Electronic Structure Calculations
An Overview

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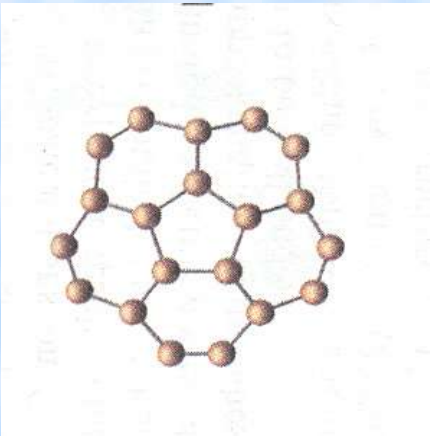
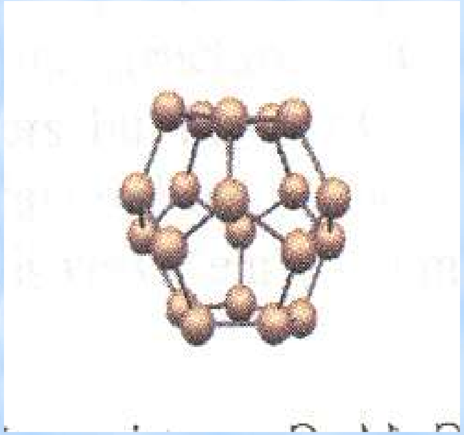
What are the questions we are interested in?

- **Properties of materials**
  - **How stable is a molecule, cluster or solid?**
    - **Binding energy (BE)**
    - **Ionization potential (IP),   electron affinity (EA)**

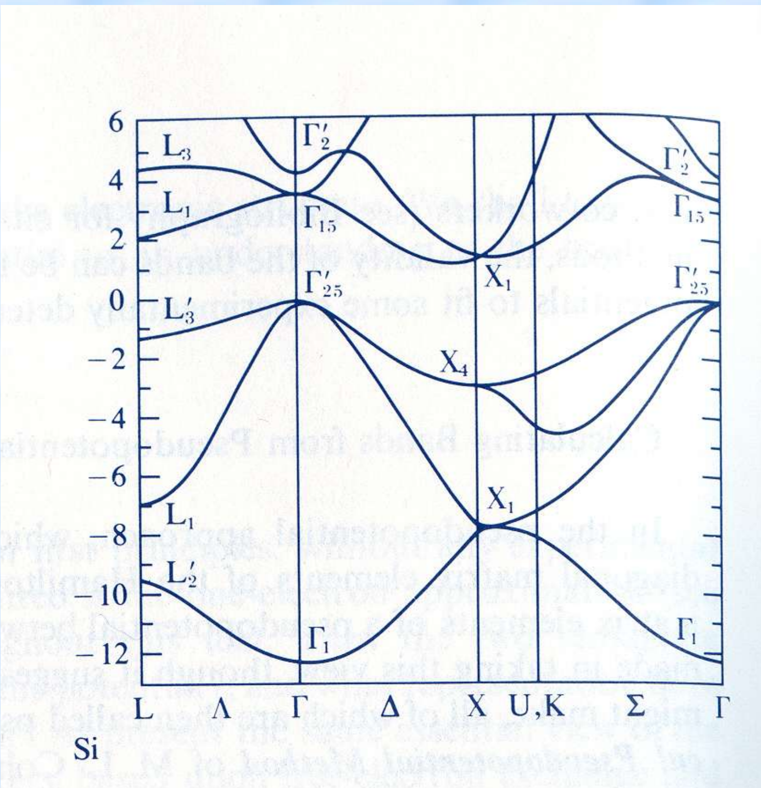




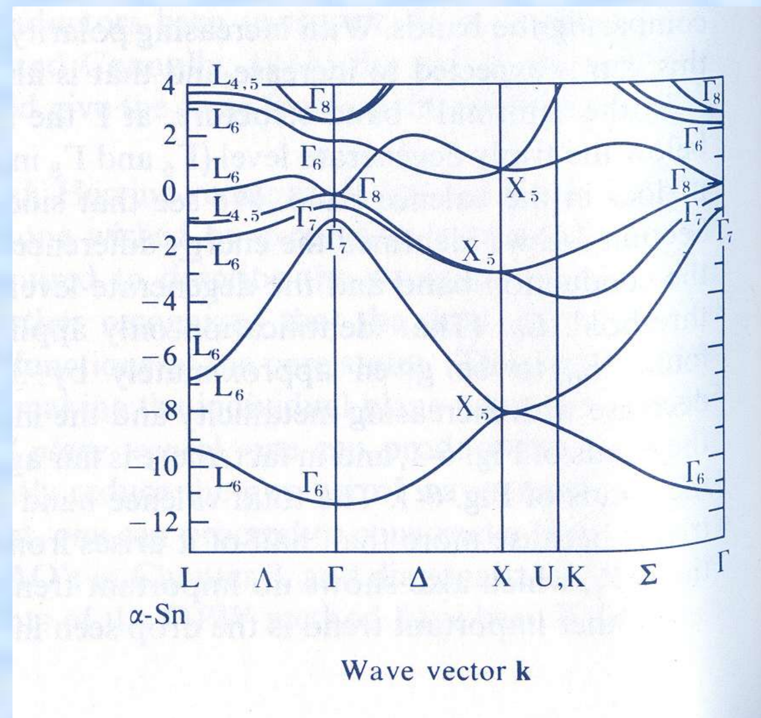
Ring **Bowl** **Cage**

C_{20} clusters

- What are the electronic energy levels in a molecule OR energy bands in a solid?
  - **Optical properties--Metal, insulator or semiconductor**



