} \rangle dk = (1/V) \sum_{\mathbf{n}} \gamma_{\mathbf{n}}$$

Because of the subtlety of electric potential = - e E x, that operator x breaks the periodicity and can not be taken expectation value of, it is quite hard to treat nonzero electric field in periodic DFT studies.

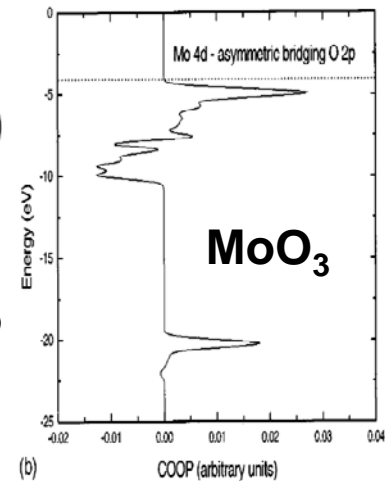
Perturbatively however, one can determine effects of electric field, such as dielectric constant, etc.

Linking Kohn-Sham wave functions to bonding:

Crystal Orbital Overlap Population (R. Hoffman)

$$\text{COOP}_{ij}(\epsilon) = \sum_{kn} \langle \psi_{kn} | \phi_{ik}^a \rangle \langle \phi_{jk}^b | \psi_{kn} \rangle S_{ij} \delta(\epsilon - \epsilon_{kn})$$

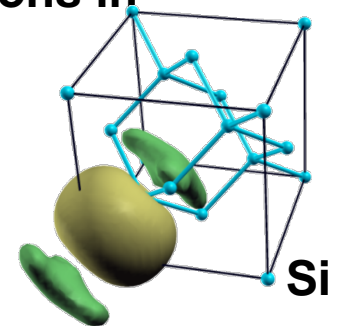
-ve: anti-bonding character, +ve: bonding character between two orbitals I and j , at an energy e .



Wannier Functions: Localized description of Kohn-Sham functions in a crystal:

$$W_n(\mathbf{r}) = \int_{\text{BZ}} d\mathbf{k} (e^{i\theta_{kn}}) \psi_{kn}(\mathbf{r})$$

Phase factors Θ 's chosen to ensure maximum localization!



Bond Orbital Overlap Population:

$$B_{lm}^I = \langle W_I | \phi_l \rangle (S^{-1})_{lm} \langle \phi_m | W_I \rangle$$

Contribution of different atomic orbitals (l, m) to bonding I :
a real-space picture of bonding

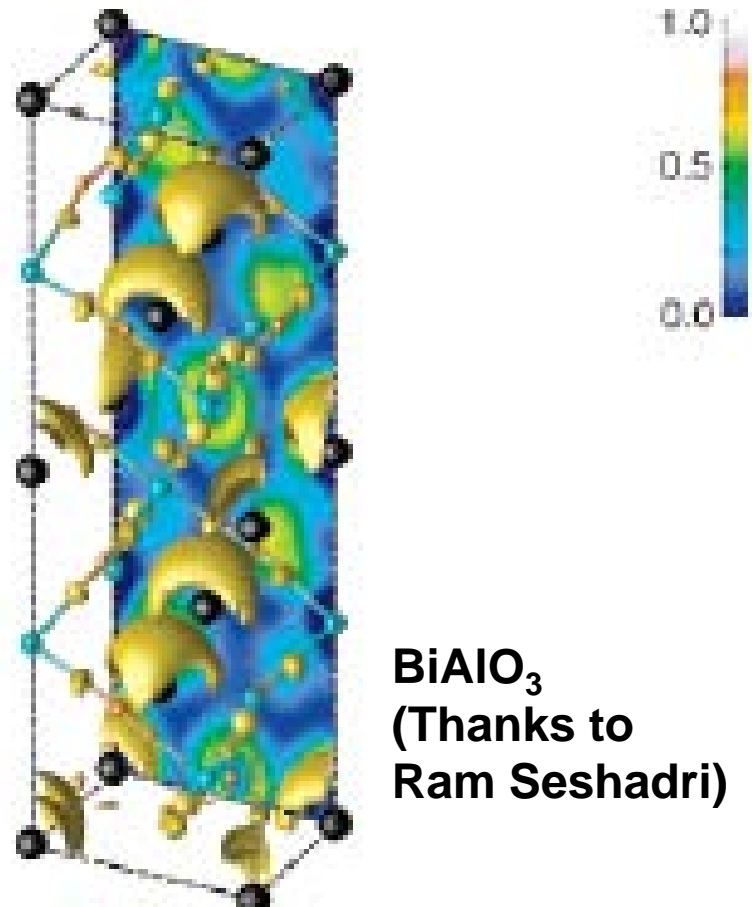
Linking Kohn-Sham wave functions to bonding (contd):

