First Principles Calculations for Condensed Matter and Nanoscience

International Center for Materials Research
University of California at Santa Barbara

August 22 - September 3, 2005

Richard M. Martin
University of Illinois at Urbana-Champaign

Density Functional theory

Today – Introduction – overview and accomplishments
Tomorrow – Behind the functionals – limits and challenges
Density Functional theory
Introduction

Richard M. Martin

Based upon
Cambridge University Press, 2004
A long way in 80 years

- E. Schrodinger – 1925, ….
- Pauli exclusion Principle - 1925
- Fermi statistics - 1926
- Thomas-Fermi approximation – 1927
- First density functional – Dirac – 1928
- Dirac equation – relativistic quantum mechanics - 1928

Quantum Mechanics ➔ Technology
Greatest Revolution of the 20th Century

• Bloch theorem – 1928
• Wilson - Implications of band theory - Insulators/metals –1931
• Wigner- Seitz – Quantitative calculation for Na - 1935
• Slater - Bands of Na - 1934 (proposal of APW in 1937)
• Bardeen - Fermi surface of a metal - 1935
• First understanding of semiconductors – 1930’s
• Invention of the Transistor – 1940’s
  – Bardeen – student of Wigner
  – Shockley – student of Slater
The Basic Methods of Electronic Structure

- **Hylleras** – Numerically exact solution for $H_2$ – 1929
  - Numerical methods used today in modern efficient methods
- **Slater** – Augmented Plane Waves (APW) – 1937
  - Not used in practice until 1950’s, 1960’s – electronic computers
- **Herring** – Orthogonalized Plane Waves (OPW) – 1940
  - First realistic bands of a semiconductor – Ge – Herrman, Callaway (1953)
- **Koringa, Kohn, Rostocker** – Multiple Scattering (KKR) – 1950’s
  - The “most elegant” method - Ziman
- **Boys** – Gaussian basis functions – 1950’s
  - Widely used, especially in chemistry
- **Phillips, Kleinman, Antoncik** – Pseudopotentials – 1950’s
  - Hellman, Fermi (1930’s) – Hamann, Vanderbilt, … – 1980’s
- **Andersen** – Linearized Muffin Tin Orbitals (LMTO) – 1975
  - The full potential “L” methods – LAPW, ….
Basis of Most Modern Calculations
Density Functional Theory

- Hohenberg-Kohn; Kohn-Sham - 1965
- Car-Parrinello Method – 1985
- Improved approximations for the density functionals
  - Generalized Gradient Approximations, . . .
- Evolution of computer power
- Nobel Prize for Chemistry, 1998, Walter Kohn

- Widely-used codes –
  - ABINIT, VASP, CASTEP, ESPRESSO, CPMD, FHI98md, SIESTA, CRYSTAL, FPLO, WEIN2k, . . .
Most Cited Papers in APS Journals

- From Physics Today, June, 2005
- 11 papers published since 1893 with > 1000 citations in APS journals

<table>
<thead>
<tr>
<th>Publication</th>
<th># cites</th>
<th>Av. age</th>
<th>Title</th>
<th>Author(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PR 140, A1133 (1965)</td>
<td>3227</td>
<td>26.7</td>
<td>Self-Consistent Equations Including Exchange and Correlation Effects</td>
<td>W. Kohn, L. J. Sham</td>
</tr>
<tr>
<td>PR 136, B864 (1964)</td>
<td>2460</td>
<td>28.7</td>
<td>Inhomogeneous Electron Gas</td>
<td>P. Hohenberg, W. Kohn</td>
</tr>
<tr>
<td>PR 108, 1175 (1957)</td>
<td>1364</td>
<td>20.2</td>
<td>Theory of Superconductivity</td>
<td>J. Bardeen, L. N. Cooper, J. R. Schrieffer</td>
</tr>
<tr>
<td>PRL 19, 1264 (1967)</td>
<td>1306</td>
<td>15.5</td>
<td>A Model of Leptons</td>
<td>S. Weinberg</td>
</tr>
<tr>
<td>PRB 12, 3060 (1975)</td>
<td>1259</td>
<td>18.4</td>
<td>Linear Methods in Band Theory</td>
<td>O. K. Anderson</td>
</tr>
<tr>
<td>PR 124, 1866 (1961)</td>
<td>1178</td>
<td>28.0</td>
<td>Effects of Configuration Interaction of Intensities and Phase Shifts</td>
<td>U. Fano</td>
</tr>
<tr>
<td>PRB 13, 5188 (1976)</td>
<td>1023</td>
<td>20.8</td>
<td>Special Points for Brillouin-Zone Integrations</td>
<td>H. J. Monkhorst, J. D. Pack</td>
</tr>
</tbody>
</table>

