Dive into computational physical chemistry

Lecture 8: Intro to electronic structure

Glen Hocky
November 7, 2024

Quantum mechanics

- Energy comes in discrete packets (quanta)

- Particles are delocalized, and they can be described by 'wave functions', which are complex functions $\Psi(x)$

- The probability of finding a particle at position x is given by $\Psi^*(x)\Psi(x)$

- For a time-independent problem, we solve the **Schrodinger equation**

  - $\widehat{H}\Psi = E\Psi$

Time-independent Schrodinger equation

$$\widehat{H}\Psi = E\Psi$$

- $\widehat{H}$ is the "Hamiltonian Operator"

- Hamiltonian is still Kinetic energy + Potential energy

- $\widehat{H} = \sum_{i=1}^{N} \frac{\hat{p}_i^2}{2\,m_i} + V(x)$

- But these are short-hands for parts of a differential equation we have to solve

- $\hat{p} = -i\,\hbar\left(\frac{d}{dx}, \frac{d}{dy}, \frac{d}{dz}\right), \hbar = \frac{h}{2\pi} \approx 1.055 \times 10^{-34} J\,s$

- So $\frac{\hat{p}_i^2}{2\,m_i} = -\frac{\hbar^2}{2m}\nabla_i^2$

Coulomb potential

$$V(x_1, x_2) = \frac{q_1 q_2}{4\pi\epsilon_0 |x_1 - x_2|}$$

$$\epsilon_0 \approx 8.85{\times}10^{-12}\,\frac{C^2}{Jm}, e = 1.602{\times}10^{-19}C$$

◦ Molecules are made of electrons and protons

◦ Except at extremely high energies, we can say that electrons and protons only interact by the Coulomb potential, which depends on the distance between particles

◦ Let i,j represent electrons and A,B represent protons then

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \frac{\hbar^2}{2}\sum_A \frac{\nabla_A^2}{2M_A} - \sum_{A,i} \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} + \sum_{A>B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r_{AB}} + \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

Born-Oppenheimer approximation

$$\widehat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \frac{\hbar^2}{2}\sum_A \frac{\nabla_A^2}{2M_A} - \sum_{A,i}\frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} + \sum_{A>B}\frac{Z_A Z_B e^2}{4\pi\epsilon_0 r_{AB}} + \sum_{i>j}\frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

◦ Electrons are much lighter than protons (~1836 times)

◦ Therefore they should "move faster"

◦ That means, if think of protons as particles at fixed positions (not delocalized), then electronic wavefunction relaxes in the potential field set by protons

◦ Protons feel forces from each other and electrons, causing them to move, and then we can solve the electron positions again

◦ One thing we will do is find the 'equilibrium' positions of the nuclei by energy minimization

Applications of electronic structure theory

The electronic wavefunction or its various derivatives are sufficient to determine the following properties:

- Geometrical structures (rotational spectra)
- Rovibrational energy levels (infrared and Raman spectra)
- Electronic energy levels (UV and visible spectra)
- Quantum Mechanics + Statistical Mechanics $\rightarrow$ Thermochemistry (ΔH, ΔS, ΔG, C_v, C_p), primarily gas phase.

- Potential energy surfaces (barrier heights, transition states); with a treatment of dynamics, this leads to reaction rates and mechanisms.
- Ionization potentials (photoelectron and X-ray spectra)
- Electron affinities
- Franck-Condon factors (transition probabilities, vibronic intensities)
- IR and Raman intensities
- Dipole moments
- Polarizabilities
- Electron density maps and population analyses
- Magnetic shielding tensors $\rightarrow$ NMR spectra

See: http://vergil.chemistry.gatech.edu/notes/intro_estruc/node3.html

Very basics idea of solving the electronic structure problem

$$\hat{H}\Psi = E\Psi$$

◦ Wave functions can be *expanded in a basis*

◦ $\Psi = \sum_i c_i \psi_i$, and so we can represent $\Psi = (c_1, c_2, \dots)$ as a vector in a space formed by the ψ's

◦ Any operator has a matrix representation such that for operator $\hat{A}$, $A_{ij} = \langle i|A|j \rangle$

◦ Want to solve the linear algebra problem of the Schrodinger equation with $\hat{H}$ a matrix, so in essence we want its eigenvalues in some basis where we can evaluate its entries

◦ In future lectures, we'll discuss the basics of Hartree-Fock and DFT in a bit more depth and how to calculate and visualize the results

Software for electronic structure

- There are many codes for solving the electronic structure problem with different specialization

- These include

  - Commercial software: GAUSSIAN, Q-CHEM, JAGUAR, …

  - Open-source software: GAMESS, NWCHEM, PSI, PySCF, …

- There are some specialization, e.g.

  - CP2K is good for AIMD

  - VASP is good for materials/band structure

Example problem

We previously talked about Lennard-Jones interaction

$$V(r) = 4\epsilon \left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right)$$

- But where does it come from, and how do we get the parameters for this term to go into an MD simulation
- First term comes from repulsion between electron clouds, while the second comes from dipole-induced dipole attraction, and the power of 6 can be derived analytically for a simple problem
- Today, we will compute it for the famous case of the Argon dimer using high level quantum theory

Today

1. Pull updates on comp-lab-class github page

https://github.com/hockyg/comp-lab-class-2024/blob/main/Week10-IntroElectronicStructure/Assignment.md

2. Do the Psi4 python tutorial

3. Compute the Ar-Ar interaction energy curve

4. Fit it to an LJ form to get interaction parameters