From Atoms to Solids

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Part II Topics

1. It’s a Quantum World: The Theory of Quantum Mechanics
2. Quantum Mechanics: Practice Makes Perfect
3. From Many-Body to Single-Particle; Quantum Modeling of Molecules
4. Application of Quantum Modeling of Molecules: Solar Thermal Fuels
5. Application of Quantum Modeling of Molecules: Hydrogen Storage
6. From Atoms to Solids
7. Quantum Modeling of Solids: Basic Properties
8. Advanced Prop. of Materials: What else can we do?
10. Application of Quantum Modeling of Solids: Solar Cells Part II
11. Application of Quantum Modeling of Solids: Nanotechnology
Lesson outline

• Briefly hydrogen storage
• Periodic potentials
• Bloch’s theorem
• Energy bands
Hydrogen Storage

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"Tonight I am proposing $1.2 billion in research funding so that America can lead the world in developing clean, hydrogen-powered automobiles.

"A simple chemical reaction between hydrogen and oxygen generates energy, which can be used to power a car producing only water, not exhaust fumes.

"With a new national commitment, our scientists and engineers will overcome obstacles to taking these cars from laboratory to showroom so that the first car driven by a child born today could be powered by hydrogen, and pollution-free.

"Join me in this important innovation to make our air significantly cleaner, and our country much less dependent on foreign sources of energy."

2003 State of the Union Address
January 28, 2003
Renault Fluence EV to be assembled in Turkey

Obama, DOE slash hydrogen fuel cell funding in new budget

by Sebastian Blanco (RSS feed) on May 8th 2009 at 7:55AM BREAKING
A History of Hydrogen as a Fuel

16th century: F. B. Paracelsus first described “an air which bursts forth like the wind”

1671: Robert Boyle published a paper in which he described the reaction between Fe filings and dilute acids which results in the evolution of gas

1766: Henry Cavendish discovers “inflammable gas from metals”

1783: Lavoisier gives the name for it J. A. C. Charles suggests using hydrogen in balloons

1793: On Nov. 25 the first balloon is sent up from British soil

1807: Dalton’s theory of atoms is published; was the symbol used for hydrogen

1839: Sir William Robert Grove invents fuel cell

1937: On May 6 the Hindenburg tragedy occurs

1960’s: NASA searches for energy supplies for the spacecraft

1980’s: numerous explosions in the dioxane factories

1986: On Jan. 28 the Challenger space shuttle catastrophe takes place

2001: Fire of NaBH₄ loaded train in Baltimore (US) Sept. 11, terrorist attack on NYC

2010: an expected dawn of the hydrogen era:
- Fossil fuels crisis
- cheap hydrogen
- cheap membrane fuel cells
- mass production of the fuel cell-powered vehicles
- hydrogen is to take 5% share of the fuel market, which equals nowadays to some $700 bln per annum, and is still growing

THE DREAM

1874: “I believe that one day hydrogen and oxygen, which together form water, will be used either alone or together as an inexhaustible source of heat and light” (Jules Verne, The mysterious island)

1900

YESTERDAY

1998-2000: Ballard Power Systems introduces 205 kW fuel cells being used in six buses in Chicago and Vancouver

May 1999: the first public liquid–hydrogen filling station has been opened in at Munich Airport

2000

TODAY

Feb. 2001: a six-month tour of a fleet of ten BMW 750iL Liquid hydrogen powered sedans around the globe starts in oil-producing Dubai, the largest petroleum producer


2003: Toyota Motor and Honda Cos. are poised to be the first to offer a pure-hydrogen fuel cell commercial vehicle to a limited public in Japan and California

THE DREAM COME TRUE?

2100
The Hydrogen Fuel Challenge

• The low volumetric density of gaseous fuels requires a storage method which densifies the fuel.
  • This is particularly true for hydrogen because of its lower energy density relative to hydrocarbon fuels
    • 3 MJ/l (5000 psi H$_2$), 8 MJ/l (LH$_2$) vs. 32 MJ/l (gasoline)

• Storing enough hydrogen on vehicles to achieve greater than 300 miles driving range is difficult.

• Storage system adds an additional weight and volume above that of the fuel.

How do we achieve adequate stored energy in an efficient, safe and cost-effective system?
How large of a gas tank do you want?