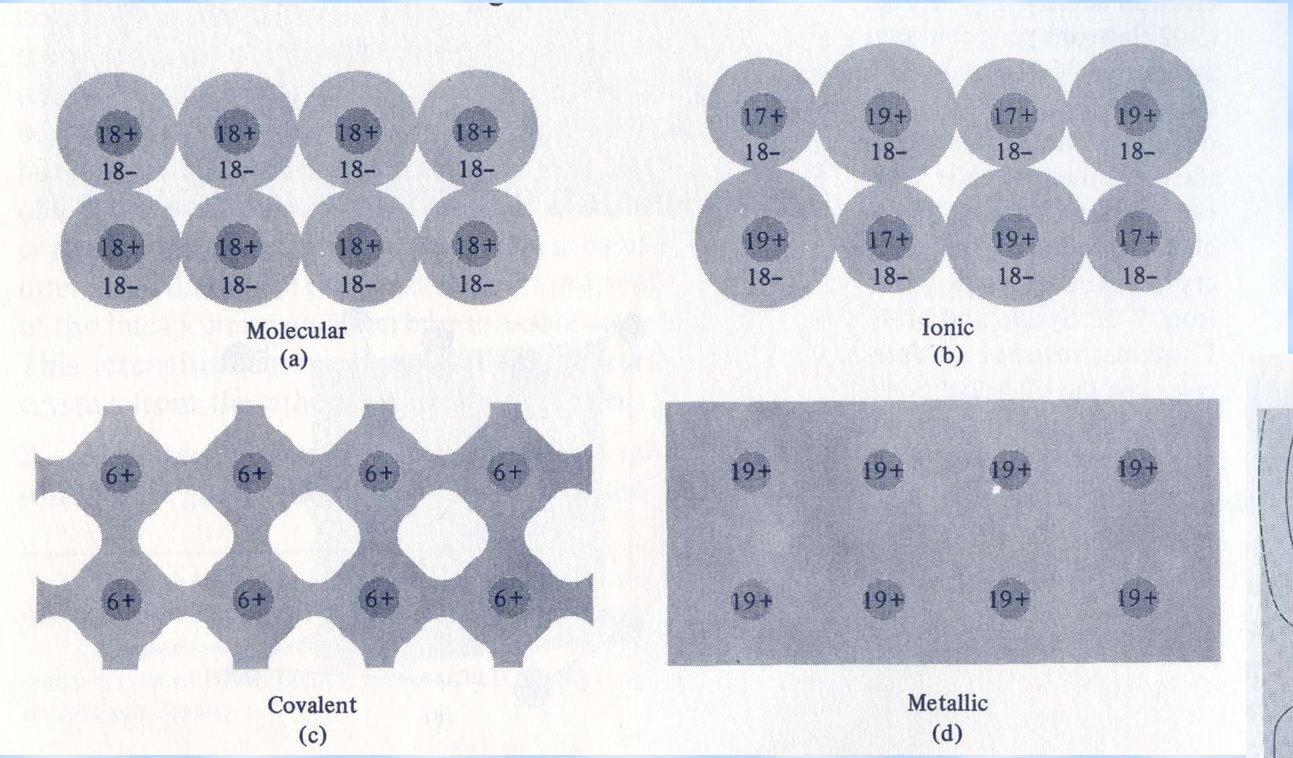
Si bands: gapped

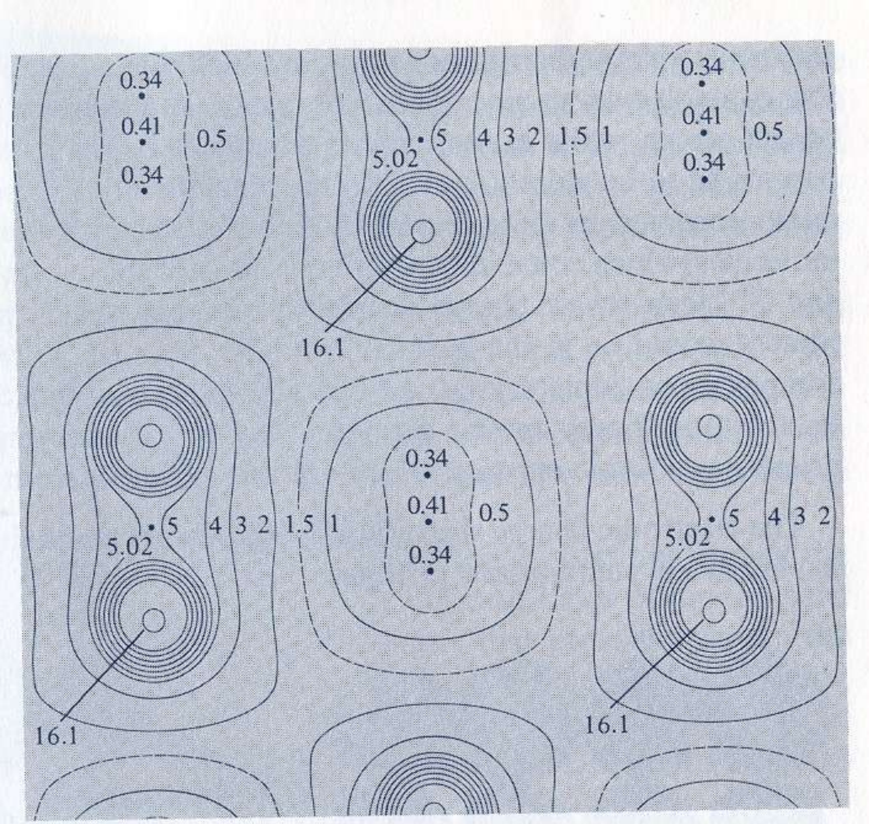


Sn bands: metallic

– **Nature of bonding**

- **Electronic charge distribution, moments**





(a)

– **Solid surfaces**

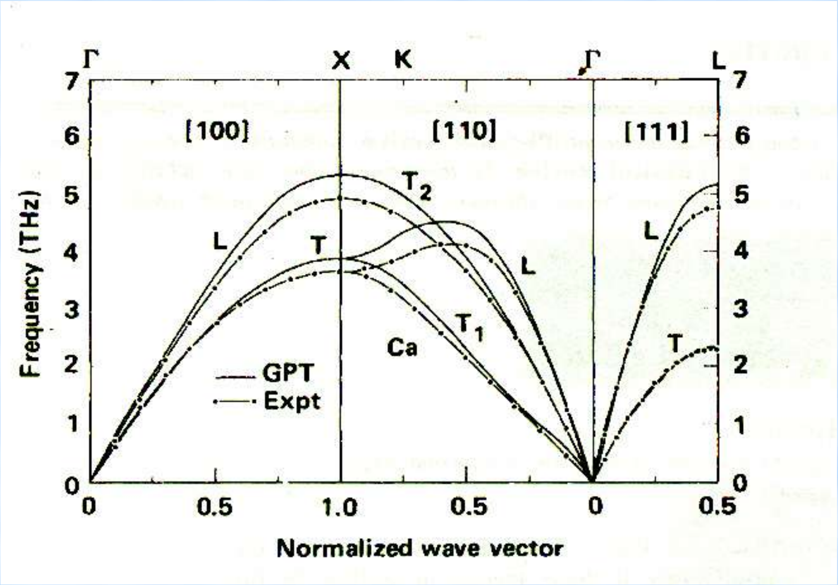
  - **Reconstruction: surface states/bands**
  - **Adsorption of atoms, molecules, adlayers**
  - **Nanowires on surfaces**

– **Motion of ion cores at zero or finite temperature**

  - **Structural relaxation OR molecular dynamics**

– **Vibrational spectrum of molecules**

– **Phonon spectrum of solids**



How do we answer these questions?

