First-Principles Methods in Materials Science

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General outline:

**Ground-state theory:**
Density Functional Theory

**Excited-state theories:**
Time-Dependent Density Functional Theory

GW method

Beyond GW:
combining first-principles and model approaches
Atoms and molecules

\( \approx 10^2 \) electrons

"Weakly correlated": Electron-gas-like Materials

Well understood within Quantum Chemistry. But Quantum Chemistry is difficult to apply to solids

Aluminium, Magnesium, Silicon, Germanium, Galium Arsenide

Well understood within available theories: Density Functional Theory, GW method

"Strongly correlated": Atomic- and electron-gas-like materials

High-temperature Superconductors, Nanomaterials, Magnetic materials, Organic solids

Not well understood \( \rightarrow \) Theoretical challenge

Bird’s-eye view

Materials science

( \( \approx 10^{23} \) electrons)
The many-electron Hamiltonian

\[
\sum_{i}^{N} \{-\nabla_{i} + V_{\text{Nuclei}}(r_{i})\} + \frac{1}{2} \sum_{i,j}^{N} \frac{1}{|r_{i} - r_{j}|} \psi_{k}(r_{1}, r_{2}, ..., r_{N}) = E_{k}\psi_{k}(r_{1}, r_{2}, ..., r_{N})
\]

In many cases it is not necessary to solve for the wave functions

• From the Green function

\[
G(\vec{r}_{1}t_{1}, \vec{r}_{2}t_{2}) = -i\langle 0 | T\hat{\psi}(\vec{r}_{1}t_{1})\hat{\psi}^{+}(\vec{r}_{2}t_{2}) | 0 \rangle
\]

1) Any expectation value of one-particle operator in the ground state
2) One-particle excitation energies
3) Ground-state energy

• From the density

According to the Hohenberg-Kohn theorem, in principle all physical quantities, including excited-state quantities, can be derived from the ground-state density
Difficulties with the many-electron wavefunction

Hydrogen molecule: 2-electron problem

\[ H (\vec{r}_1, \vec{r}_2) = H_0 (\vec{r}_1) + H_0 (\vec{r}_2) + H_1 (\vec{r}_1, \vec{r}_2) \]

\[ H_0 = - \frac{1}{2} \nabla^2 - \frac{1}{|\vec{R}_1 - \vec{r}|} - \frac{1}{|\vec{R}_2 - \vec{r}|} \]

\[ H_1 = \frac{1}{|\vec{r}_1 - \vec{r}_2|} \]

Coulomb interaction
Without the Coulomb interaction the problem can be easily solved. It is equivalent to a one-electron problem.

\[
\Psi (\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(1) & \psi_1(2) \\ \psi_2(1) & \psi_2(2) \end{vmatrix} \quad \text{Slater determinant}
\]

\[
H_0 \psi_n (\vec{r}) = \varepsilon_n \psi_n (\vec{r}) \quad \leftrightarrow \text{One-electron problem}
\]

\[
[ H_0(\vec{r}_1) + H_0(\vec{r}_2) ] \Psi (\vec{r}_1, \vec{r}_2) = E_0 \Psi (\vec{r}_1, \vec{r}_2)
\]

With the Coulomb interaction \( \Psi (\vec{r}_1, \vec{r}_2) = ? \)

1 dimension requires \( \sim 10 \) points \( \rightarrow \)
For \( N \) electrons there are \( 2N \) dimensions \( \rightarrow \) \( \sim 10^{3N} \)
Quantum Chemistry Method

Example: Hydrogen molecule. Consider all possible configurations. The wave function is written as a linear combination of these configurations with certain weights.

\[ |\Psi\rangle = \]

Each site has a set of orbitals: 1s, 2s, 2p, 3s, 3p, 3d etc.
For real materials the number of possible configurations becomes very large to be handled by present computers or even future computers.

\[ E = \int dx_1 dx_2 \Psi^*(x_1, x_2) H \Psi(x_1, x_2) \]

Minimise the total energy with respect to the weight of each configuration.

