Density Functional Theory (DFT)

An Introduction by
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Irbid, Aug, 2nd, 2009
Density Functional Theory

- Revolutionized our approach to the electronic structure of atoms, molecules and solid materials.
- Plethora of publications reporting very successful applications in a wide range of fields in physics, chemistry, biology and others.
- Its appeal is in the simplicity and accuracy over the traditional methods: HF and CI.
Walter Kohn: Founder of DFT

- 1998 Nobel Prize in Chemistry for the development of DFT.
- Thousands of citations.
Iterative minimization techniques for \textit{ab initio} total-energy calculations: molecular dynamics and conjugate gradients

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Reviews of Modern Physics, Vol. 64, No. 4, October 1992  
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References: Texts

1. Density-Functional Theory of Atoms and Molecules
   - Robert G. Parr
   - Weitao Yang
   - Oxford Science Publications

2. Electronic Structure
   - Basic Theory and Practical Methods
   - Richard M. Martin
   - Cambridge
References: Texts

Downloadable eBooks
http://www.freescience.
Info/Physics.php?id=30

Presentations, tutorials
and more …see the web
The DFT acronym

Take care when searching the web for DFT, for you might hit:

- Discrete Fourier Transform
- Decision Field Theory.
- The UK's Department for Transport
- Design For Test
- DFT Digital Film Technology
- Deep Flow Technique

and many others. Advise: Use the full name
Function vs Functional

\[ f(x) = x^2; \quad f(2) = 4 \]

\[ F[f] = \int_0^1 f(x) \, dx; \quad F[x^2] = \frac{1}{3} \]
The Basic Many Body Problem

Ground state properties of a system of $N$ charged fermions (electrons, positrons, protons, ...) moving in an external field.
The Hamiltonian

\[ H = T + V + U \]

\[ = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} v(r_i) + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{1}{r_{ij}} \]

\( T \): Diff. one body operator.
\( V \): Multiplicative one body operator
\( U \): Multiplicative two body operator.
Atomic Units Confusion!

• We use atomic Hartree units:

\[ \hbar = 1, \ m_e = 1, \ e^2 = 1 \]

• Not the atomic Rydberg units:

\[ \hbar = 1, \ m_e = 1/2, \ e^2 = 2 \]

• \( E_o(\text{Hdrgn}) = -13.6 \text{ eV} = 1 \text{ Ryd} = 0.5 \text{ Hart} \)
T.I.S.E: \( H\Psi = E\Psi \)

- To compute any property, we need the many body wave function \( \Psi_0(x_1, \ldots, x_N) \), which is a function of \( 4N \) independent variables.

\[ O = O[\Psi] = \langle \Psi | O | \Psi \rangle \]
No rigorous analytic solution

• No! there isn’t, even for N=2 (Helium atom)
• What about N = $10^{24}$.
• The bottle neck is the interaction term $U$.

$$U = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{1}{r_{ij}}$$

Approximate treatment is needed.
One Body Operator

Non-differential (multiplicative) one body operator (e.g. the external potential)

\[
\langle V \rangle = \langle \Psi | \sum v(r_i) | \Psi \rangle \\
= \sum \int \Psi^*(x_1, x_2, ..., x_N) v(r_i) \Psi(x_1, x_2, ..., x_N) dx_1 ... dx_i ... dx_N \\
= \sum \int v(r_i) dx_i \int |\Psi(x_1, x_2, ..., x_N)|^2 dx_1 ... dx_N \\
= \int v(r) n(r) dr \\

\_\_\_ V \_\_\_ = V[n]
\]
Can we generalize?

• Is the total energy a functional of the density?

\[ E = E[\Psi] \quad \text{ok} \]

\[ E = E[n] \quad ? \]
Thomas Fermi Model (1927)

- Is an approximation!
- **Basic postulate**: electrons are distributed uniformly in phase space with \( \frac{2e}{\hbar^3} \).

\[
T_{TF} [n] \propto \int n^{5/3} (\vec{r}) \ d\vec{r}
\]
The Density Functional Approach

• $\Psi_0(r_1, \ldots, r_N)$ has much more information than actually needed.

