It’s A Quantum World: The Theory of Quantum Mechanics

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3.021 Content Overview

I. Particle and continuum methods
   1. Atoms, molecules, chemistry
   2. Continuum modeling approaches and solution approaches
   3. Statistical mechanics
   4. Molecular dynamics, Monte Carlo
   5. Visualization and data analysis
   6. Mechanical properties – application: how things fail (and how to prevent it)
   7. Multi-scale modeling paradigm
   8. Biological systems (simulation in biophysics) – how proteins work and how to model them

II. Quantum mechanical methods ← we are here

Welcome to Part 2!

The next 11 lectures will cover atomistic quantum modeling of materials.

Note: there will be a substitute lecturer on Tuesday, April 10 and no class on Thursday, April 12.
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

- Why quantum mechanics?
- Wave aspect of matter
- Interpretation
- The Schrödinger equation
- Simple examples
Multi-scale modeling

Macro-scale structural engineering

Ultra-scale structural engineering

Energy $U$

$1/r^{12}$ (or exponential)

repulsion

Radius $r$
(distance between atoms)

$1/r^6$

attraction

O(100 m)

O(10 m)

O(1 m)

O(1 nm)

O(100 nm)

O(0.01 m)

quantum modeling

It’s a quantum world!
Motivation

If we understand electrons, then we understand everything.

(almost) ...
Quantum modeling/simulation

- Mechanical properties
- Electrical properties
- Optical properties
A simple iron atom ...
Why Quantum Mechanics?

Accurate/predictive structural/atomistic properties, when we need to span a wide range of coordinations, and bond-breaking, bond-forming takes place.

(But beware of accurate energetics with poor statistics !)

EDIP Si potential  
Tight-binding

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Electronic, optical, magnetic properties

Jahn-Teller effect in porphyrins (A. Ghosh)

Non-resonant Raman in silicates (Lazzeri and Mauri)
Reactions

1,3-butadiene + ethylene → cyclohexene

See Lecture 1 video for animation. © James E. Kendall/MSC Caltech. All rights reserved. This content is excluded from our Creative Commons license. For more information, see http://ocw.mit.edu/help/faq-fair-use/.
Standard Model of Matter

• Atoms are made by MASSIVE, POINT-LIKE NUCLEI (protons+neutrons)

• Surrounded by tightly bound, rigid shells of CORE ELECTRONS

• Bound together by a glue of VALENCE ELECTRONS (gas vs. atomic orbitals)
It’s real!

Cu-O Bond
(experiment)

Ti-O Bond
(theory)

Importance of Solving for this Picture with a Computer

• It provides us microscopic understanding
• It has predictive power (it is “first-principles”)
• It allows controlled “gedanken” experiments
• Challenges:
  › Length scales
  › Time scales
  › Accuracy
Why quantum mechanics?

**Classical mechanics**

Newton’s laws (1687)

\[
\vec{F} = \frac{d(m\vec{v})}{dt}
\]

Problems?
Why quantum mechanics?

Problems in classical physics that led to quantum mechanics:

- “classical atom”
- quantization of properties
- wave aspect of matter
- (black-body radiation), ...
Quantum mechanists

Werner Heisenberg, Max Planck, Louis de Broglie, Albert Einstein, Niels Bohr, Erwin Schrödinger, Max Born, John von Neumann, Paul Dirac, Wolfgang Pauli (1900 - 1930)
“Classical atoms”

Problem:
accelerated charge causes radiation, atom is not stable!

hydrogen atom
Quantization of properties

photoelectric effect

\[ E = \hbar(\omega - \omega_A) = \hbar(\nu - \nu_A) \]

\[ \hbar = 2\pi\hbar = 6.6 \cdot 10^{-34} \text{ Wattsec}^2 \]

Einstein: photon \[ E = \hbar\omega \]
Quantization of properties

atomic spectra
Quantization of properties

\[ E = \hbar \omega \]

possible energy states

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The Double-Slit Experiment

Dr Quantum explains the double-slit experiment. From the film: *What the bleep do we know?* See Lecture 1 video for full clip.
"Anyone who is not shocked by quantum theory has not understood it"