**BUT:** The number of configurations grows exponentially with the number of electrons

For real materials the number of possible configurations becomes very large to be handled by present computers or even future computers.

Quantum Monte Carlo: (→Anders Sandvik)
Mean-field methods:
Reducing the many-body problem to a one-body problem

Hartree approximation (1926)

\[ V_H (r) = v_{\text{nuclei}} (r) + \int dr' \frac{n(r')}{|r - r'|} \]

Hartree-Fock approximation (include exchange but no correlations) (1927)

\[ V_{\text{ex}} (r, r') = -v(r - r') \sum_{n=1}^{\text{occupied}} \psi_n^*(r)\psi_n (r') \]

Slater \( X_\alpha \) method: approximate exchange by a one-particle potential (1956)

\[ V_{\text{ex}} (r) = \alpha n^{1/3} (r) \]

For atoms and molecules the Hartree-Fock approximation is generally better than the Hartree approximation because screening is weak but for solids the Hartree approximation is often better than the Hartree-Fock because exchange and correlations cancel each other to some extent. Correlations are essential in real materials
Density Functional Theory:
The density as the basic variable
(Walter Kohn 1964)

No many-electron wave function, only the electron density is needed.

Compare many-electron wave function and density

\[ \Psi (x_1, x_2, \ldots, x_N) \Leftrightarrow n(x) \]

Hohenberg and Kohn, Phys. Rev. 136, B864 (1964)
Kohn and Sham, Phys. Rev. 140, A1133 (1965)
Jones and Gunnarsson, Rev. Mod. Phys. 61, 689 (1989)
Breakthrough: Density Functional Theory (DFT, 1965)

[1] The ground-state electron density \( n(r) \) is *uniquely determined by the external potential* \( v(r) \) and *all properties* of a material can, *in principle*, be derived from it.

[2] For ground-state properties, the interacting many-body problem can be mapped to a *non-interacting* problem with the same electron density.

The Hohenberg-Kohn Theorem (1964)

The *ground-state density* $n(r)$ of a (bound) system of interacting electrons moving in some external potential $v(r)$ is determined by this potential uniquely.

$$n(\vec{r}) \leftrightarrow v(\vec{r})$$

There is a one-to-one correspondence between the ground-state density and the external potential.

Since $v(r)$ determines the many-electron Hamiltonian then *all properties, not only ground-state properties*, are determined by $n(r)$.
Changing the external potential by more than a constant will change the ground-state electron density.
Proof of the Hohenberg-Kohn Theorem

The many-electron Schroedinger equation

\[
\sum_{i}^{N} \left\{ -\nabla_i + v(r_i) \right\} + \frac{1}{2} \sum_{i,j}^{N} \frac{1}{|r_i - r_j|} \right] \psi(r_1, r_2, \ldots, r_N) = E \psi(r_1, r_2, \ldots, r_N)
\]

Consider a system of electrons moving in an external potential \(v(r)\) with a ground-state density \(n(r)\) corresponding to the ground state \(\Psi\) and energy \(E\). Assume that there exists another potential \(v'(r)\) that gives the same density.

Density \(n(r)\)
Assume a non-degenerate ground state.

\[ E = \langle \Psi | H | \Psi \rangle \]
\[ = \int dr \; v(r)n(r) + \langle \Psi | T + U | \Psi \rangle \]

\[ E' = \langle \Psi' | H' | \Psi' \rangle \quad \text{Assume that there exists another system with} \]
\[ \text{the same density but different external potential } v'(r) \]
\[ = \int dr \; v'(r)n(r) + \langle \Psi' | T + U | \Psi' \rangle \]

From the Rayleigh-Ritz variational principle

\[ E < \langle \Psi' | H | \Psi' \rangle = \int dr \; v(r)n(r) + \langle \Psi' | T + U | \Psi' \rangle \]

\[ E < E' + \int dr \; [v(r) - v'(r)]n(r) \quad \text{\{ } E + E' < E + E' \text{\}} \]
\[ E' < E + \int dr \; [v'(r) - v(r)]n(r) \quad \text{\{} \text{contradiction} \text{\}} \]
The Hohenberg-Kohn Variational Principle

\[ E = \min_{\Psi[n]} \langle \Psi[n] | H | \Psi[n] \rangle \]

Minimise \( E \) with respect to the \textit{density}, instead of the wave function.