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

• **Today**
  – 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

• **Tomorrow**
  – 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

\[
\hat{H} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i,F} \frac{Z_i e^2}{|r_i - R_F|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} 
- \sum_F \frac{\hbar^2}{2M_F} \nabla_F^2 + \frac{1}{2} \sum_{F \neq J} \frac{Z_F Z_J e^2}{|R_F - R_J|}
\]

- 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
The basis of most modern calculations
Density Functional Theory (DFT)

- Hohenberg-Kohn (1964)

\[ V_{\text{ext}}(r) \xrightleftharpoons[\text{HK}]{\downarrow} n_0(r) \]
\[ \Psi_i(\{r\}) \Rightarrow \Psi_0(\{r\}) \]

- All properties of the many-body system are determined by the ground state density \( n_0(r) \)

- Each property is a functional of the ground state density \( n_0(r) \) which is written as \( f[n_0] \)

- A functional \( f[n_0] \) maps a function to a result: \( n_0(r) \rightarrow f \)
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
  \[ n_0(r) = \sum_{\sigma} \sum_{i=1} |\psi_i^\sigma(r)|^2, \]

\[
\begin{array}{cccc}
V_{\text{ext}}(r) & \overset{HK}{\leftrightarrow} & n_0(r) & \overset{KS}{\leftrightarrow} & n_0(r) & \overset{HK_0}{\leftrightarrow} & V_{KS}(r) \\
\downarrow & & \uparrow & & \uparrow & & \downarrow \\
\Psi_i (\{r\}) & \Rightarrow & \Psi_0 (\{r\}) & & \psi_i = 1, N_e (r) & \Leftarrow & \psi_i (r)
\end{array}
\]

- 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

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

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

Equations for independent particles - soluble

Exchange-Correlation Functional – Exact theory but unknown functional!

- The new paradigm – find useful, approximate functionals
The Kohn-Sham Equations

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

\[ n_0(r) = \sum_\sigma \sum_i |\psi_i^\sigma(r)|^2, \]

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

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

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

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

\[ V_{KS}^\sigma(\mathbf{r}) = V_{ext}(\mathbf{r}) + \frac{\delta E_{Hartree}}{\delta n(\mathbf{r},\sigma)} + \frac{\delta E_{xc}}{\delta n(\mathbf{r},\sigma)} \]

\[ = V_{ext}(\mathbf{r}) + V_{Hartree}(\mathbf{r}) + V_{xc}^\sigma(\mathbf{r}). \quad (4) \]

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
• 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

\[ \psi_{i,k}(\mathbf{r}) \propto \sum_m c_{i,m}(k) \times \exp(i(k + \mathbf{G}_m) \cdot \mathbf{r}) \]  \hspace{1cm} (1)

\[ \sum_{m'} H_{m,m'}(k)c_{i,m'}(k) = \varepsilon_i(k)c_{i,m}(k) \]  \hspace{1cm} (2)

\[ H_{m,m'}(k) = \frac{\hbar^2}{2m_e} |k + \mathbf{G}_m|^2 \delta_{m,m'} + V_{eff}(\mathbf{G}_m - \mathbf{G}_{m'}). \]  \hspace{1cm} (3)

• Kohn-Sham Equations in a crystal

• 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) – use in solid
  2. Pseudopotential can be constructed to be weak
     - Can be chosen to be smooth
     - Solve Kohn-Sham equations in solid directly in Fourier space
Examples of Modern Calculations

