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
- 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

![Phonon Spectrum Diagram](image)
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

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

– 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 \( \Psi \) 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
      
      \[ \Psi = (N!)^{-1/2} \begin{vmatrix} \chi_1(x_1) & \chi_1(x_2) & \ldots & \chi_1(x_N) \\ \chi_2(x_1) & \chi_2(x_2) & \ldots & \chi_2(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_N(x_1) & \chi_N(x_2) & \ldots & \chi_N(x_N) \end{vmatrix} \equiv |\chi_1, \chi_2, \ldots, \chi_N\rangle \]
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 \( P(\uparrow\downarrow) \neq 0 \)
  - Zero if the spins are parallel \( P(\uparrow\uparrow) = 0 \)

- 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)
\[
E[\rho] = \int \nu_n(\vec{r}) \rho(\vec{r}) \, d\vec{r} + V_{ee}[\rho] + T[\rho]
\]
- Minimize \(E\) but the functionals \(V\) and \(T\) are unknown
- Kohn-Sham method of solution: noninteracting electrons moving in
\[
\nu_{\text{eff}}(\vec{r}) = \nu_n(\vec{r}) + \frac{\int \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} \, d\vec{r}' + \nu_{xc}(\vec{r})
\]
- We need to solve:
\[
\left[ -\frac{1}{2} \nabla^2 + \nu_{\text{eff}}(\vec{r}) \right] \psi_i = \epsilon_i \psi_i \quad \text{with} \quad \rho(\vec{r}) = \sum_{\text{occ}} |\psi_i(\vec{r})|^2
\]

Exchange-correlation pot.
• Again, we do not know $\nu_{xc}$

• Local Density Approximation (LDA): exch-corr energy in each infinitesimal vol = exch-corr energy of a homogeneous e-gas with same density as in the infinitesimal 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 $\sim 1.1$ eV

LDA Gap $\sim 0.5$ eV

LDA underestimates band-gap
• **Binding energy/stability**
  
  – Cohesive energy of bulk Si (eV/atom)

<table>
<thead>
<tr>
<th>Method</th>
<th>HF</th>
<th>LDA</th>
<th>expt</th>
</tr>
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<tr>
<td></td>
<td>4.02</td>
<td>5.28</td>
<td>4.62(8)</td>
</tr>
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</table>

• **Si(100) surface**
  
  – Reconstruction
Nature of bonding

- Ga clusters

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

- Happens in other systems: Al wire vs. bulk

Breaux et al PRL '03
Chako et al PRL '04
Sen et al '01
Predicting new materials

- Pentagonal nanowires
  - Motivated by experiments on Au wires
  - Experimentally confirmed recently by Gonzalez et al. PRL '04

- Experimentally confirmed recently by Sen et al '02

Kondo & Takayanagi Sc. 2000
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 systems
    - 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 $\Psi$ is anti-symmetric

♦ Local energy is constant for an eigenfunction

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

⇒ $\Psi$ should obey e-e and e-n cusp conditions

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

♦ Example: H atom 1s 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
  \[ \Psi_T = \exp \left[ \sum_I \sum_{i<j} u(r_{il}, r_{jl}, r_{ij}) \right] D^{SL} \]
  where
  \[ u(r_{il}, r_{jl}, r_{ij}) = -\frac{C}{\gamma} e^{-\gamma r_{ij}} + \sum_{k<l, m} c_{klm} \left[ \alpha_k(r_{il}) \alpha_l(r_{jl}) + \alpha_k(r_{jl}) \alpha_l(r_{il}) \right] \beta_m(r_{ij}) \]
  - First term in $u$: e-e cusp conditions
  - $C=1/4$ for like $=1/2$ for unlike spins
  - Remaining part introduces correlations
  - $\gamma$ and $c_{klm}$ are variational parameters
Exponential Pade' functions

\[ \frac{a^x}{1 + a^x} \]

Pade' functions

\[ \exp\left[\frac{x}{(1+x)^2}\right] \]

\[ \exp\left[-\frac{x}{(1+x)^2}\right] \]
Variational Monte Carlo (VMC)

- We need to evaluate integrals like:
  - Where $R_i$ are distributed according to $\Psi^2$
  - Use stochastic methods to evaluate this multi (3N)-dim integral

- $\gamma$ and $c_{klm}$'s are optimized by minimization of variance of the local energy

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

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

\[
\sigma_{VMC}^2 \approx \frac{1}{M} \sum_{i=1}^{M} [E_L(\vec{R}_i) - E_{VMC}]^2
\]
Cohesive energy of bulk Si (eV/atom)

<table>
<thead>
<tr>
<th>Method</th>
<th>DMC</th>
<th>LDA</th>
<th>HF</th>
<th>Expt</th>
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<td>4.63(2)</td>
<td>5.28</td>
<td>4.02</td>
<td>4.62(8)</td>
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Binding energy of TiO molecule.

Binding energies (eV) from various methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Energy (eV)</th>
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<tbody>
<tr>
<td>HF</td>
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<tr>
<td>DFT (LSDA)</td>
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<td>DFT (PW91)</td>
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<tr>
<td>QMC</td>
<td>6.7(1)</td>
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<tr>
<td>Experiment</td>
<td>6.98(17)</td>
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QMC provides the best theoretical value to date though expensive!

Wagner & Mitas '03
• $C_{20}$ 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
- Si$_{12}$ cages encapsulating TM atoms
  - even number of e: singlets
  - odd number of e: doublets
  - “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

WSi$_{12}$ (Japan)
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