From a given set of densities \( n(r) \):

1. Choose a density \( n(r) \) and minimise \( E \) with respect to all \( \Psi \) that yield \( n(r) \)

\[ E = \min_{\Psi \to n} \langle \Psi[n] | H | \Psi[n] \rangle \]

2. Minimise \( E \) over the given set of \( n(r) \):
   repeat (1) with different densities to find the lowest \( E \)

\[ E = \min_n \langle \Psi[n] | H | \Psi[n] \rangle \]

Levy and Lieb (1982)
What to do with the Hohenberg-Kohn Theorem and the Variational Principle?

Kohn and Sham (1965):
Consider a system of non-interacting electrons

\[ E[n] = \int dr \ v(r)n(r) + \langle \Psi[n] | T_s | \Psi[n] \rangle \]

\[ \delta E[n] = \int dr \ \delta n(r) \left\{ v(r) + \frac{\delta}{\delta n(r)} T_s[n(r)] - \varepsilon \right\} = 0 \]

The ground-state density and energy can be obtained from solving the Kohn-Sham equation

\[ \left[ -\nabla^2 + v(r) - \varepsilon_i \right] \phi_i(r) = 0 \]

\[ n(r) = \sum_{i=1}^{N} |\phi_i(r)|^2 ; \quad E = \sum_{i=1}^{N} \varepsilon_i \]

\[ T_s[n(r)] = -\sum_{i=1}^{N} \int dr \phi_i^* \nabla^2 \phi_i \]
For interacting electrons

\[
E[n] = \int dr \ n(r) v(r) n(r) + T_s[n] + \frac{1}{2} \int drdr' \frac{n(r)n(r')}{|r-r'|} + E_{xc}[n]
\]

The ground-state density and energy can be obtained from solving
the Kohn-Sham equation:

\[
[-\nabla^2 + v_{\text{eff}}(r) - \varepsilon_i] \phi_i(r) = 0
\]

\[
n(r) = \sum_{i=1}^{N} |\phi_i(r)|^2; \quad T_s[n(r)] = -\sum_{i=1}^{N} \int dr \phi_i^* \nabla^2 \phi_i
\]
The Local Density Approximation (LDA)

Total Energy: \[ E[\rho(r)] = T[\rho] + E_H[\rho] + E_{xc}[\rho] \]

- Kinetic energy
- Electrostatic energy
- Exchange-correlation energy (unknown)

Approximate \( E_{xc}[\rho] \) by the Local Density Approximation (LDA):
For the electron gas \( E_{xc}[\rho] \) can be calculated very precisely.

Real density \( \rho \)

Local Density Approximation

Electron gas with average density \(<\rho>\)
Summary of Density Functional Theory

Kinetic energy (non-interacting)

\[ T[\rho] = -\frac{1}{2} \sum_{n=1}^{N} \int d^3r \phi_n(\vec{r}) \nabla^2 \phi_n(\vec{r}) \]

Electrostatic energy (Hartree energy)

\[ E_H[\rho] = \frac{1}{2} \int d^3rd^3r' \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + \int d^3r \ V_{ext}(\vec{r})\rho(\vec{r}) \]

Exchange-correlation energy

\[ E_{XC}[\rho] = \alpha \int d^3r \ [\rho(\vec{r})]^{4/3} + ... \]

\[ \rho(r) = \sum_{n=1}^{N} |\phi_n(r)|^2 \]

density
The Kohn-Sham equation

\[ \left[ -\nabla^2 + V_{\text{eff}}(r) \right] \phi_n(r) = \varepsilon_n \phi_n(r) \]

Self-consistency

\[ n(r) = \sum_{n=1}^{N} |\phi_n(r)|^2 \]

\[ V_{\text{eff}}(r) = V_{\text{ext}}(\vec{r}) + \int d^3r' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + (4\alpha/3)[\rho(\vec{r})]^{1/3} + \ldots \]

Total energy

\[ E[\rho(r)] = T[\rho] + E_H[\rho] + E_{\text{xc}}[\rho] \]

(1) The total energy is not the same as that of the auxiliary non-interacting system.