- Molecules or solids consist of atoms, which consist of electrons and nuclei
  - Quantum mechanical objects obeying Schroedinger's equation

$$H = -\frac{\hbar^2}{2m_e}\sum_i \nabla^2{}_i - \sum_{i,I}\frac{Z_I e^2}{|\vec{r}_i - \vec{R}_I|} + \frac{1}{2}\sum_{i \neq j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \frac{\hbar^2}{2M_I}\sum_I \nabla_I^2 + \frac{1}{2}\sum_{I \neq J}\frac{Z_I Z_J e^2}{|\vec{R}_I - \vec{R}_J|}$$

  - The task is to find the eigenvalues and eigenvectors of this Hamiltonian

$$H\Psi = E\Psi$$

- We cannot solve this exactly, make approximations:
  - I. Decouple electronic and nuclear motions (BO)
    - Electronic Hamiltonian (a.u.)

$$H = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_{i,I}\frac{Z_I}{r_{iI}} + \sum_{i<j}\frac{1}{r_{ij}}$$

    - Total energy

$$\epsilon_{tot} = \langle\Psi|H|\Psi\rangle + \sum_{I<J}\frac{Z_I Z_J}{R_{IJ}}$$

  - Ground state wavefunction is Ψ that gives the lowest total energy

We cannot (exactly) solve the electronic problem either

- Further approximation
  - We know
    - Many electron wavefunction is antisymmetric

$$\Psi(X_1, X_2, \ldots, X_i, \ldots, X_j, \ldots, X_N) = -\Psi(X_1, X_2, \ldots, X_j, \ldots, X_i, \ldots, X_N)$$

$$X_i = \{\vec{r}_i, \sigma_i\}$$

    - For non-interacting electrons a single (Slater) determinant of spin orbitals is the exact wavefunction

$$\Psi = (N!)^{-1/2} \begin{vmatrix} \chi_1(x_1) & \chi_1(x_2) & \cdots & \chi_1(x_N) \\ \chi_2(x_1) & \chi_2(x_2) & \cdots & \chi_2(x_N) \\ \vdots & \vdots & & \vdots \\ \chi_N(x_1) & \chi_N(x_2) & \cdots & \chi_N(x_N) \end{vmatrix}$$

$$\equiv |\chi_1, \chi_2, \ldots, \chi_N\rangle$$

- II. HF approx, Claim: Even in the interacting system, a single determinant is the correct form of the wavefunction
  - Minimize energy to calculate the optimum spin-orbitals
  - Constraint: spin orbitals are orthonormal

  ⇒ Electrons move in an **effective 1-body, nonlocal** potential

- We have a scheme to find a solution to S' equation
- What does HF imply?
- Probability of finding two electrons at the same point in space
  - Non-zero if the spins are opposite **P(↑↓)** ≠0
  - Zero if the spins are parallel **P(↑↑)** =**0**
- **HF incorporates exchange effect but no correlation**

Another approach to interacting electron system: Density Functional Theory

- G.S. energy of a system of interacting electrons is a functional of its density (Hohenberg-Kohn)

$$E[\rho]=\int v_n(\bar{r})\rho(\bar{r})d\bar{r}+V_{ee}[\rho]+T[\rho]$$

- Minimize *E* but the functionals *V* and *T* are unknown
- Kohn-Sham method of solution: noninteracting electrons moving in

$$v_{eff}(\bar{r})=v_n(\bar{r})+\frac{\int\rho(\bar{r}')}{|\bar{r}-\bar{r}'|}d\bar{r}'+v_{xc}(\bar{r})$$

Exchange-correlation pot.

- We need to solve:

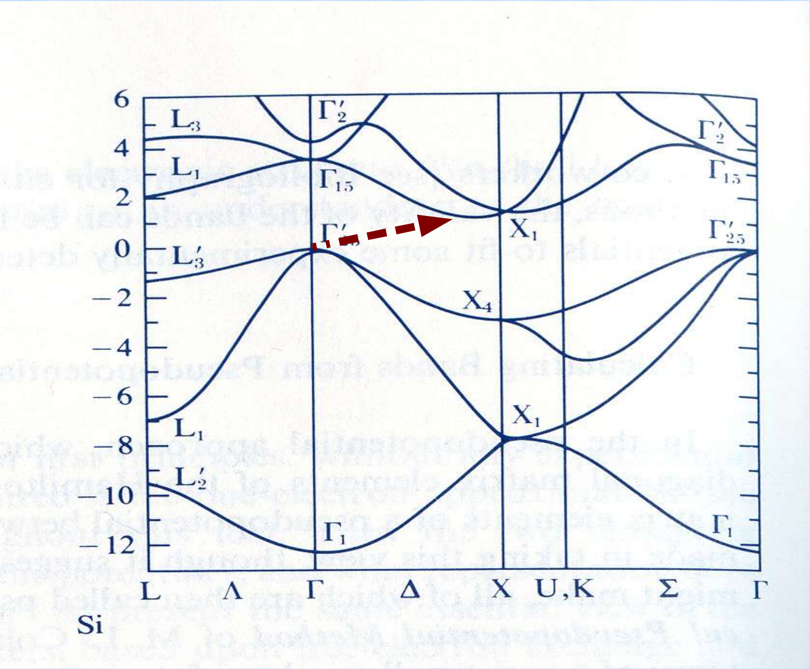
$$\left[\frac{-1}{2}\nabla^2+v_{eff}(\bar{r})\right]\psi_i=\epsilon_i\psi_i \text{ with } \qquad \rho(\bar{r})=\sum_{occ}|\psi_i(\bar{r})|^2$$

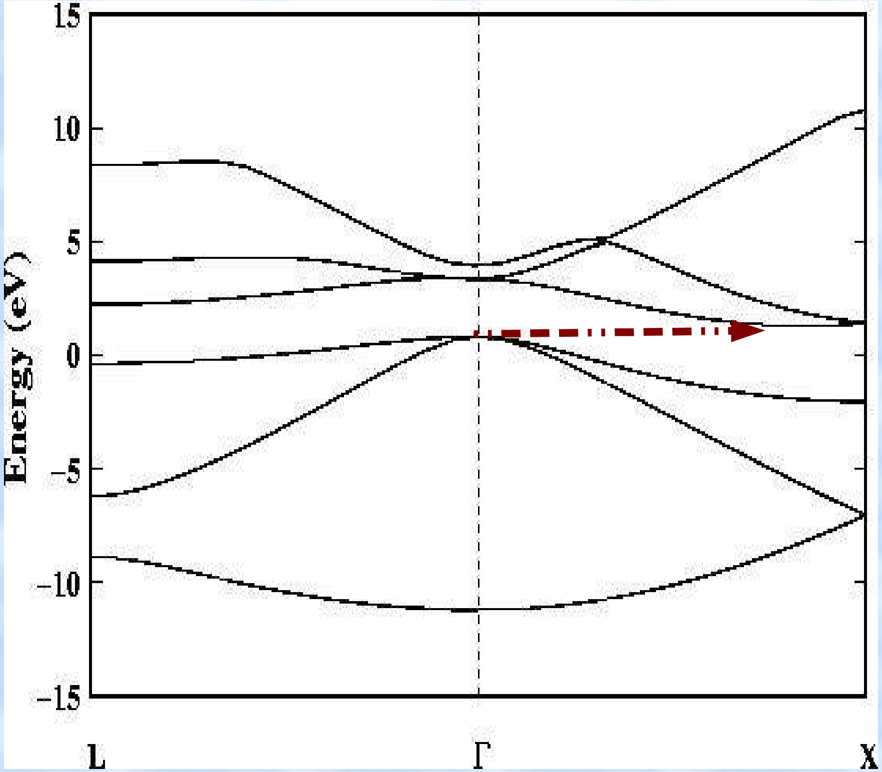
- **Again, we do not know v_{xc}**
- **Local Density Approximation (LDA)**: exch-corr energy in each infinitisimal vol = exch-corr energy of a *homogeneous* e-gas with same density as in the infinitisimal vol.
- LDA includes both exchange and correlation, but simplistically. Improvement---
  - **GGA's**
- Though extremely simple, LDA has been remarkably successful
- No qualitative improvement with GGA's