Volume Comparisons for 4 kg Vehicular H₂ Storage

**Figure 1** Volume of 4 kg of hydrogen compacted in different ways, with size relative to the size of a car. (Image of car courtesy of Toyota press information, 33rd Tokyo Motor Show, 1999.)


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Packaging volume and safety are key issues.
Only the light elements.
- Short list: Li, Be, B, C, N, O, F, Na, Mg, Al, Si, and P.
- No toxicity!

List becomes only eight elements.
- Not a lot of room to do chemistry!
Lots of Materials Choices

- Crystalline Nanoporous Materials
- Polymer Microspheres
- Self-Assembled Nanocomposites
- Advanced Hydrides
- Inorganic – Organic Compounds
- BN Nanotubes
- Hydrogenated Amorphous Carbon
- Mesoporous Materials
- Bulk Amorphous Materials (BAMs)
- Iron Hydrolysis
- Nanosize Powders
- Metallic Hydrogen
- Hydride Alcoholysis

From Patrovic & Milliken (2003)
# Lots of Materials Choices

<table>
<thead>
<tr>
<th>Formula</th>
<th>Formula wt.% Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>25</td>
</tr>
<tr>
<td>H₃BNH₃</td>
<td>19.5</td>
</tr>
<tr>
<td>LiBH₄</td>
<td>18.3</td>
</tr>
<tr>
<td>(CH₃)₄NBH₄</td>
<td>18</td>
</tr>
<tr>
<td>NH₃</td>
<td>17.7</td>
</tr>
<tr>
<td>Al(BH₄)₃</td>
<td>16.8</td>
</tr>
<tr>
<td>Mg(BH₄)₂</td>
<td>14.8</td>
</tr>
<tr>
<td>LiH</td>
<td>12.6</td>
</tr>
<tr>
<td>CH₃OH</td>
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<tr>
<td>H₂O</td>
<td>11.2</td>
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<tr>
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<tr>
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<td>7.6</td>
</tr>
<tr>
<td>NaAlH₄</td>
<td>7.4</td>
</tr>
</tbody>
</table>
Example: BN Nanotubes

Figure 1 The morphologies of BN nanotubes: (a) multiwall nanotubes and (b) bamboo-like nanotubes. Scale bar: 100 nm.

Figure 2 The hydrogen adsorption as a function of pressure in multiwall BN nanotubes and bamboo nanotubes at 10 MPa is 1.8 and 2.6 wt %, respectively, in sharp contrast to the 0.2 wt % in bulk BN powder. The values reported here have an error of <0.3 wt %.

Figures removed due to copyright restrictions.

Sodium alanate doped with Ti is a reversible material hydrogen storage approach.

\[ 3\text{NaAlH}_4 \rightarrow \text{Na}_3\text{AlH}_6 + 2\text{Al} + 3\text{H}_2 \rightarrow 3\text{NaH} + \text{Al} + \frac{3}{2}\text{H}_2 \]

3.7 wt% 1.8 wt%

Low hydrogen capacity and slow kinetics are issues
Metal Hydrides

• Some metals absorb hydrogen to form metal hydrides

• These release the hydrogen gas when heated at low pressure and relatively high temperature

• Thus the metals soak up and release hydrogen like a sponge

• Hydrogen becomes part of the chemical structure of the metal itself and therefore does not require high pressures or cryogenic temperatures for operation

BUT: irreversibility problem!
There is no ONE material yet.

• There is, as yet, no material known to meet simultaneously all of the key requirements and criteria.

• Palladium metal has long been viewed as an attractive hydrogen-storage medium, exhibiting reversible behavior at quite low temperature. However, its poor storage efficiency (less than 1 wt %) and the high cost of palladium ($1000 per ounce) eliminate it from any realistic consideration.

• On the other hand, the composite material “Li3Be2H7” is a highly efficient storage medium (ca. 8.7 wt % of reversibly stored H), but it is highly toxic and operates only at temperatures as high as 300 °C.
There is no ONE material yet.

• Or take AlH3: the compound is a relatively low temperature (150 °C), highly efficient (10.0 wt %) storage material and contains cheap Al metal ($1300 per tonne), but, unfortunately, its hydrogen uptake is almost completely irreversible.

• Similarly, an alkaline solution of NaBH4 in H2O constitutes a super-efficient storage system (9.2 wt % hydrogen), and full control may be gained over H2 evolution by use of a proper catalyst, but the starting material cannot be simply (economically) regenerated.