(2) The total energy may be lower than the exact one for approximate Exc.
V-Representability:
Can we always find an effective potential such that the ground-state density is the same as the interacting density?

\[ n(r) = \sum_{n=1}^{N} |\phi_n(r)|^2 \quad ? \text{ Yes} \]

N-Representability:
Can we always find a set of one-particle orbitals such that

\[ \sum_{i=1}^{N} n_{ii} = \sum_{i=1}^{N} n_{ii} \]

There are examples of densities which are not purely V-representable, i.e., cannot be represented as a non-degenerate ground-state density.

But if we allow the density to be ensemble V-representable then for discrete systems (lattice) all positive definite densities are \( \nu \)-representable

\[ n(r) = \sum_{n=1}^{M} c_n \rho_n(r); \quad \rho_n(r) = \sum_{i=1}^{N} |\phi_i^n(r)|^2 \]

Linear combination of degenerate ground-state densities
From the total energy we can calculate many physical properties

*Molecular and materials structure:*
Example: protein structure

*Dynamic simulations:*
Follow how atoms and molecules move under various conditions

*Predict materials state:*
Metal or insulators/semiconductors

*Chemical reactions:*
Not yet achievable within the present density functional theory
TABLE IV. Total energies in first-row atoms (Ry). Experimental energies $E_{\text{expt}}$ and the estimated relativistic corrections $\Delta E_{\text{rel}}$ are from Scherr et al. (1962); Hartree-Fock (HF) energies with relativistic corrections $E_{\text{HF}}^{\text{rel}}$ are from Clementi and Roetti (1974).

<table>
<thead>
<tr>
<th>Atom</th>
<th>$E_{\text{expt}}$</th>
<th>$\Delta E_{\text{rel}}$</th>
<th>$E_{\text{HF}}^{\text{rel}}$</th>
<th>$E_{\text{LSD}}^{\text{nonrel}}$</th>
<th>$E_{\text{expt}} - E_{\text{HF}}^{\text{rel}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>$-14.957$</td>
<td>0.001</td>
<td>$-14.866$</td>
<td>$-14.706$</td>
<td>0.091</td>
</tr>
<tr>
<td>Be</td>
<td>$-29.339$</td>
<td>0.004</td>
<td>$-29.150$</td>
<td>$-28.909$</td>
<td>0.188</td>
</tr>
<tr>
<td>B</td>
<td>$-49.318$</td>
<td>0.011</td>
<td>$-49.070$</td>
<td>$-48.653$</td>
<td>0.248</td>
</tr>
<tr>
<td>C</td>
<td>$-75.715$</td>
<td>0.025</td>
<td>$-75.404$</td>
<td>$-74.958$</td>
<td>0.310</td>
</tr>
<tr>
<td>N</td>
<td>$-109.228$</td>
<td>0.050</td>
<td>$-108.856$</td>
<td>$-108.298$</td>
<td>0.373</td>
</tr>
<tr>
<td>O</td>
<td>$-150.225$</td>
<td>0.090</td>
<td>$-149.716$</td>
<td>$-149.064$</td>
<td>0.508</td>
</tr>
<tr>
<td>F</td>
<td>$-199.618$</td>
<td>0.150</td>
<td>$-198.982$</td>
<td>$-198.336$</td>
<td>0.635</td>
</tr>
</tbody>
</table>