Topological Analysis (Bader) of charge density and of Electron Localization Function (ELF) (Silvi and Savin, 94):

ELF: Measure of another electron of the same spin to be localized near the reference point.

Exhibits shell structure for atoms and molecules.

Critical points of the density and ELF can be used to define bonds



Main Data Sets in a DFT calculation

- $\Psi_{kn}(x,y,z)$ (largest in size $\propto N_{\text{atom}}^2$)

Band index $n = 1, N_e$

Bloch vector $k = 1, M$ (size of the periodic supercell)

x,y,z inside a unit cell

- $\rho(x,y,z), V(x,y,z)$

(size $\propto N_{\text{atom}}$)

Kohn Sham Equations: $H \psi_{kn} = \epsilon_{kn} \psi_{kn}$

Eigenvalue problem



Method of solution depends on how you represent ψ_{kn} 's:

*** basis set:**

Plane wave ($e^{i\mathbf{G}\cdot\mathbf{r}}$): H is not sparse

Localized orbitals (eg. Gaussian): H is sparse

*** represent on a grid: H (kinetic energy) is sparse**

Parallelization: I

- Largest data-sets:

Kohn-Sham wave-fns $\psi_{k,n}(\vec{r})$

- Operations done often:

1. Orthogonalization: $\langle \psi_{k,m} | \psi_{k,n} \rangle = \delta_{mn}$ **$O(N^3)$**

2. Obtain $H_{KS} \cdot \psi_{k,n}$:

Sparsity: Localized basis/grid-based codes **$O(N^2)$**

FFTs: Plane wave basis **$O(N^2 \log N)$**

3. Charge density:

$$\rho(\vec{r}) = \sum_{kn} |\psi_{k,n}(\vec{r})|^2 \quad \mathbf{O(N^2)}$$

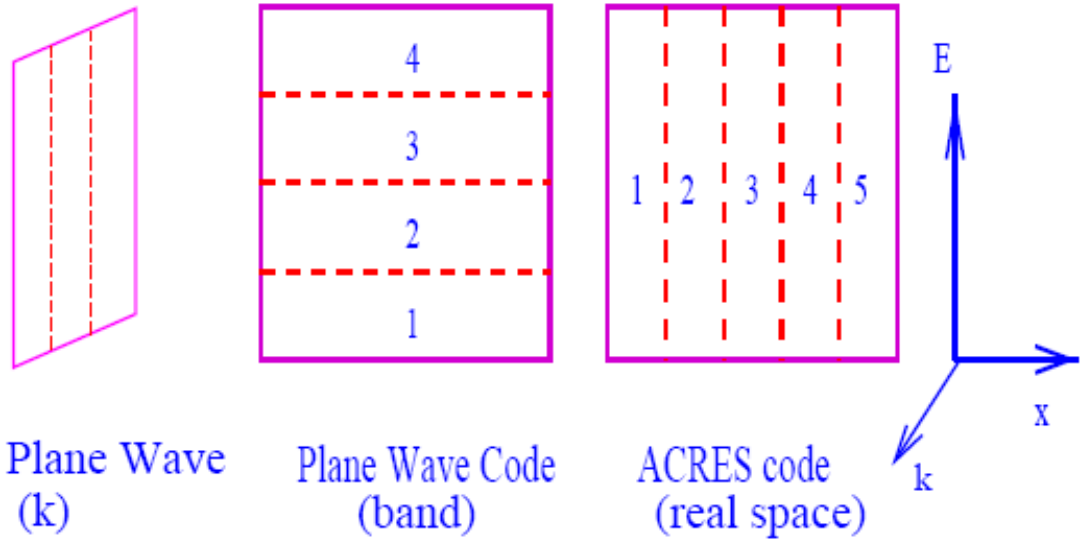
4. Hartree potential:

Solve Poisson equation OR **$O(N)$**

use fourier transform with FFT **$O(N \log N)$**

Parallelization II

- Large systems: 1 k-point
- Small systems: *many* k-points
- Scales:



- Different Advantages: wide applications

DFT-based Molecular Dynamics

- **Classical Molecular Dynamics of ions**
- **Force (Hellman Feynman) field and energy are determined from DFT calculation on the fly**

Ab Initio MD (AIMD):

A self-consistent DFT solution is obtained at a given set of ionic positions. Hence, the forces are very accurate, trajectory of ions is “exact”.

Car Parrinello MD (CPMD):

Electrons are also treated through a fictitious dynamics by defining a Lagrangian for parameters that define Kohn-Sham wave functions. At a given step/configurations, Kohn-Sham wave functions are approximate solutions, hence less accurate forces than AIMD.

However, the ionic trajectory remains in the neighborhood of the exact one in a stable way.

As a result, CPMD is usually faster than AIMD.

Thermodynamic simulations of materials.

Various methods and codes based on DFT

1. All-electron vs. Valence electrons-only codes:

In the former, the entire electronic Hamiltonian is solved whereas in the latter, the interaction between core electrons + nucleus and valence electrons is treated using a **pseudopotential**.

Note that pseudopotential is the second biggest approximation in most common DFT calculations.

2. Basis Set vs. Grid-based codes:

In the former, Kohn-Sham wave functions are written in terms of basis functions, while they are represented on a mesh or a grid in the latter.

All Electron codes: Stuttgart-LMTO, FP-LAPW (**WIEN-2K**),
HARES, TOMBO mixed basis, FPLO

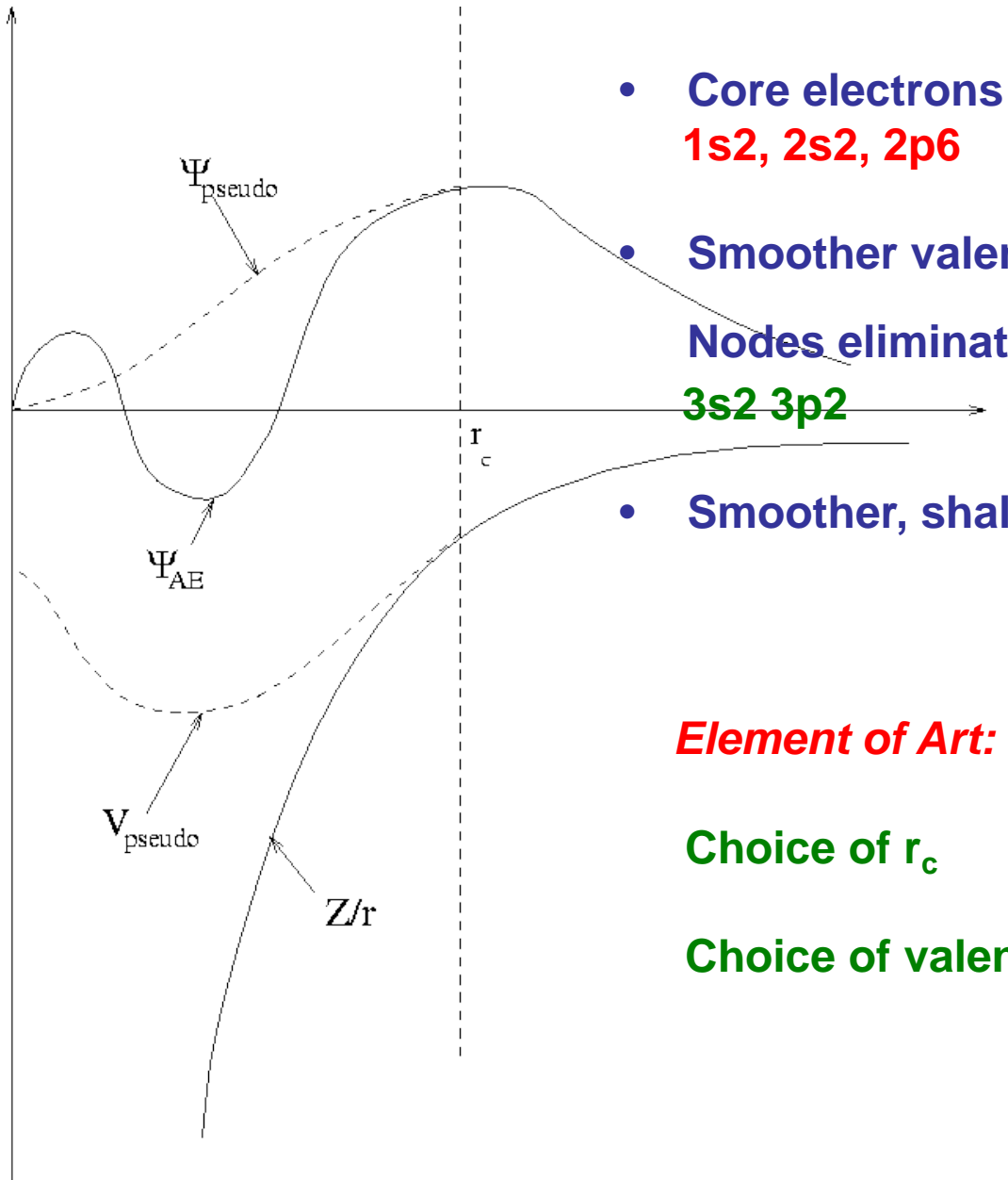
Pseudopotential codes:

ABINIT, QUANTUM-ESPRESSO, FHI98MD, SOCORRO,
CPMD, **CASTEP**, vasp,
SIESTA, HARES

Concept of a pseudopotential

Eg. Si:

$1s^2, 2s^2, 2p^6, 3s^2, 3p^2$



- Core electrons eliminated:
 $1s^2, 2s^2, 2p^6$
- Smoother valence wave-functions:
Nodes eliminated easier to represent
 $3s^2, 3p^2$
- Smoother, shallow potentials

Element of Art:

Choice of r_c

Choice of valence states

-
- All Electron DFT calculations are more accurate than the pseudopotential - based ones (assuming both done numerically well).
- A pseudopotential has to be tested in a well-known chemical environment close to what you may be interested in. It should give results identical/close to the results of AE calculations, wherever available.
- Localized basis (like in Siesta) give a sparse matrix representation of the KS hamiltonian, hence lead to very efficient [$O(N)$] methods; unfortunately the basis set has to be chosen with a lot of care and tested.
- Plane wave basis is most unbiased, in the sense that it is not dependent on a system of study. They allow very fast computation of forces and hence are most commonly used in the DFT-based MD codes. They are always used along with pseudopotentials to keep the size of the basis set in practical limits.
- Grid-based (or localized orbitals) codes are easy to parallelize by distributing the large data-set on different compute nodes.

When to use which code? *

A complex material with many atoms per cell and structural parameters,
Determination of structure, other simple ground state properties:

- **PWSCF/ESPRESSO** with ultra-soft pseudopotentials or **VASP**

Relatively simple materials, dielectric, other nontrivial properties, constrained
Structural determination:

ABINIT, PWSCF/ESPRESSO

Full phonon dispersion and thermodynamic modeling:

ABINIT, PWSCF; SIESTA+VIBRA

Electronic structure of complex oxides, insights into bonding, coupling
to tools for strong correlation:

FP-LMTO (Stuttgart)

Very large systems, determination of structure from a not-so-good guess:

SIESTA

Optimally, use a combination of methods: cross-checking, efficiency

* Note that this may not be exhaustive and should be used as a guideline!

