Dive into computational physical chemistry

Lecture 11: Ab Initio MD

Glen Hocky
November 30, 2023

Reminder: What is a classical Molecular Dynamics (MD) Simulation?

Classical particles obey Newton's Equations of Motion

$$F = m\,a$$

But really 3N differential equations

$$F_i^x = m_i\,\frac{d^2x_i}{dt^2}\,;\ F_i^y = m_i\,\frac{d^2y_i}{dt^2}\,;\ F_i^z = m_i\,\frac{d^2z_i}{dt^2}$$

What are the forces?

$$\vec{F} = -\nabla U$$

$$\Rightarrow F_i^x = -\frac{dU(x_1,y_1,z_1,\ldots,x_N,y_N,z_N)}{dx_i}\text{, etc.}$$

Good reference: https://livecomsjournal.org/index.php/livecoms/article/view/v1i1e5957

Reminder: Two key variables, position (q) and momentum (p)

Momentum is "mass times velocity" – total momentum is conserved (doesn't change in time) if there are no external forces.

$$\vec{q_i} = \{x_i, y_i, z_i\}, \vec{p_i} = m_i \frac{dq_i}{dt}$$

"Microstate" or "phase space point" of the system is current position and momentum: $X(t) = \{\vec{q_1}, \vec{q_2}, \ldots, \vec{q_N}, \vec{p_1}, \vec{p_2}, \ldots, \vec{p_N}\}$

If following Newton's equations - knowing $U(X)$ and $X(0)$, know everything from $X(-\infty)$ to $X(\infty)$

Reminder: Electronic structure in Born Oppenheimer approximation

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

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

Or: use DFT to find electron density that minimizes this energy

Ab Initio Molecular Dynamics

- In the Born-Oppenheimer approximation, nuclei are classical already

- That means we can do classical MD, if only we knew the forces

$$F_i^x = -\frac{dU(x_1, y_1, z_1, ..., x_N, y_N, z_N)}{dx_i}, \text{ etc.}$$

- How does the energy change with nuclear position? Need to calculate this quantity from electronic structure

- Hellmann-Feynman theorem: $\frac{dE_\lambda}{d\lambda} = \left\langle \psi_\lambda \left| \frac{dH_\lambda}{d\lambda} \right| \psi_\lambda \right\rangle$

- This applies to eigenfunctions of H, but can be extended to variational theories, so it is okay for HF and DFT

- For "BOMD", only electron-nucleus and nucleus-nucleus interaction contribute

- Note: CPMD (1985) differs in that it treats the electrons as dynamical variables

Hybrid QM/MM approaches

- Original idea: Warshel & Levitt, 1976 (Nobel Prize 2013)

- Treat part of the system quantum mechanically, and most using forcefield, plus an interaction between the QM and MM regions

- How do we combine the two parts?

- Simple approach: $E = E^{QM}(QM) + E^{MM}(QM + MM) - E^{MM}(QM)$

- In practice, additive method: $E(QM) + E(MM) + E(QM - MM)$, where the interaction between QM and MM is from interaction of QM region with classical point charges and interaction on MM is from charge density applied to protons, plus VDW and bonded interactions across the boundary

Example AIMD problem for the week

- AIMD on water using DFT

  - Can try to predict features of water using first principles, can give insight into structure of water, diffusion constant, spectrum etc

  - Need to include quantum mechanical protons to get some properties correct

- AIMD on proton in water

  - Famously, diffusion of hydronium ion is faster than other ions

  - This is due to Grotthuss mechanism (1806!)

  - Still vigorous discussion of whether the solvated hydronium is like $H_9O_4^+$ (Eigen) or $H_5O_2^+$ (Zundel)
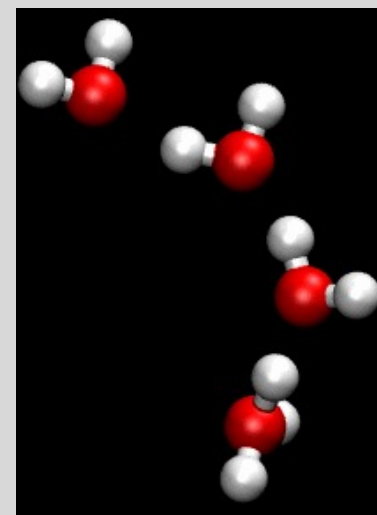
Today

1. Work on independent project or

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

https://github.com/hockyg/comp-lab-class-2023/blob/main/Week12/Assignment.md

   1. Run AIMD on water

   2. Run AIMD on water + proton

   3. Visualize in VMD and calculate structure, comparing to experiment