Niels Bohr
Schrödinger’s Cat

"I don't like it, and I'm sorry I ever had anything to do with it," Schrödinger, on the cat paradox.
EPR Paradox

Einstein–Podolsky–Rosen

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Wave-Particle Duality

• Waves have particle-like properties:
  • Photoelectric effect: quanta (photons) are exchanged discretely
  • Energy spectrum of an incandescent body looks like a gas of very hot particles

• Particles have wave-like properties:
  • Electrons in an atom are like standing waves (harmonics) in an organ pipe
  • Electrons beams can be diffracted, and we can see the fringes
Interference Patterns

Wave Interactions

Constructive Interference

Destructive Interference

Resultant $A_1 + A_2$

Resultant $A_1 - A_2$

Image by MIT OpenCourseWare.
Interference Patterns
Bucky- and soccer balls

Courtesy of the University of Vienna. Used with permission.
When is a particle like a wave?

Wavelengths:

- Electron: $10^{-10}$ m
- C60 Fullerene: $10^{-12}$ m
- Baseball: $10^{-34}$ m
- Human wavelength: $10^{-35}$ m

20 orders of magnitude smaller than the diameter of the nucleus of an atom!
Classical vs. quantum

It is the mechanics of waves rather than classical particles.
Wave aspect of matter

light
matter

wave character

particle character

monochromatic planar wave (e.g. a laser)
screen with two slits
optical screen

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Mechanics of a Particle

\[ m \frac{d^2 \mathbf{r}}{dt^2} = F(\mathbf{r}) \quad \rightarrow \quad \mathbf{r}(t) \quad \mathbf{v}(t) \]

The sum of the kinetic and potential energy is conserved.
Description of a Wave

The wave is an excitation (a vibration): We need to know the amplitude of the excitation at every point and at every instant

$$\Psi = \Psi(r, t)$$
Mechanics of a Wave

Free particle, with an assigned momentum:

\[ \Psi(r, t) = A \exp[i(k \cdot r - \omega t)] \]
Wave aspect of matter

**particle:** $E$ and momentum $\vec{p}$

**wave:** frequency $\nu$ and wavevector $\vec{k}$

\[
E = h\nu = \hbar\omega
\]

\[
\vec{p} = \hbar\vec{k} = \frac{h \vec{k}}{\lambda |\vec{k}|}
\]

de Broglie: free particle can be described as planewave
\[
\psi(\vec{r}, t) = Ae^{i(\vec{k} \cdot \vec{r} - \omega t)} \quad \text{with} \quad \lambda = \frac{h}{mv}
\]
How do we describe the physical behavior of particles as waves?
The Schrödinger equation

a wave equation: second derivative in space
first derivative in time

\[ -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}, t) \psi(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) \]

\[ H = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}, t) = \]

\[ = \frac{p^2}{2m} + V = T + V \]

\[ \vec{p} = -i\hbar \nabla \]

Hamiltonian
In practice ...

$H$ time independent: $\psi(\vec{r}, t) = \psi(\vec{r}) \cdot f(t)$

\[
\dot{f}(t) = \frac{i\hbar}{f(t)} \frac{H\psi(\vec{r})}{\psi(\vec{r})} = \text{const.} = E
\]

$H\psi(\vec{r}) = E\psi(\vec{r})$

$\psi(\vec{r}, t) = \psi(\vec{r}) \cdot e^{-\frac{i}{\hbar}Et}$

time independent Schrödinger equation
stationary Schrödinger equation
Particle in a box

boundary conditions
\[ \psi(0) = \psi(L) = 0 \quad (4) \]
\[ \psi(x) = A \sin(kx) \quad (5) \]
\[ \psi(L) = A \sin(kL) = 0 \quad (6) \]

general solution
\[ \psi(x) = A \sin(kx) + B \cos(kx) \]
\[ E = \frac{k^2 \hbar^2}{2m} \quad (3) \]

Schrödinger equation
\[ -\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \quad (1) \]