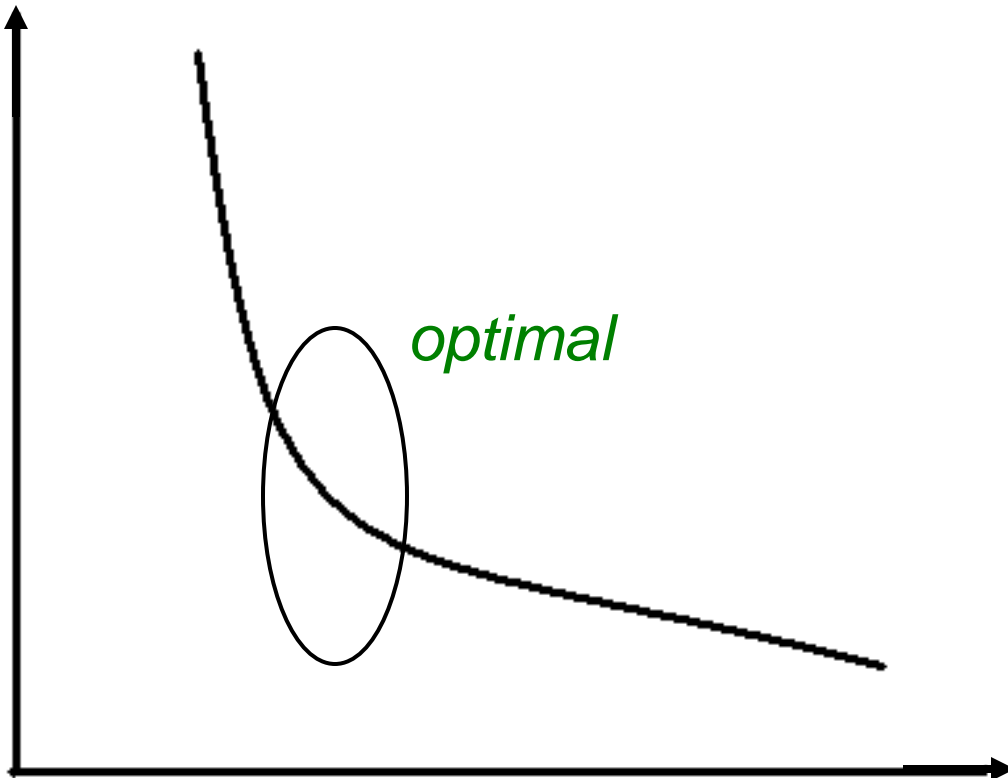
SUMMARY

First-principles Density Functional Theory based calculations:

Inputs: Atomic numbers and Atomic masses
and candidate structures

Output: Total energy, its derivatives (eg. Forces)
→ Structure, Electronic structure
→ Various properties
→ Molecular Dynamics: thermodynamics

**Computational
Cost**



optimal

Error



Accuracy

Direct use of first-principles DFT energy function in MD or Monte Carlo Simulations is often expensive.

Example, a DFT total energy calculation of a system with 200 atoms takes about 1 day on a 64-bit cpu (2010)

More importantly, a brute force simulation may not give much insights into the physics/chemistry of the material

Modeling is a good idea!

I Ab Initio Approaches

Electronic Problem: First-principles Methods
(Density Functional Theory)

Symmetries

Microscopic Picture:
Bonding, Couplings, Instabilities

integrate out DoF

H_{eff} : Effective Hamiltonian (model)
Focus on relevant phase subspace

eg. Ising,
Heisenberg
Lattice Dyna

Simulations

MD, Monte Carlo, FEM

Macroscopic, $T \neq 0$ Response,
Different length Scales phenomena
(Material-specific)