- Properties of crystals – many calculations are now “routine”
  - Definitive tests of the theory – comparisons with experiments
- Calculations for complex systems
  - Theory provides key role along with experiments
  - Understanding
  - Predictions
  - Direct simulation of atomic scale quantum phenomena
- Examples
  - Surfaces, interfaces, defects, …
  - Thermodynamic phase transitions, Liquids, Melting, …
  - Nanostructures – in real environments, …
  - Large complex molecules – in solution, …
Examples of Modern Calculations

Electron density in silicon


In Si the black and grey atoms are identical
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
  - Very similar results with pseudopotentials
Comparisons – LAPW – PAW - - Pseudopotentials  (VASP code)

<table>
<thead>
<tr>
<th>Method</th>
<th>C</th>
<th>Si</th>
<th>CaF$_2$</th>
<th>bcc Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a$</td>
<td>$B$</td>
<td>$a$</td>
<td>$B$</td>
</tr>
<tr>
<td>NCPP$^a$</td>
<td>3.54</td>
<td>460</td>
<td>5.39</td>
<td>98</td>
</tr>
<tr>
<td>PAW$^a$</td>
<td>3.54</td>
<td>460</td>
<td>5.38</td>
<td>98</td>
</tr>
<tr>
<td>PAW$^b$</td>
<td>3.54</td>
<td>460</td>
<td>5.40</td>
<td>95</td>
</tr>
<tr>
<td>USPP$^b$</td>
<td>3.54</td>
<td>461</td>
<td>5.40</td>
<td>95</td>
</tr>
<tr>
<td>LAPW$^a$</td>
<td>3.54</td>
<td>470</td>
<td>5.41</td>
<td>98</td>
</tr>
<tr>
<td>EXP$^a$</td>
<td>3.56</td>
<td>443</td>
<td>5.43</td>
<td>99</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$a$</th>
<th>$B$</th>
<th>$m$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.75$^c$</td>
<td>226$^c$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.75</td>
<td>247</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>2.72</td>
<td>237</td>
<td>2.08</td>
</tr>
<tr>
<td></td>
<td>2.72$^d$</td>
<td>245$^d$</td>
<td>2.04$^d$</td>
</tr>
<tr>
<td></td>
<td>2.87$^d$</td>
<td>172$^d$</td>
<td>2.12$^d$</td>
</tr>
</tbody>
</table>

- $a$ – lattice constant;  $B$ – bulk modulus;  $m$ – magnetization
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!
Examples of Modern Calculations

**Phonons**

Comparison of theory and experiment

- Calculated from the response function – “Density functional perturbation theory”
- Now a widely-used tool in ABINIT

De Gironcoli, et al.
Examples of Modern Calculations

• Instability and predicted ferroelectric displacement in \( \text{BaTiO}_3 \) - calculated with the SIESTA and LAPW codes
  – Provided by R. Weht and J. Junquera

Perovskite structure

Many calculations done with ABINIT, . . .
Examples of Modern Calculations

Atomic scale Au wires on Si (557) surface

STM image of self-assembled atomic “wires” on a Si surface

Theoretical prediction – using SIESTA code - of structure in very good agreement with experiment– done later!

Explains one-dimensional metallic bands observed by photoemission
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 lnN instead of N² or N³
  – 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)
Example of Thermal Simulation

- Phase diagram of carbon
- Full Density Functional “Car-Parrinello” simulation
Examples of Modern Calculations

• **Unraveling the steps in the Ziegler-Natta reaction**
  – **Industrial process for production of polyethylene**
  – Simulations with Car-Parrinello MD – plane wave pseudopotentials – M. Boero, et al.

\[ \pi \text{-complex} \quad \rightarrow \quad \text{Transition} \quad \rightarrow \quad \text{insertion} \]

Adds one ethylene unit to polymer
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

Conclusions to this point

• A long way in 80 years!
• **Electronic Structure** is the quintessential many-body problem of quantum mechanics
  – Interacting electrons → real materials and phenomena
• **Density functional theory** is by far the most widely applied “*ab intio*” method used for “real materials” in physics, chemistry, materials science
  – Approximate forms have proved to be very successful
  – BUT there are shortcomings and failures!
• Momentous time for theory
  – New opportunities and challenges
  – Requires care and understanding of limitations