• All what we need is the ground state density $n(r)$ which is a function of 3 variables only!
Fundamental Statement
(Hohenberg and Kohn)

\[ n_o (\vec{r}) \leftrightarrow v(\vec{r}) \]

\[ E_o = \min (E[n]) \]
Formal Proof

• Consider two different Hamiltonians

\[ H = T + V + U \]
\[ H' = T + V' + U \]

Corresponding to two different wave functions

\[ E'_0 = \langle \Psi'_0 | H' | \Psi'_0 \rangle \]
\[ E_0 = \langle \Psi_0 | H | \Psi_0 \rangle \]
If we assume that $n = n'$ we get a contradiction!
DFT is a theory of existence but NOT a calculation recipe. The explicit functional form is, so far, unknown!!
The Kohn-Sham Scheme

- A further simplification towards this problem is introduced in the second cornerstone paper by Kohn and Sham.
- Since $n_0(r)$ is the thumbnail of any system:
  "Two systems with the same ground state density should have the same physical properties".
Now consider the two systems A and B:

\[ H_A = T + V + U \]

\[ H_B = T_{KS} + V_{KS} \]

\[ E_A = E_B \Rightarrow T + V + U = T_{KS} + V_{KS} \]
The KS scheme ...

\[ T + V + U = T_{KS} + V_{KS} \]

\[ V_{KS} = V + U + (T - T_{KS}) \]

\[ = V + J + \tilde{U} + (T - T_{KS}) \]

\[ = V + J + E_{xc} \]

\[ J[n] = \frac{1}{2} \int \int \frac{1}{r_{12}} n(r_1)n(r_2) dr_1 dr_2 \]
The KS potential

\[ v_{ks}(\mathbf{r}) = \frac{\delta V_{ks}[n]}{\delta n(\mathbf{r})} \]

\[ v_{ks}(\mathbf{r}) = \frac{\delta V[n]}{\delta n(\mathbf{r})} + \frac{\delta J[n]}{\delta n(\mathbf{r})} + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \]

\[ = v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}) \]

- The dilemma is now “how to evaluate \( v_{xc} \)!”
The Local Density Approximation (LDA) is the exchange-correlation energy per particle in a uniform electron gas of density $n$.

$$E_{xc}[n] = \int n(r) \varepsilon_{xc}(n(r)) \, dr$$

$$\varepsilon_{xc}(n(r))$$ is the exchange-correlation energy per particle in a uniform electron gas of density $n$. 
LDA Example

Uniform e-Gas

$n_1$

Our System with Four Diff. Den.

$n_1$  $n_3$

$n_2$  $n_4$

Uniform e-Gas

$n_3$

$n_4$

$E_{xc} = n_1 \varepsilon_{xc}(n_1) + n_2 \varepsilon_{xc}(n_2) + n_3 \varepsilon_{xc}(n_3) + n_4 \varepsilon_{xc}(n_4)$
LDA: Success and failure!

- The simplest and lightest!
- Designed for a slowly varying densities but it works well beyond this limit!
- Fails to reproduce atomic Rydberg series (wrong $1/r$ potential tail)
- $E_{\text{gap}}$, $E_c$, $B$, $a$: Estimation errors!
- Workaround: SIC
The Generalized Gradient Approximation (GGA)

\[ E_{xc} = E_{xc} \left[ n(r) + \nabla n(r) \right] \]

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>GGA</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>-1%, -3%</td>
<td>+1%</td>
</tr>
<tr>
<td>(B)</td>
<td>+10, +40%</td>
<td>-20%, +10%</td>
</tr>
<tr>
<td>(E_c)</td>
<td>+15%</td>
<td>-5%</td>
</tr>
<tr>
<td>(E_{\text{gap}})</td>
<td>-50%</td>
<td>-50%</td>
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</tbody>
</table>
LDA Complete failure (bcc Iron)

- LDA: Fe is nonmagnetic fcc.
- GGA: Fe is a ferromagnetic bcc.
- Experiment: GGA prediction is correct!
Quantum Monte Carlo (QMC) and Exact Exchange (EXX)