Energy, forces
Ab Initio MD,
Monte Carlo

Ab Initio
Modeling

II Hybrid Approaches: Quasicontinuum Methodology

Atomistic
treatment



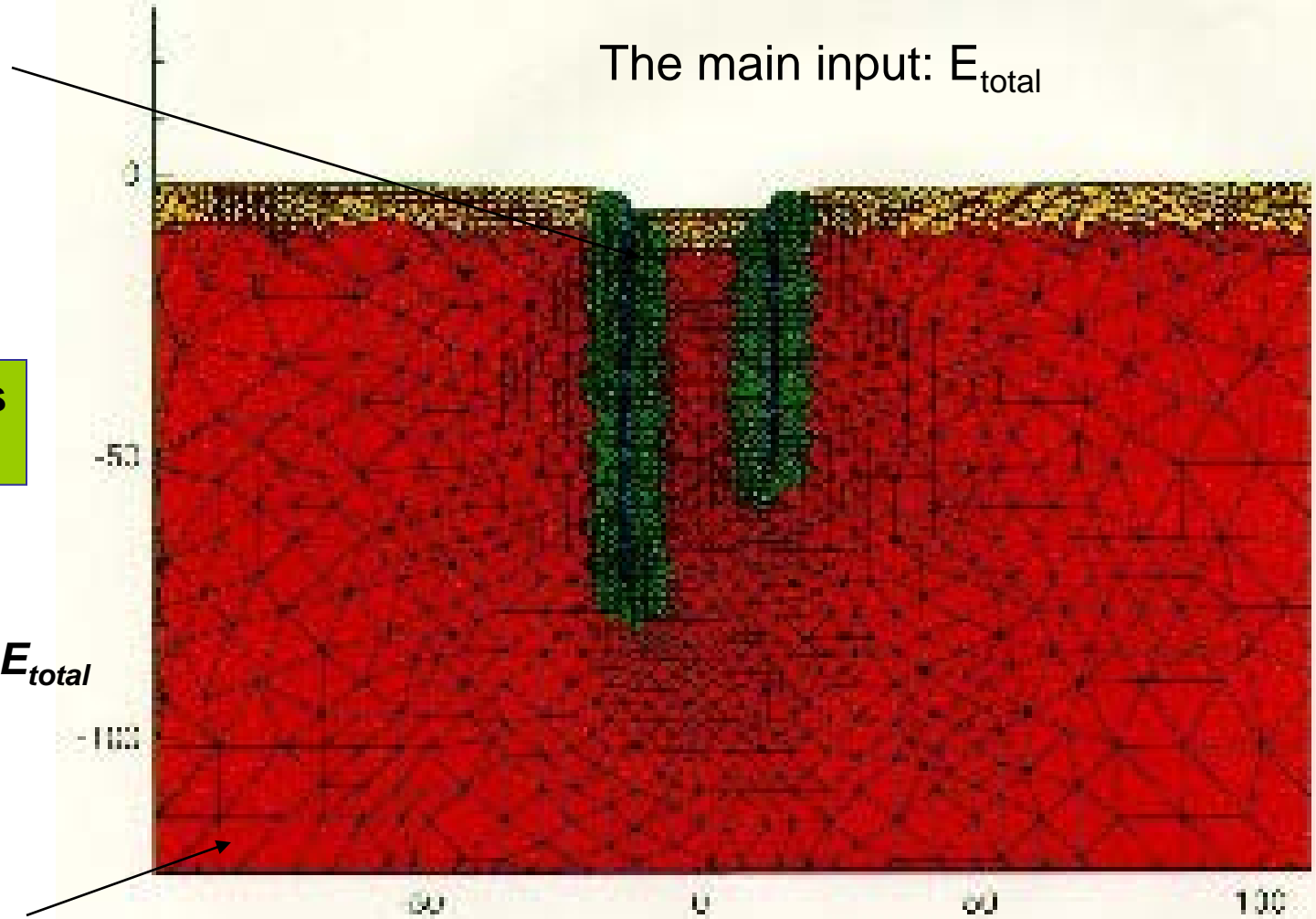
First-principles
methodology



Coarse-grained E_{total}



Continuum
treatment



Limitations: No dynamics, finite Temperature

<http://www.qcmethod.com/>

III Use of phenomenological theories with first-principles E_{tot} for a few *key configurations* as input

Properties such as ductility vs brittleness

- dislocation nucleation, motion
stacking fault energies
- Griffith criterion for Brittle failure
surface energies

Search of new materials:

- Too many possibilities
- Use a few microscopic indicators

Summary

DFT-based simulations or more generally computational materials science have now become a powerful way of doing science, like experimental and theoretical approaches.

Experimentalists still make decisions on “What is right” and make the major new discoveries!