Taken from Jones and Gunnarsson, Rev. Mod. Phys. 61 (1989)
<table>
<thead>
<tr>
<th>Molecule</th>
<th>Expt. (^a)</th>
<th>LSD(^b)</th>
<th>Xα(^b)</th>
<th>HF(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)</td>
<td>4.75</td>
<td>4.91</td>
<td>3.59</td>
<td>3.64</td>
</tr>
<tr>
<td>Li(_2)</td>
<td>1.07</td>
<td>1.01</td>
<td>0.21</td>
<td>0.17</td>
</tr>
<tr>
<td>Be(_2)</td>
<td>0.10</td>
<td>0.50</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>B(_2)</td>
<td>3.09</td>
<td>3.93</td>
<td>3.79</td>
<td>0.89</td>
</tr>
<tr>
<td>C(_2)</td>
<td>6.32</td>
<td>7.19</td>
<td>6.00</td>
<td>0.79</td>
</tr>
<tr>
<td>N(_2)</td>
<td>9.91</td>
<td>11.34</td>
<td>9.09</td>
<td>5.20</td>
</tr>
<tr>
<td>O(_2)</td>
<td>5.22</td>
<td>7.54</td>
<td>7.01</td>
<td>1.28</td>
</tr>
<tr>
<td>F(_2)</td>
<td>1.66</td>
<td>3.32</td>
<td>3.04</td>
<td>-1.37</td>
</tr>
</tbody>
</table>

\(^a\)Huber and Herzberg (1979); Bondybey and English (1984), Be\(_2\).
\(^b\)Painter and Averill (1982).
\(^c\)Total energies for experimental geometry from Cade and Wahl (1974).
FIG. 25. Pair correlation function $g(r)$ for (a) amorphous and (b) liquid Si (after Car and Parrinello, 1987).
### TABLE IX. Ground-state properties of diamond, Si, and Ge: lattice constant, $a$; cohesive energy, $E_c$; and bulk modulus $B$.

<table>
<thead>
<tr>
<th></th>
<th>$a$ (a.u.)</th>
<th>$E_c$ (eV)</th>
<th>$B$ (Mbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Diamond</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experiment$^a$</td>
<td>6.740</td>
<td>7.37</td>
<td>4.43</td>
</tr>
<tr>
<td>ASA-HL$^b$</td>
<td>6.67</td>
<td>8.5</td>
<td>4.90</td>
</tr>
<tr>
<td>pseud-W$^c$</td>
<td>6.807</td>
<td>7.58</td>
<td>4.33</td>
</tr>
<tr>
<td>ASA-BH$^d$</td>
<td>6.709</td>
<td>8.43</td>
<td>4.64</td>
</tr>
<tr>
<td>BH$^e$</td>
<td>6.744</td>
<td></td>
<td>4.42</td>
</tr>
<tr>
<td><strong>Silicon</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experiment$^a$</td>
<td>10.26</td>
<td>4.63</td>
<td>0.99</td>
</tr>
<tr>
<td>ASA-HL$^b$</td>
<td>10.22</td>
<td>4.8</td>
<td>0.98</td>
</tr>
<tr>
<td>pseud-W$^c$</td>
<td>10.30</td>
<td>4.84</td>
<td>0.98</td>
</tr>
<tr>
<td>ASA-BH$^d$</td>
<td>10.29</td>
<td>4.94</td>
<td>0.95</td>
</tr>
<tr>
<td>pseud-CA$^f$</td>
<td>10.20</td>
<td>5.28</td>
<td>0.94</td>
</tr>
<tr>
<td><strong>Germanium</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experiment$^g$</td>
<td>10.68</td>
<td>3.85</td>
<td>0.770</td>
</tr>
<tr>
<td>ASA-HL$^b$</td>
<td>10.78</td>
<td>3.6</td>
<td>0.660</td>
</tr>
<tr>
<td>pseud-W$^c$</td>
<td>10.69</td>
<td>4.02</td>
<td>0.730</td>
</tr>
<tr>
<td>pseud-CA$^f$</td>
<td>10.58</td>
<td>4.67</td>
<td>0.730</td>
</tr>
</tbody>
</table>