Applications are too many to list

Some random examples

- Band structure of Si





Expt Gap ~1.1 eV

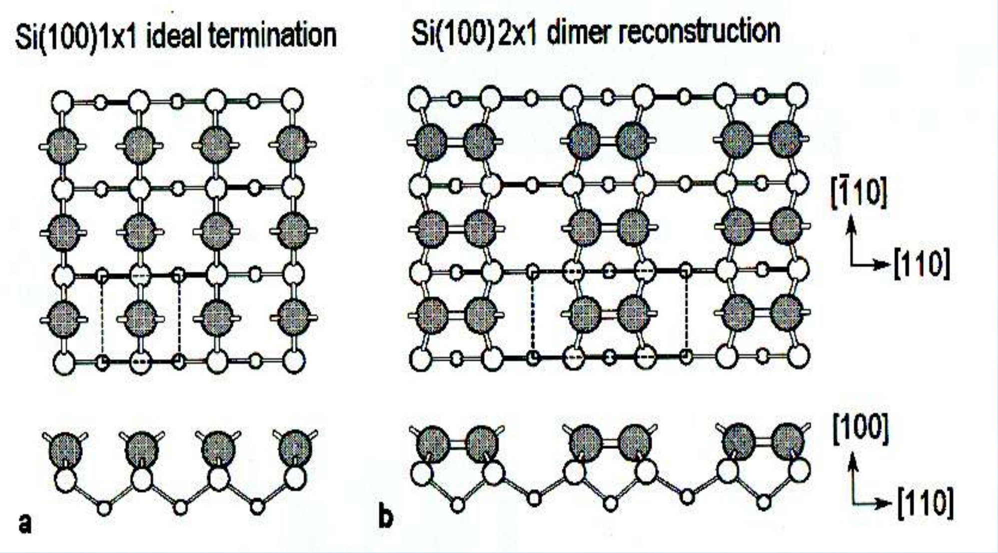
LDA Gap ~0.5 eV

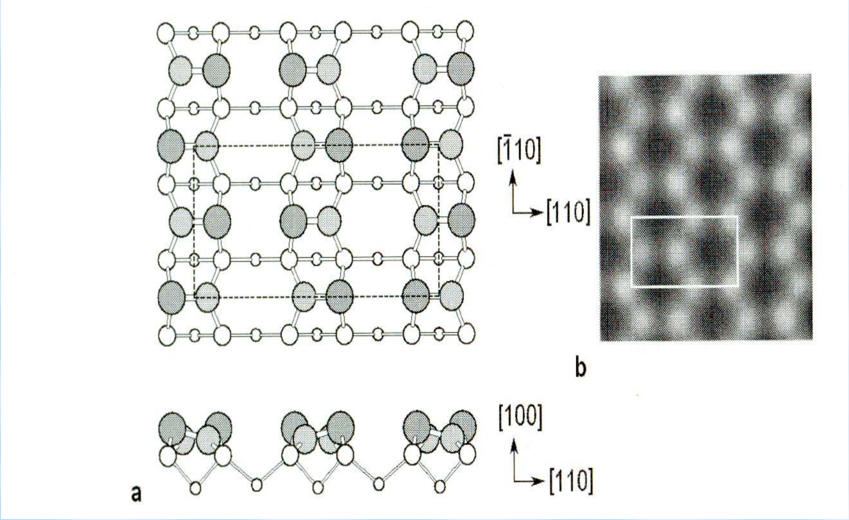
LDA underestimates band-gap

- Binding energy/stability
  - Cohesive energy of bulk Si (eV/atom)

HF	LDA	expt
4.02	5.28	4.62(8)

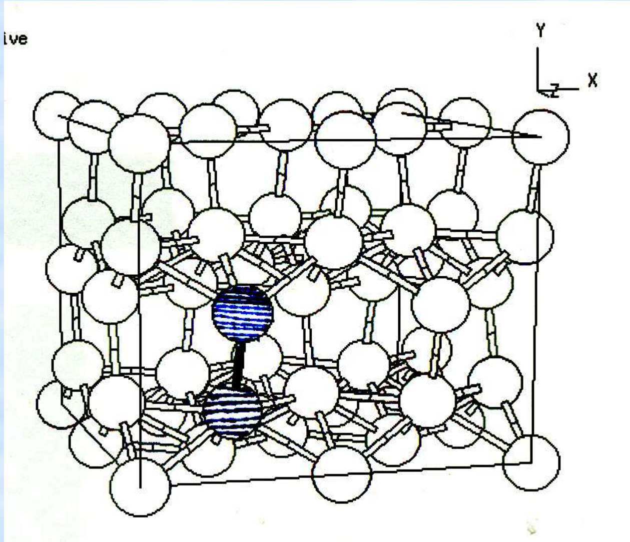
- Si(100) surface
  - Reconstruction



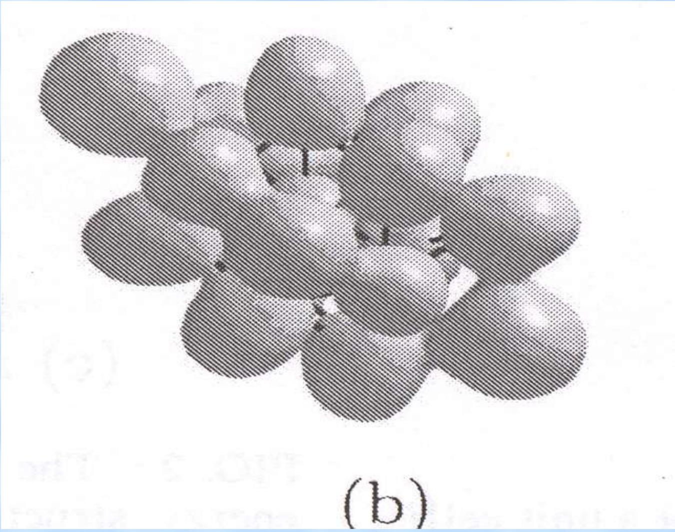


Nature of bonding

- **Ga clusters**
  - Ga clusters melt at higher T compared to bulk Ga!!