• Finally, pure water contains 11.1 wt % of H, but its decomposition requires much thermal, electric, or chemical energy.

• Recently advanced technology of hydrogen storage in nitrides and imides allows for effective (6.5-7.0 wt % H) but high-temperature (around 300 °C) storage.
PERFECT Problem for Computational Quantum Mechanics!

- Hydrogen storage: store hydrogen in a lightweight and compact manner for mobile applications.
- Bulk materials are often too stable.
  - E.g. MgH$_2$: 7.7wt%, $\Delta H^0_d = 75$ kJ/mol, $T_d \sim 300$ °C
  - Desirable $\Delta H^0_d = 20 - 50$ kJ/mol
  - $\Delta H^0_d$ can be tuned by the size of nanoparticles.

\[ \text{MgH}_2 \rightarrow \text{H} \text{(kJ/mol H)}_2 \]

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Alloying and Nanostructuring May be the Key, but Phase Space is Enormous

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Wagner, Allendorf, and JCG, PCCP (2012)
From Atoms to Solids
The ground state electron configuration of a system is constructed by putting the available electrons, two at a time (Pauli principle), into the states of lowest energy.
Energy bands

occupied
empty

Metal
Insulator
Semiconductor

NB: boxes = allowed energy regions
Crystal symmetries

A crystal is built up of a unit cell and periodic replicas thereof.

lattice  unit cell

Image of Sketch 96 (Swans) by M.C. Escher removed due to copyright restrictions.
Since a crystal is periodic, maybe we can get away with modeling only the unit cell?
Crystal symmetries

CUBIC
a = b = c
α = β = γ = 90°

TETRAGONAL
a = b ≠ c
α = β = γ = 90°

ORTHORHOMBIC
a ≠ b ≠ c
α = β = γ = 90°

HEXAGONAL
a = b ≠ c
α = β = 90°
γ = 120°

MONOCLINIC
a ≠ b ≠ c
α = γ = 90°
β ≠ 120°

TRICLINIC
a ≠ b ≠ c
α ≠ β ≠ γ ≠ 90°

S = simple
BC = body centered
FC = face centered

4 Types of Unit Cell
P = Primitive
I = Body-Centred
F = Face-Centred
C = Side-Centred

7 Crystal Classes
→ 14 Bravais Lattices

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Lattice and basis

simple cubic

face centered cubic

Images by MIT OpenCourseWare.
The inverse (or “reciprocal”) lattice

Associated with each real space lattice, there exists something we call a **reciprocal lattice**.

The reciprocal lattice is the set of wave-vectors which are commensurate with the real space lattice.

It is defined by a set of vectors $a^*$, $b^*$, and $c^*$ such that $a^*$ is perpendicular to $b$ and $c$ of the Bravais lattice, and the product $a^* \times a$ is 1.
The inverse lattice

The real space lattice is described by three basis vectors:
\[ \mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \]

The inverse lattice is described by three basis vectors:
\[ \mathbf{G} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3 \]

\[ b_1 = 2\pi \frac{a_2 \times a_3}{a_1 \cdot (a_2 \times a_3)} \quad b_2 = 2\pi \frac{a_3 \times a_1}{a_2 \cdot (a_3 \times a_1)} \quad b_3 = 2\pi \frac{a_1 \times a_2}{a_3 \cdot (a_1 \times a_2)} \]

\[ e^{i \mathbf{G} \cdot \mathbf{R}} = 1 \]

\[ \psi(\mathbf{r}) = \sum_j c_j e^{i \mathbf{G}_j \cdot \mathbf{r}} \]

automatically periodic in \( \mathbf{R} \)!
The inverse lattice

real space lattice (BCC)  inverse lattice (FCC)
The Brillouin zone is a special unit cell of the inverse lattice.
Reciprocal Lattice & Brillouin Zone

It is defined by a set of vectors \(a^*, b^*, \) and \(c^*\) such that \(a^*\) is perpendicular to \(b\) and \(c\) of the Bravais lattice, and the product \(a^* \times a\) is \(1\).

In particular: \[ a^* = \frac{b \times c}{a \cdot b \times c} \]

Surfaces of the first, second, and third Brillouin zones for body-centered cubic and face-centered cubic crystals. Images are in the public domain.
The Brillouin zone

Brillouin zone of the FCC lattice
Periodic potentials

metallic sodium

\[
\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi = E\psi
\]
Periodic potentials

It becomes much easier if you use the periodicity of the potential!