$^e$Christensen et al. (1987).
$^g$Cited by Hybertsen and Louie (1984).
FIG. 1. Methanol inside a cage of the zeolite sodalite. Zeolites are crystalline arrays of cages built of silicon (blue), aluminum (yellow), and oxygen (red) atoms. For each Al atom one must have a positive counter ion [in this case H⁺ (white)]. A methanol molecule is inside the cage (carbon is green) where it can react with the proton. DFT calculations have assigned and clarified the IR spectra, have determined the binding sites of methanol, and have calculated the activation energy for the reaction. Acid catalysis in zeolites is widely used in the chemical industry (after E. Nusterer, P. Bloechl, and K. Schwarz, 1996, Angew. Chem. 35, 175) [Color].
FIG. 2. The geometric structure of the clathrate $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ (Sr, red; Ga, blue; Ge, white) and its charge density in a plane bisecting the centers of the cages. DFT calculations have shown that the Sr atoms are weakly bound and scatter phonons effectively, thereby lowering thermal conductivity. However, contrary to intuitive expectations, the Sr atoms do not donate electrons to the frame and are practically neutral. Conductivity is due to electrons traveling through the frame, not through the one-dimensional Sr “wires” in the structure; there is thus little scattering of conduction electrons by Sr vibrations. For these reasons, the compound is a metal with a large Seebeck coefficient (unlike ordinary metals). The calculation suggests that other compounds of this type may be even better thermoelectrics (theory by N. P. Blake and H. Metiu, submitted for publication) [Ceder].
FIG. 3. Fully hydroxylated aluminum (0001) surface (red, O; blue, interior Al; Al; gray, H atoms; the green lines are H bonds). Each surface A atom in Al₂O₃ has been replaced by three H atoms. The figure represents a superposition of configurations in a molecular-dynamics simulation at regular intervals of 1 ps. These calculations help to understand the complex dynamics of water adsorption on aluminum [K. C. Haas et al., Science 282, 265 (1998)] [Color].
Why does the LDA work so well?

\[ E_{xc} [\rho (r)] = \frac{1}{2} \int d^3 r d^3 r' \frac{\rho (\vec{r}) \rho (\vec{r}')}{|\vec{r} - \vec{r}'|} \int_0^1 d \lambda [g (\vec{r}, \vec{r}'; \lambda) - 1] \]

\[ = \frac{1}{2} \int d^3 r d^3 r' \frac{\rho (\vec{r}) \rho_{xc} (\vec{r}, \vec{r}' - \vec{r})}{|\vec{r} - \vec{r}'|} \]

\[ = \frac{1}{2} \int d^3 r \rho (\vec{r}) \int dRR \ 2 \frac{1}{R} \int d\Omega \rho_{xc} (\vec{r}, \vec{R}) \]

1) The exchange-correlation energy only depends on the **spherical average** of the xc-hole.

2) Sum rule

\[ \int d^3 r' \rho_{xc} (\vec{r}, \vec{r}' - \vec{r}) = -1 \]

Gunnarsson and Lundqvist PRB 13, 4247 (1976)
FIG. 7. Exact (solid line) and approximate (dashed line) exchange hole $n_x(r, r'-r)$ [Eq. (3.10)] for a spin-up electron in a nitrogen atom for $r = 0.13$ and 0.63 a.u. The top figure shows the hole along a line through the nucleus and the electron. The arrow indicates the nuclear position and $r - r' = 0$ gives the electron position. The exact hole has a large weight at the nucleus, while the approximate hole is centered at the electron. The lower figure shows the spherical average of the hole around the electron. The area under the curve is proportional to the exchange energy. The figure also shows the value of $\langle 1/R \rangle$, defined in Eq. (3.13).
Comparison between the exact Vxc and the LDA Vxc

Beryllium

FIG. 36. Accurate exchange-correlation potential $V_{xc}$ compared with the local density (LD) $V_{xc}$ for Be. The dotted line gives the radial density. The upper part of the figure gives the correlation potential (Almbladh and Pedroza, 1984).