Bulk



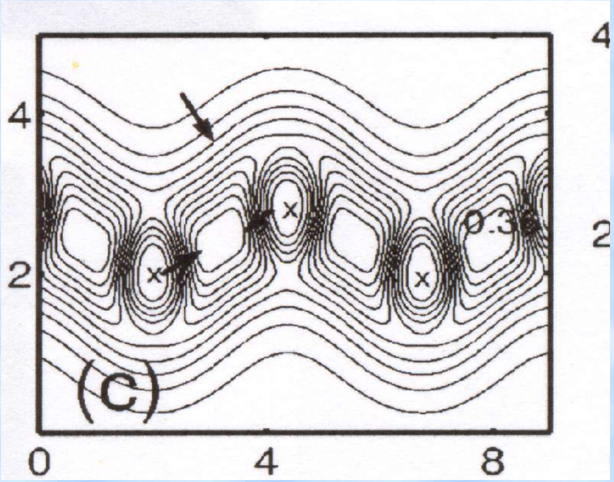
Breaux et al PRL '03
Chako et al PRL '04

Ga_{17} cluster

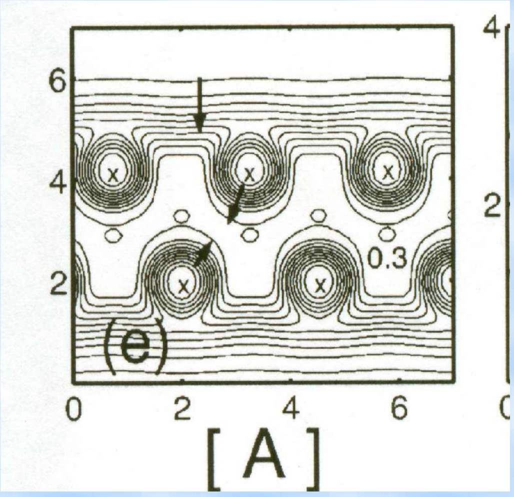
- **Happens in other systems: Al wire vs. bulk**

Sen et al '01

Bulk



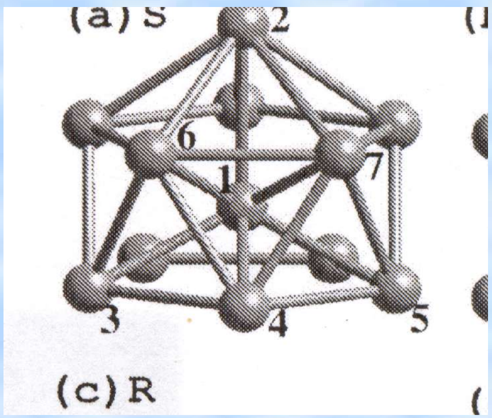
Wires



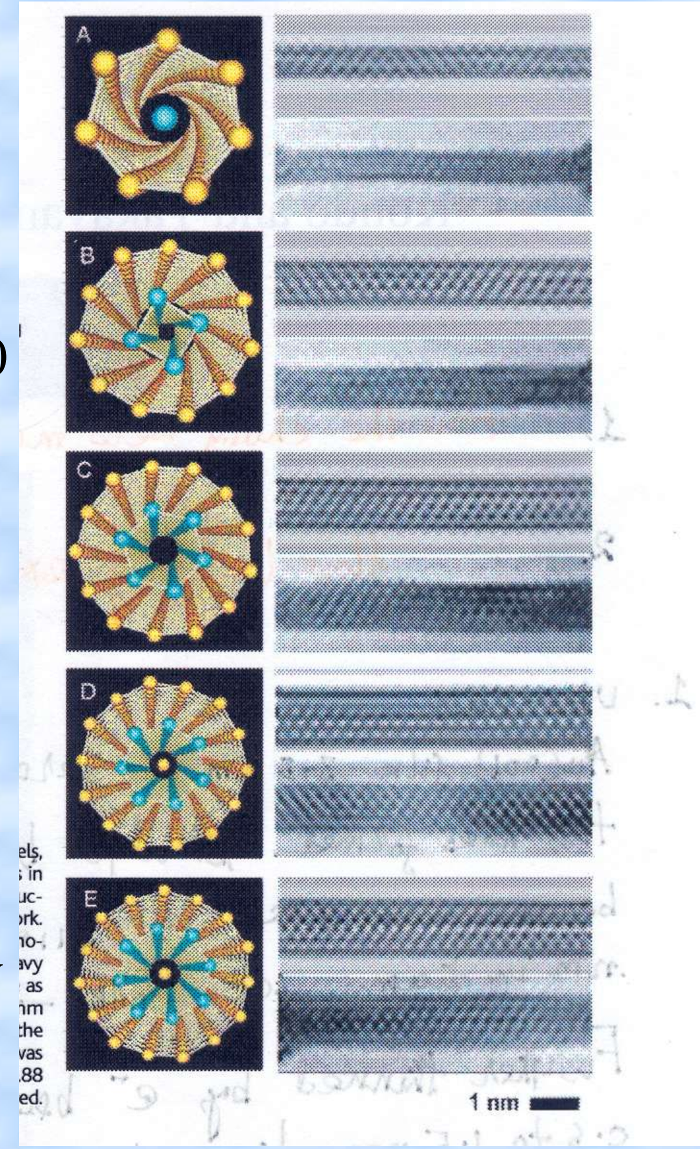
Predicting new materials

- Pentagonal nanowires
  - Motivated by experiments on Au wires

Kondo & Takayanagi Sc. 2000



Sen et al '02



- Experimentally confirmed recently by

Gonzalez et al. PRL '04

Can we incorporate correlation effects over HF?