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

Results in a VERY important new concept.

Bloch’s Theorem
Bloch’s Theorem

Reciprocal lattice vectors have special properties of particular value for calculations of solids.

We write the reciprocal lattice vector:

\[ G = 2\pi n \mathbf{a}^* + 2\pi m \mathbf{b}^* + 2\pi o \mathbf{c}^* \]

We added the 2 simply for convenience, and the n, m, o, are integers.

Now consider the behavior of the function \(\exp(iG\mathbf{r})\).
Bloch’s Theorem

\[
\exp(iG \cdot \mathbf{r}) = \exp\left[ i(2\pi n a^* + 2\pi m b^* + 2\pi o c^*) \cdot (\alpha a + \beta b + \gamma c) \right] \\
= \exp\left[ i(2\pi n \alpha + 2\pi m \beta + 2\pi o \gamma) \right] \\
= \cos(2\pi n \alpha + 2\pi m \beta + 2\pi o \gamma) + i \sin(2\pi n \alpha + 2\pi m \beta + 2\pi o \gamma)
\]

As \( \mathbf{r} \) is varied, lattice vector coefficients (\( \alpha, \beta, \gamma \)) change between 0 and 1 and the function \( \exp(iG \cdot \mathbf{r}) \) changes too.

However, since \( n, m, \) and \( o \) are integral, \( \exp(iG \cdot \mathbf{r}) \) will always vary with the periodicity of the real-space lattice.

\[
e^{i\mathbf{G} \cdot \mathbf{R}} = 1 \quad \quad \psi(\mathbf{r}) = \sum_j c_j e^{i\mathbf{G}_j \cdot \mathbf{r}}
\]

automatically periodic in \( \mathbf{R} \)!
Bloch’s Theorem

The periodicity of the lattice in a solid means that the values of a function (e.g., density) will be identical at equivalent points on the lattice.

The wavefunction, on the other hand, is periodic but only when multiplied by a phase factor.

This is known as Bloch’s theorem.

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

\[
u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{R})
\]
Periodic potentials

Results of the Bloch theorem:

\[ \psi_{\vec{k}}(\vec{r} + \vec{R}) = \psi_{\vec{k}}(\vec{r}) e^{i\vec{k} \cdot \vec{R}} \]

\[ |\psi_{\vec{k}}(\vec{r} + \vec{R})|^2 = |\psi_{\vec{k}}(\vec{r})|^2 \]

Charge density is lattice periodic

if solution \( \psi_{\vec{k}}(\vec{r}) \) \( \longrightarrow \) \( \psi_{\vec{k}+\vec{G}}(\vec{r}) \) also solution

with \( E_{\vec{k}} = E_{\vec{k}+\vec{G}} \)
Periodic potentials

Schrödinger equation

hydrogen atom

spherical symmetry

periodic solid

translational symmetry

quantum number

\[ [H, L^2] = HL^2 - L^2H = 0 \]

\[ [H, L_z] = 0 \]

\[ [H, T] = 0 \]

\[ \psi_{n,l,m}(\vec{r}) \]

\[ \psi_{n,\vec{k}}(\vec{r}) \]
Periodic potentials

Bloch’s theorem

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

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

\[ \lambda = 2\pi/k \]

Image by MIT OpenCourseWare.
The band structure

Different wave functions can satisfy the Bloch theorem for the same $k$: eigenfunctions and eigenvalues labelled with $k$ and the index $n$

\[
\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r})\right] \psi_{\vec{k}}(\vec{r}) = \epsilon_{\vec{k}} \psi_{\vec{k}}(\vec{r}) \quad \Rightarrow \quad \psi_{n,\vec{k}}(\vec{r}) \quad \epsilon_{n,\vec{k}} \]

energy bands
The band structure

energy levels in the Brillouin zone

Silicon

Image by MIT OpenCourseWare.
The band structure

energy levels
in the Brillouin zone
Literature

• Charles Kittel, Introduction to Solid State Physics

• Richard M. Martin, Electronic Structure

• wikipedia, “solid state physics”, “condensed matter physics”, ...

• Simple band structure simulations: http://phet.colorado.edu/simulations/sims.php?sim=Band_Structure