Boundary conditions cause quantization!
Particle in a box

quantization

\[ k = \frac{n\pi}{L} \quad \text{where} \quad n \in \mathbb{Z}^+ \quad (7) \]

normalization

\[ 1 = \int_{-\infty}^{\infty} |\psi(x)|^2 \, dx = |A|^2 \int_{0}^{L} \sin^2(kx) \, dx = |A|^2 \frac{L}{2} \]

solution

\[ \psi_n(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{n\pi x}{L} \right) \quad (9) \]

\[ E_n = \frac{n^2\hbar^2\pi^2}{2mL^2} = \frac{n^2\hbar^2}{8mL^2} \quad (10) \]

quantum number

Image adapted from Wikimedia Commons, http://commons.wikimedia.org.
Simple examples

electron in square well

\[ \infty \rightarrow \infty \]

\[ n = 5 \quad 58.8 \text{ eV} \]
\[ n = 4 \quad 37.6 \text{ eV} \]
\[ n = 3 \quad 21.4 \text{ eV} \]
\[ n = 2 \quad 9.4 \text{ eV} \]
\[ n = 1 \quad 2.6 \text{ eV} \]

Infinite Well

electron in hydrogen atom

\[ 1 \rightarrow n = 5 \]
\[ 2 \rightarrow n = 4 \]
\[ 3 \rightarrow n = 3 \]
\[ 4 \rightarrow n = 2 \]
\[ 5 \rightarrow n = 1 \]

Balmer series

Paschen series

Brackett series

Pfund series

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Harmonic oscillator

\[ V(x) = \frac{1}{2} m \omega^2 x^2 \]

\[ H = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 x^2 \]

\[ E_n = \hbar \omega \left( n + \frac{1}{2} \right) \]

\[ \langle x | \psi_n \rangle = \sqrt{\frac{1}{2^n n!}} \cdot \left( \frac{m \omega}{\pi \hbar} \right)^{1/4} \cdot \exp \left( -\frac{m \omega x^2}{2 \hbar} \right) \cdot H_n \left( \sqrt{\frac{m \omega}{\hbar}} x \right) \]
Harmonic oscillator

Graphs of the quantum harmonic oscillator potential and wavefunctions.

Image by MIT OpenCourseWare.
Interpretation of a wavefunction

\[ \psi(\vec{r}, t) \] wave function (complex)

\[ |\psi|^2 = \psi\psi^* \] interpretation as probability to find particle (that is, if a measurement is made)

\[ \int_{-\infty}^{\infty} \psi\psi^* dV = 1 \]

Image by MIT OpenCourseWare.
Connection to reality?

potential: \( \frac{1}{r} \)

hydrogen atom

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## Many Interpretations of Quantum Mechanics!

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<td>Ensemble interpretation</td>
<td>Max Born, 1926</td>
<td>No</td>
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<td>Yes</td>
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<td>No</td>
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<td>Copenhagen interpretation</td>
<td>Niels Bohr, Werner Heisenberg, 1927</td>
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<td>de Broglie-Bohm theory</td>
<td>Louis de Broglie, 1927, David Bohm,</td>
<td>Yes</td>
<td>Yes(^5)</td>
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<td>von Neumann interpretation</td>
<td>John von Neumann, 1932</td>
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<td>Many-worlds interpretation</td>
<td>Hugh Everett, 1957</td>
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<td>Stochastic mechanics</td>
<td>Edward Nelson, 1966</td>
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<td>Many-minds mechanics</td>
<td>H. Dieter Zeh, 1970</td>
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<td>Interpretational(^4)</td>
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<td>Consistent histories</td>
<td>Robert B. Griffiths, 1984</td>
<td>Agnostic(^1)</td>
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<td>Objective collapse theories</td>
<td>Ghirardi-Rimini-Weber, 1986</td>
<td>No</td>
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<td>Transactional interpretation</td>
<td>John G. Cramer, 1986</td>
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<td>Relational interpretation</td>
<td>Carlo Rovelli, 1994</td>
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<td>Incomplete measurements</td>
<td>Christophe de Dinechin, 2006</td>
<td>No</td>
<td>No(^11)</td>
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Summary
Review

- Why quantum mechanics?
- Wave aspect of matter
- Interpretation
- The Schrödinger equation
- Simple examples
Literature

- Greiner, Quantum Mechanics: An Introduction
- Thaller, Visual Quantum Mechanics
- Feynman, The Feynman Lectures on Physics
- wikipedia, “quantum mechanics”, “Hamiltonian operator”, “Schrödinger equation”, ...