Beyond density functional theory

1. **Time-dependent density functional theory: excited electronic states, transport, better description of correlation, etc.**
2. **Dynamical Mean Field Theory: treating electron correlations more accurately, understand trends in the properties of strongly correlated materials**
3. **Many body theory (pert) based corrections to DFT: energy gaps are estimated accurately.**
4. **Quantum Monte Carlo: essentially exact solution of many e problem**
5. **Non-equilibrium Green function: transport properties of molecules, nano...**
6. **Meta-dynamics: expand the time-scales achievable with AIMD or CPMD**

Useful Resources

Links to all sorts of softwares relating to Density Functional Theory:

<http://electronicstructure.org/software.asp>

Time dependent density functional theory:

<http://www.tddft.org/>

Symmetry and Crystallography of materials:

<http://www.cryst.ehu.es/>

Quantum Monte Carlo Methods:

<http://www.tcm.phy.cam.ac.uk/~mdt26/cqmc.html>

Numerical Methods/Recipes:

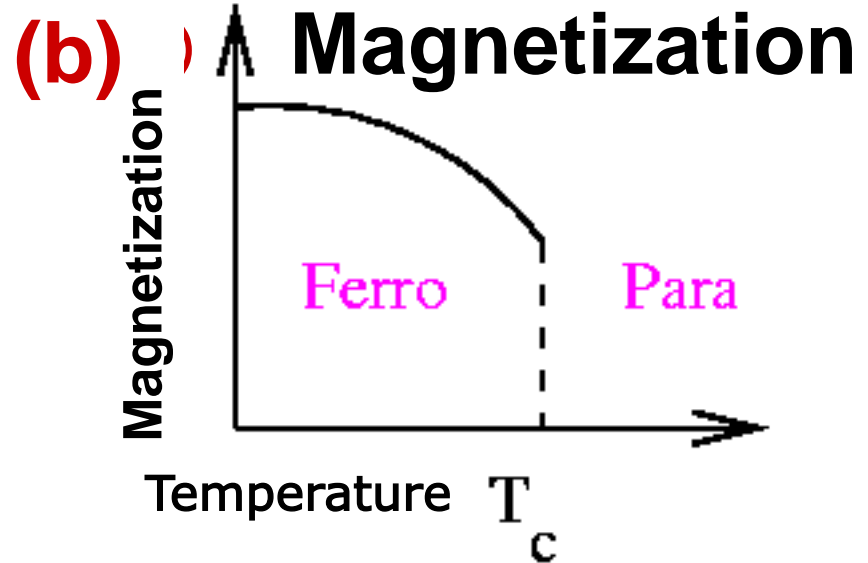
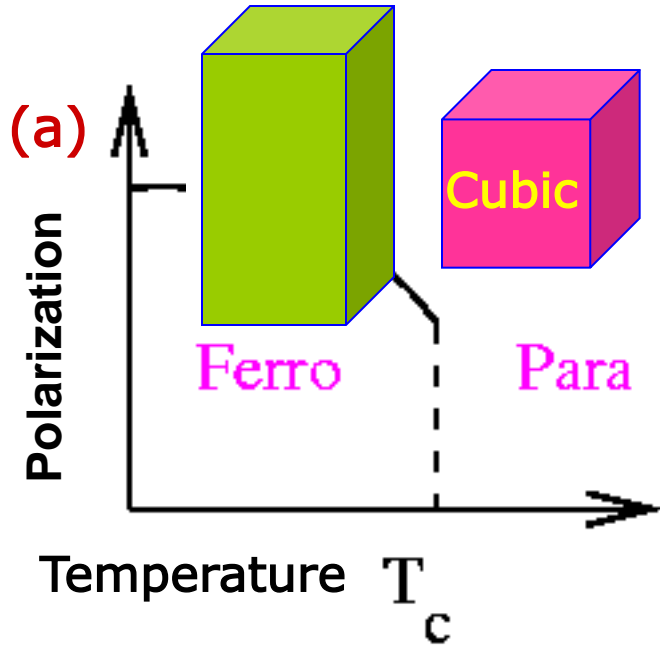
<http://www.nr.com/>