Rev. Mod. Phys., Vol. 61, No. 3, July 1989
FIG. 6. The effective exchange, exchange-correlation, and correlation potentials of beryllium deduced from the Hartree-Fock and configuration-interaction densities shown in Fig. 4. The solid curve is the exchange-correlation potential, the short-dashed curve is the exchange potential, and the long-dashed curve is the correlation potential which is magnified ten times.
FIG. 8. The effective exchange, exchange-correlation, and correlation potentials of neon deduced from the Hartree-Fock and configuration-interaction densities shown in Fig. 7. The solid curve is the exchange-correlation potential, the short-dashed curve is the exchange potential, and the long-dashed curve is the correlation potential which is magnified 10 times.
The unoccupied orbitals are bound

→ In DFT, they are too low in energy.
Recent progress: van der Waals force in DFT

TABLE I. QC (Ref. 14) and vdW-DF interaction energies (in kcal/mol) for a subset of the S22 data set. Note: some vdW-DF calculations do not include full geometry optimizations, which would account for 1–2 kcal/mol differences in interaction energies.

<table>
<thead>
<tr>
<th>Dimer</th>
<th>QC</th>
<th>vdW-DF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adenine · thymine WC ($C_1$)</td>
<td>−16.37</td>
<td>−15.2</td>
</tr>
<tr>
<td>Benzene·CH$_4$ ($C_3$)</td>
<td>−1.50</td>
<td>−1.57</td>
</tr>
<tr>
<td>Benzene dimer ($C_{2h}$)</td>
<td>−2.73</td>
<td>−2.74</td>
</tr>
<tr>
<td>Benzene·H$_2$O ($C_3$)</td>
<td>−3.28</td>
<td>−2.72</td>
</tr>
<tr>
<td>Uracil dimer ($C_2$)</td>
<td>−10.12</td>
<td>−7.03</td>
</tr>
<tr>
<td>Adenine · thymine stack ($C_1$)</td>
<td>−12.23</td>
<td>−9.55</td>
</tr>
<tr>
<td>Benzene dimer ($C_{2v}$)</td>
<td>−2.74</td>
<td>−2.28</td>
</tr>
</tbody>
</table>

*The 180° point from the solid black triangle curve for UU in Fig. 5, with no further structural relaxations.

*The 135° point from the open green triangle curve for AT in Fig. 6, with no further structural relaxations.

Applications to DNA:

M. Dion et al, PRL 92, 246401 (2004)
T. Thonhauser et al, PRB 76, 125112 (2007)
Local Density Approximation (LDA):

• Very successful in describing structural properties.
• Very useful for atomistic simulation of materials.

Confession time:

Difficulties with LDA?

We can now do accurate GW calculations for complex systems containing ~20-30 atoms/unit cell, e.g., VO2.
Metal-Insulator Transition of VO$_2$

Example of LDA failure: both phases are predicted to be metal

Conductivity

J. Morin (1959)

High T: Tetragonal (R) (metallic)

Low T: Monoclinic (M$_1$) (insulating)

Dimerisation of V, doubling of the unit cell

Figures taken from Eyert 2002
APPLICATIONS of VO2

Intelligent window coating:
Allows all visible wavelengths of light through but reflects infrared light when the temperature rises over 29°C

Ultrafast electrical and optical switch:
VO2 changes from a transparent to a mirror-like state in less than the time it takes light to travel a tenth of a millimeter

Futuristic applications:
VO2 nanoparticles as microscopic thermometers
Insulating VO$_2$: Peierls or Mott-Hubbard?

VO$_2$: d$^1$ configuration

- **Strong Correlation Scenario**
  
  *(A. Zylbersztejn and N. F. Mott 1980, T. M. Rice *et al.* 1999)*

- **Peierls Scenario** *(J. B. Goodenough 1979)*

Dimerization of two V atoms leads to bonding-antibonding splitting of $a_{1g}$ bands.

Peierls Picture *(Goodenough 1979)*

Metallic VO$_2$

Insulating VO$_2$

$t_{2g}(3)$

$e^\pi_g(2)$

$\alpha_{1g}(1)$

$E_F$
Kinetic energy

Potential energy

LDA:

\[- \nabla^2 \phi_n (r) + V_{LDA} (r) \phi_n (r) = \varepsilon_n \phi_n (r),\]

\[- \nabla^2 \phi_n (r) + \int dr' \Sigma (r, r'; \varepsilon_n) \phi_n (r') = \varepsilon_n \phi_n (r),\]

All interaction effects are included in \(\Sigma\) (“Self-energy”), which is *non-local* and *energy dependent*. 