- **Different approach taken in quantum Monte Carlo methods**

- QMC methods rely on (many-body)wavefunctions
  - Exact wavefunctions are unknown for interacting system
  - Exact equations are impossible to solve (otherwise we would not need approximate methods)
  - Wavefunctions may be complicated quantities, particularly for large systems

- Let's see how much we know about wavefunctions and what we actually can do

- **Relevant properties of many-electron wave functions**

- **Many-body Ψ is anti-symmetric**

- Local energy is constant for an eigenfunction

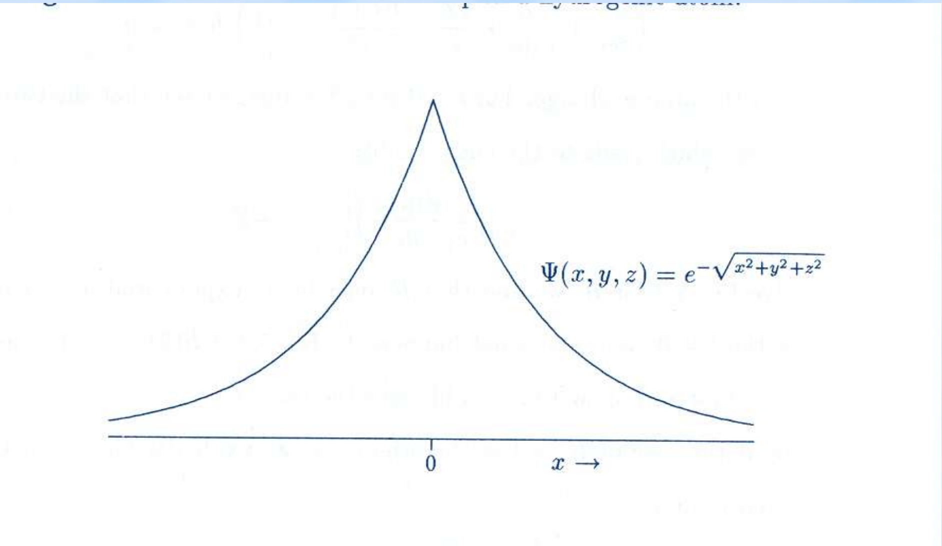
$$E_L = \frac{H\Psi_i(\vec{R})}{\Psi_i(\vec{R})} = \frac{E_i\Psi_i(\vec{R})}{\Psi_i(\vec{R})} = E_i$$

$\Rightarrow$ Ψ should obey e-e and e-n cusp conditions

- Singularities in V (1/r) should be canceled by those from KE

  - Example: H atom 1*s*

wavefunction



Slater-Jastrow wavefunction

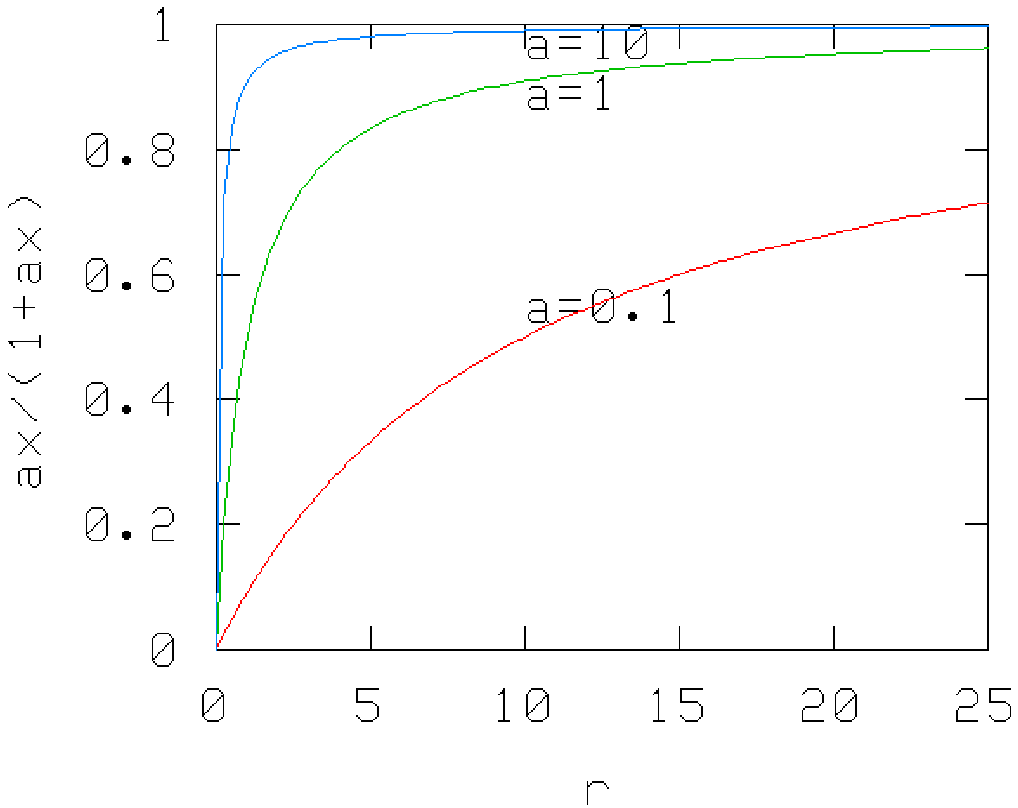
- Slater wavefunction cannot have e-e cusp
  - As there is no r_{ij} dependence
- The functional form we use for the trial function

$$\Psi_T = \exp\left[\sum_I \sum_{i<j} \boldsymbol{u}(\boldsymbol{r}_{iI}, \boldsymbol{r}_{jI}, \boldsymbol{r}_{ij})\right] \boldsymbol{D}^{SL}$$

where

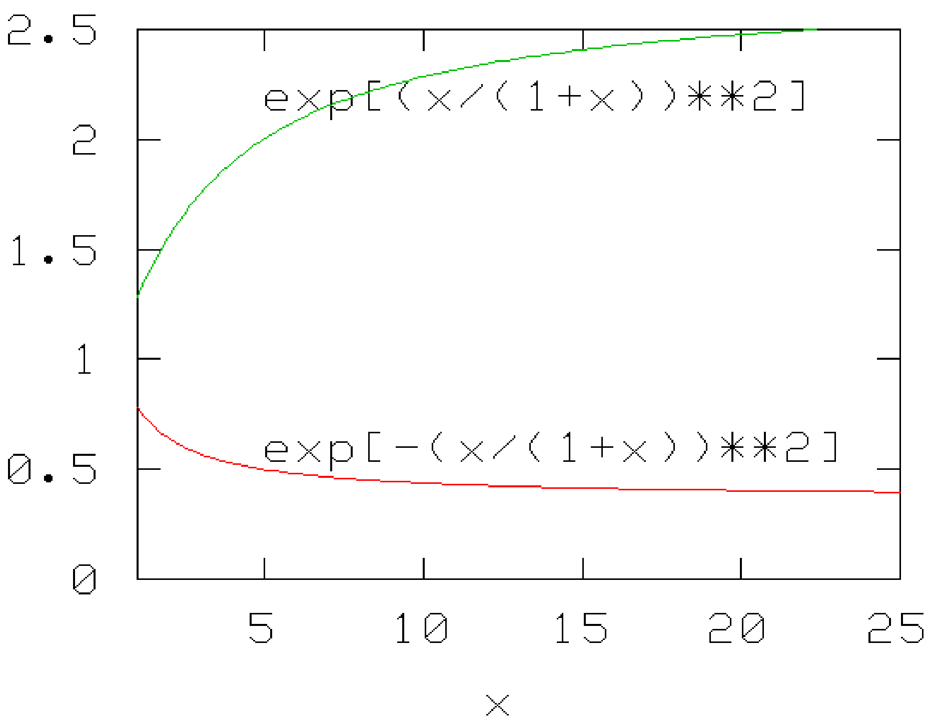
$$\boldsymbol{u}(\boldsymbol{r}_{iI}, \boldsymbol{r}_{jI}, \boldsymbol{r}_{ij}) = -\frac{\boldsymbol{C}}{\gamma} \mathrm{e}^{-\gamma r_{ij}} + \sum_{k<l,m} \boldsymbol{c}_{klm}\left[\alpha_k(\boldsymbol{r}_{iI})\alpha_l(\boldsymbol{r}_{jI}) + \alpha_k(\boldsymbol{r}_{jI})\alpha_l(\boldsymbol{r}_{iI})\right]\beta_m(\boldsymbol{r}_{ij})$$

