Contents

1 Introduction

1.1 What do we care about?

Things chemistry/materials-related:

- What are the properties of atoms?
- What molecules do they make? What other substances do they make?
- What are the shapes of those molecules? Structures of those solids? Properties of them?
- How do those substances react with each other?
- What are the energies of those reactions?
- What are the rates of those reactions?
- What is the strongest substance?
- How do we make a substance to do. . . .?
- add your own questions. . . .

Things that relate to the *chemical* properties of substances.

1.2 How are we going to figure these out? With only a computer?

1926 Erwin Schrödinger equation: $\hat{H}\Psi = E\Psi$

1929 Paul Dirac, British physicist

> The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus *completely known*, and the difficulty lies only in the fact that application of these laws leads to equations that are *too complex to be solved*.
>
> It therefore becomes desirable that *approximate practical methods* of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

1930's-1950's Elaboration, analytical applications

1950's Computers start to appear for technical applications

1960's-1970's Numerical solutions of Schrödinger equation for atoms/molecules—expert users

1980's "Supercomputer" era—routine use of computational chemistry software becomes possible

Figure 1: Ohio State Cray Y-MP supercomputer, ca. 1989. World's fastest computer at the time. 333 MFlop top speed, 512 Mb RAM

1990's "Chemical accuracy" era—very precise solutions routinely available, for a cost! See Schneider, *J. Phys. Chem.*, **1994**.

1990's Density functional theory (DFT) allows applications to solids/surfaces/liquids to become common. See Hass, *Science*, **1998**

1990's Visualization moves to the desktop

2000's Computational "screening", materials "discovery." See Greeley, *J. Phys. Chem. C*, **2009**. Also see Gurkan, *J. Phys. Chem. Lett.*, **2010**.

Today Computational "chemistry" widely integrated into all aspects of chemical, materials, biological research

"Computational chemistry" is now so vast it is impossible to cover everything completely. We limit ourselves to quantum-mechanics-based calculations.

1.3 Our goals

1. Understand when it is appropriate to use quantum-mechanics methods.
2. Be able to state the basic theoretical, mathematical, and numerical concepts behind quantum mechanical "wavefunction theory" (WFT) and "density functional theory," (DFT) calculations.
3. Understand the terminology and practical issues associated with doing quantum chemical simulations.
4. Get hands-on experience with these concepts using popular computational tools of today, including GAMESS for molecular systems and Vasp for condensed phase systems.
5. Learn how to apply the results of quantum chemical simulations to calculate things you care about.
6. Demonstrate an ability to formulate a problem and apply QM methods to it.
7. Develop the skills to understand a literature paper in the area.

1.4 Reading resources

- These notes
- Chris Cramer, *Essentials of Computational Chemistry*, Wiley, 2004

- Sholl and Steckel, *Density Functional Theory: A Practical Introduction*, Wiley, 2009
- Kitchin book, http://kitchingroup.cheme.cmu.edu/dft-book/

1.5 Software tools

1.5.1 Molecular methods

- Avogadro environment http://avogadro.cc/wiki/Main_Page
- GAMESS code http://www.msg.ameslab.gov/GAMESS/GAMESS.html

1.5.2 Supercell methods

- ASE environment https://wiki.fysik.dtu.dk/ase/
- Vasp code http://www.vasp.at/

1.5.3 Great for getting started

- Webmo http://www.webmo.net/