- Elaborate and Heavy computations.
- Nearly exact atomic KS potentials (QMC).
- Excellent band gap (EXX).
- Recent developments:
  - Generating excellent atomic KS potentials using (LDA + SIC)
  - Reformulating EXX in terms of ground state orbitals. (approximate correlation!)
The KS equations

The KS Hamiltonian is separable into $N$ independent Hamiltonians $\{h_i\}$ each satisfying the one particle SE:

$$\left[ -\frac{\nabla^2}{2} + v_{KS}[n](\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

Physical significance of $\{\varphi_i\}$ and $\{\varepsilon_i\}$?
Basis Set Expansion

- Numerically it is more efficient to expand \( \{ \varphi_i \} \) in a suitable basis set (depending on the symmetry):
  - STO’s (Slater Type Orbitals) or atomic orbitals.
  - Gaussians.
  - Plane waves.

\[ \varphi_i = \{ c_1, c_2, \ldots, c_m \}; \text{ Complex Numbers.} \]

*Increase m to achieve convergence!*
The Self-Consistent cycle

\[ \phi_i = \{c_1, c_2, \ldots, c_m\}; \]

\[ n(r) = \sum_{i} |\varphi_i(r)|^2 \]

\[ v_{KS}[n](r) = v(r) + v_H[n](r) + v_{XC}[n](r) \]
The Solids Complicated Problem

♦ $\nu(r)$ depends on the moving nuclei: Coupled electronic and Nuclear degrees of freedom. (Born-Oppenheimer approximation)

♦ Very deep in the vicinity of the nuclei => wiggling orbitals => $m$ is large. (Pseudopotentials)

♦ Infinite number of electrons => infinite number of extended wave functions. (Bloch’s Theorem)
The Born-Oppenheimer Approximation

\[
\frac{M_\alpha}{m_e} \gg 1
\]

\[
\Rightarrow \text{Nuclei much slower than the electrons}
\]

\[
\frac{v_{\text{electron}}}{v_{\text{nucleus}}} \gg 1
\]

\[
v_{\text{electron}} \approx v_F \approx 10^8 \text{ cm/s}
\]

\[
v_{\text{nucleus}} \approx 10^5 \text{ cm/s}
\]

At any moment the electrons will be in their ground state for that particular instantaneous ionic configuration.

Solve electronic equations assuming fixed positions for nuclei

Move the nuclei as classical particles in the potential generated by the e⁻
Solids: The Periodic Matter

- An ideal periodic solid contains infinite numbers of atoms and electrons.
- We need infinite number of wave functions that extend over the entire solid (infinite space).
- Using the periodicity character (symmetry) Block resolved those singularities!
Bloch’s Theorem

\[ V(\vec{r}) = V(\vec{r} + \vec{R}) \]

\[ \psi_{n,k}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_{n,k}(\vec{r}) \]

\[ u_{n,k}(\vec{r} + \vec{R}) = u_{n,k}(\vec{r}) \]

\[ \varepsilon_{n,k + k'} = \varepsilon_{n,k} \]

\[ \psi_{n,k+k'}(\vec{r}) = \psi_{n,k}(\vec{r}) \]

- Infinite number of wave functions => Finite number of wave functions at an infinite number of k points.
The Monkhorst-Pack mesh

For adjacent $k$ points $\psi_{n,k}$ is almost the same

$\Rightarrow$ Divide the $k$-space into small volumes

and chose one point in each volume to

represent $\psi_{n,k}$ over this volume.

$\int d\vec{k} \rightarrow \sum_{\vec{k}} \Delta \vec{k}$

How many $k$-points? Check convergence!
Supercells: Enforcing periodicity

M. C. Payne et al., Rev. Mod. Phys., 64, 1045 (1992)
Acknowledgment

The flash animations are from:
http://www.educypedia.be/education/chemistryjava
    list.htm

Some illustrations are from:
http://www.authorstream.com/Presentation/Maitan
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    properties-matter-theoretical-methods-firmly-
rooted-fundamental-equations-as-
Entertainment-ppt-powerpoint/
Thank you