- First term in u: e-e cusp conditions
  - C=1/4 for like =1/2 for unlike spins
- Remaining part introduces correlations
- γ and c_{klm} are variational parameters



Pade' functions

Exponential Pade' functions



Variational Monte Carlo (VMC)

- We need to evaluate integrals like:

$$E_{VMC}=\frac{\int \psi_T^2[H\psi_T/\psi_T]\,d\vec{R}}{\int \psi_T^2\,d\vec{R}}$$

  - Where R_i are distributed according to $\Psi_T^{\,2}$

$$E_{VMC}=\lim_{M\to\infty}\frac{1}{M}\sum_{i=1}^{M}E_L(\vec{R}_i)$$

  - Use stochastic methods to evaluate this multi (3N)-dim integral

- γ and c_{klm}'s are optimized **by minimization of variance of the local energy**

$$\sigma_{VMC}^2\approx\frac{1}{M}\sum_{i=1}^{M}\left[E_L(\vec{R}_i)-E_{VMC}\right]^2$$

- Cohesive energy of bulk Si (eV/atom)

DMC	LDA	HF	Expt
4.63(2)	5.28	4.02	4.62(8)

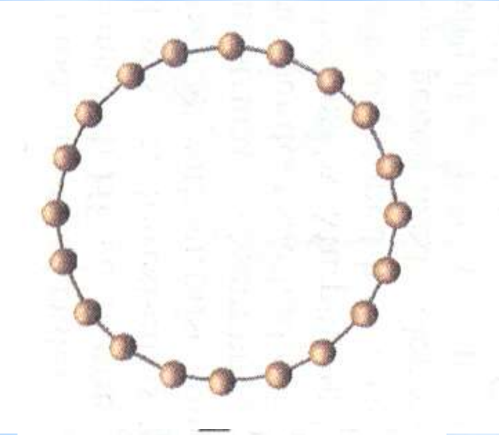
- Binding energy of ***TiO*** molecule.
  - **Binding energies (eV) from various methods**

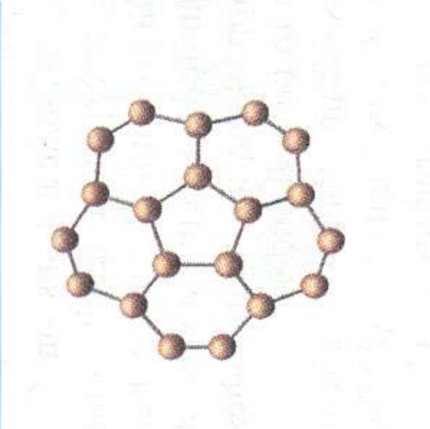
HF	**2.64**
DFT (LSDA)	**9.11**
DFT (PW91)	**7.45**
QMC	**6.7(1)**
Experiment	**6.98(17)**

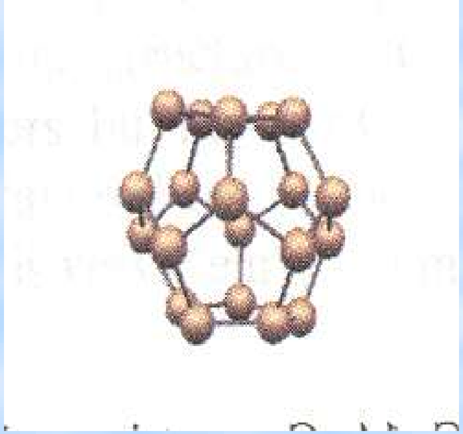
Wagner & Mitas '03

- QMC provides the best theoretical value to date though expensive!

- C_{20} clusters







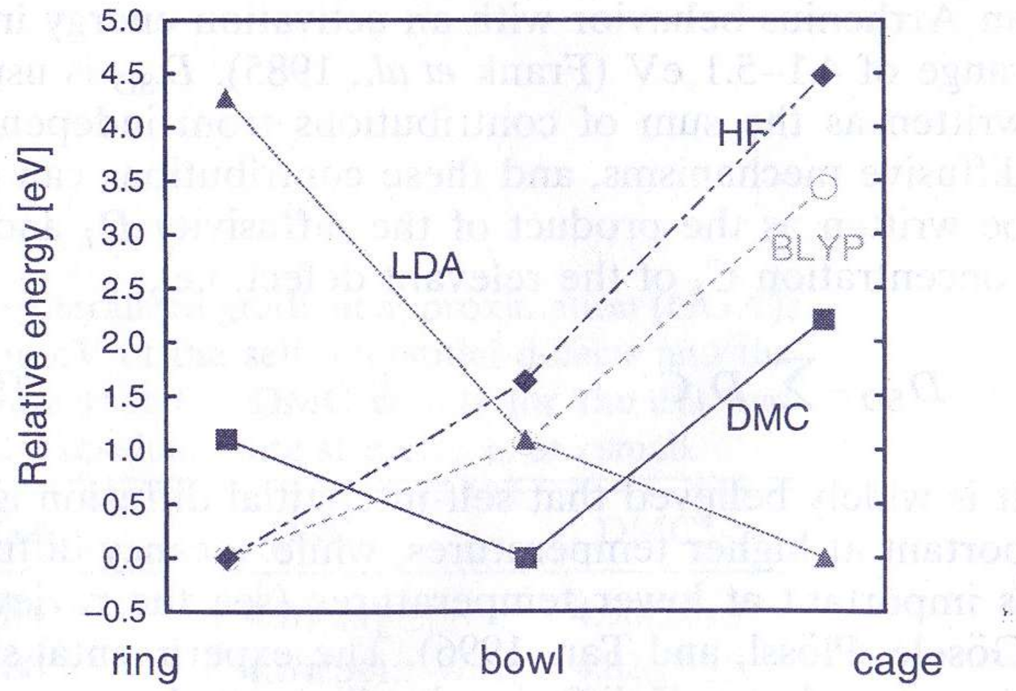


FIG. 15. Relative energies of C_{20} isomers from the HF, LDA, BLYP, and DMC methods. The energies are given relative to the lowest-energy isomer within the given theory. From Grossman, Mitas, and Raghavachari, 1995.