References

- M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, *Rev. Mod. Phys.* **64**,pp 1045-1097 (1992).
- X. Gonze, *Adv. in Quantum Chemistry* **33**,pp 225-239 (1999).
- S. Baroni, S. de Girancoli and A. Dal Corso, *Rev. Mod. Phys.* **73**, 515 (2001).
- R. M. Martin, *Electronic Structure: Basic Theory and Practical Methods*, Cambridge Univ. Press (2004).
- E. Kaxiras, *Electronic and Atomic Structure*

Extra slides

Phase Transitions, Symmetry Breaking: Landau Theory



Change in symmetry at T_c :

inversion symmetry broken in (a)

time reversal symmetry broken in (b)

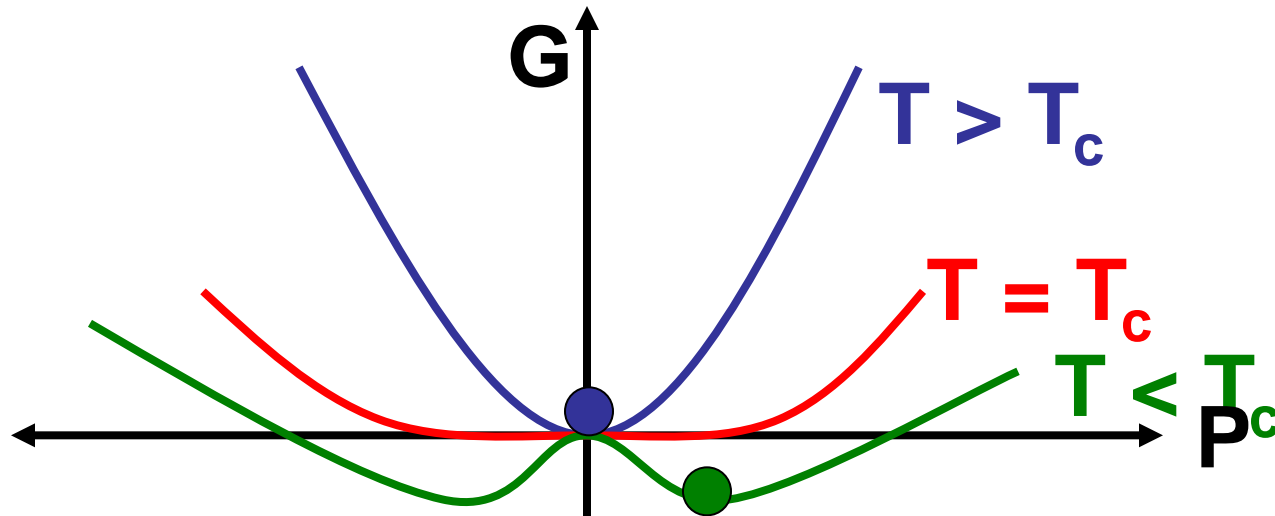
Low-T state is connected with the high-T state:

order parameter P and M .

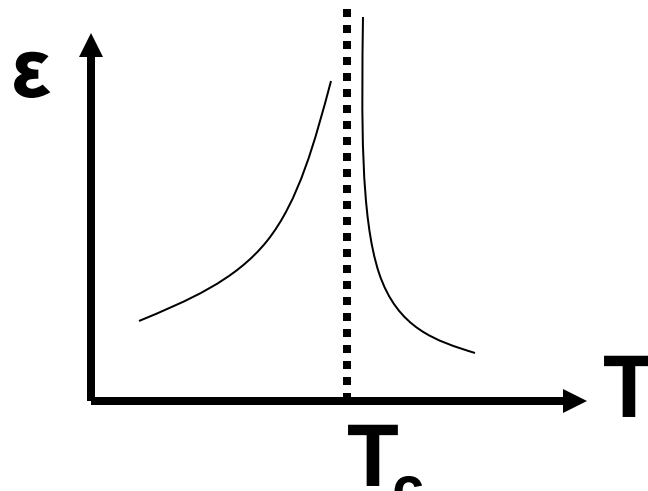
Landau free energy: $G = G_0 + A (T-T_c)P^2 + B P^4$

Landau Theory [phenomenology]:

Form of the free energy G is completely determined by symmetry.



$$\frac{1}{\varepsilon} = \frac{\partial^2 G}{\partial P^2} \Big|_{P=P_0}$$



Near a transition, susceptibility diverges: important to technology