Grossman & Mitas PRL '95

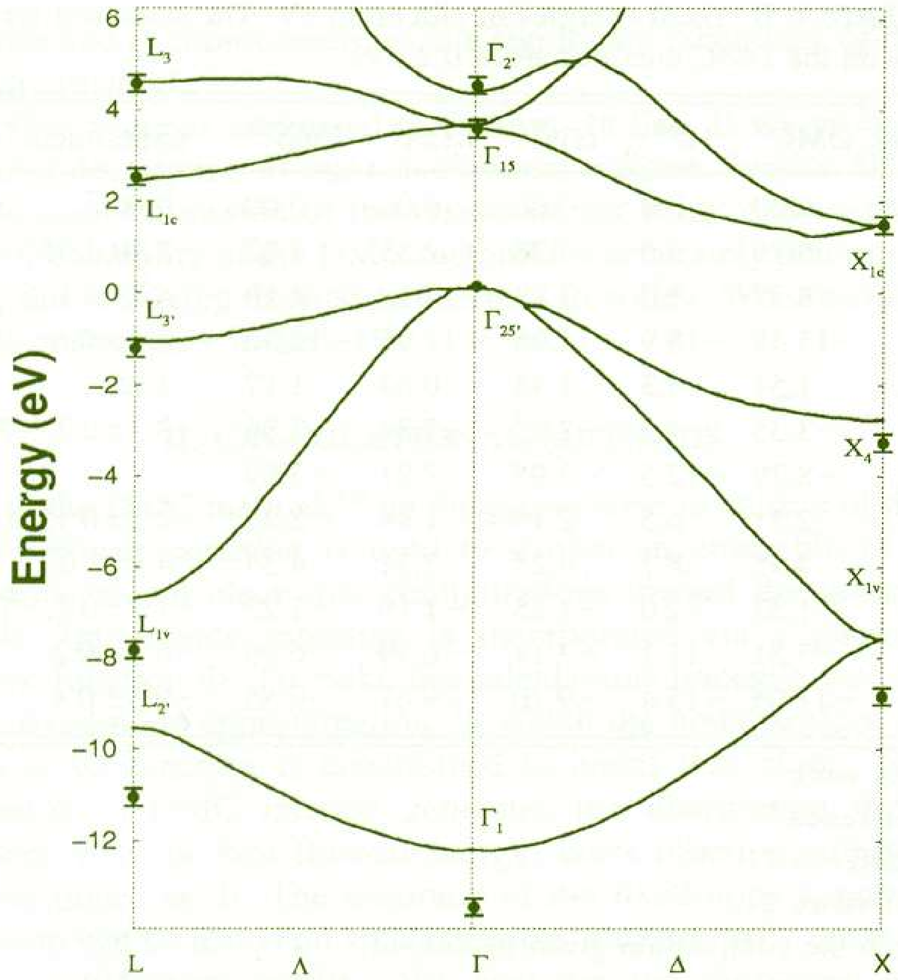


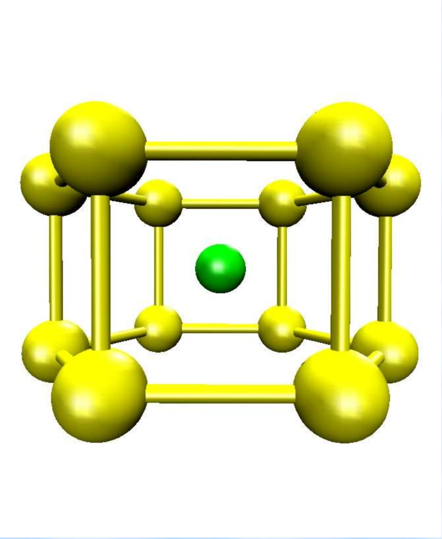
FIG. 1. The DMC band structure (filled circles with error bars). As a guide to the eye, we also show empirical pseudopotential data (Ref. 21) (solid lines).

Williamson et al '98

QMC energy bands of Si

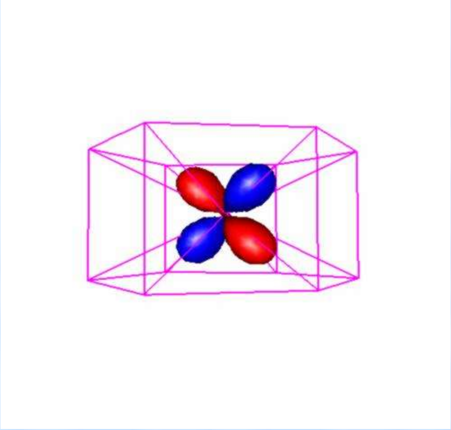
Si$_{12}$ cages encapsulating TM atoms

WSi$_{12}$ (Japan)



- even number of e: singlets
- odd number of e: dublets
- “18-e rule” not valid in general
- exception: Ti,Zr--singlet and triplet close

  - TiSi$_{12}$: singlet or triplet?

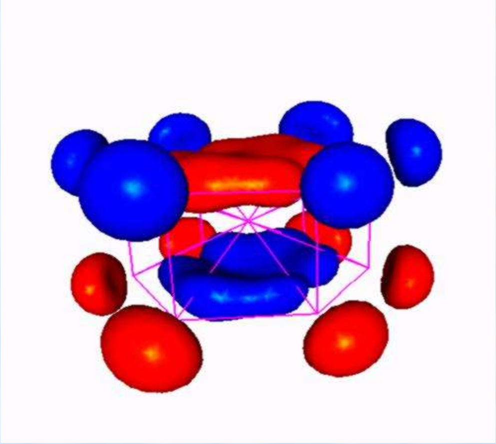


HF and B3LYP: triplet

Competition between

localized *d* on TM and

sp states on Si cage



DMC supports that only TiSi$_{12}$ is a triplet

Sen & Mitas '03

Summary

- Goal: essentially to solve Schroedinger's equation for interacting electrons in presence of *external* field of the ion cores and hence calculate properties of materials
- Different approaches
  - Find the wavefunction variationally: HF and beyond
  - Minimize energy with respect to charge density: DFT with LDA/GGA.
    - These are "mean field" methods
  - Work with many-electron wavefunctions, include "many-body" exchange-correlation effects: QMC methods

QMC is by far the most accurate method