Molecular Dynamics: The Quantum Coupling

A (hopefully) lightweight introduction to the world of multiscale modeling.

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Outline

Recap of Molecular Dynamics
  Basics
  Why do we need quantum mechanics?

Introducing Quantum Mechanics
  Difference from Newtonian Mechanics
  Challenges

Parameterizing Potentials using Quantum Mechanics
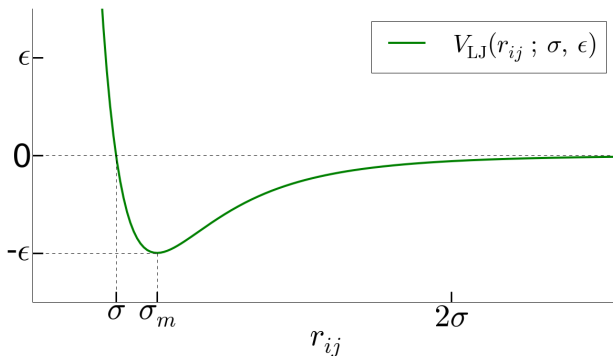 Connecting the scales
  Examples!
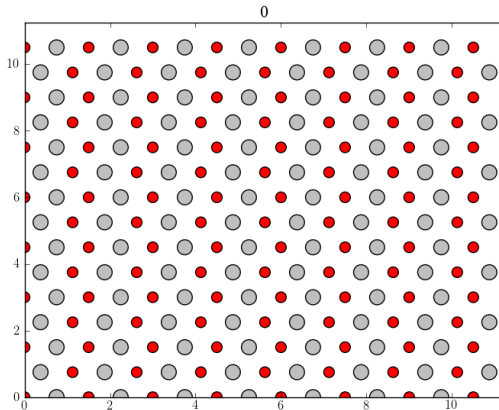 The Nobel prize in chemistry 2013

Recap of Molecular Dynamics

Basics

- Integrate Newton's equations for a dynamic set of point particles.

- Molecular interactions are described by potentials.

Why do we need quantum mechanics?

- Allows for studying complex chemical reactions.

- Reveals most energy efficient configurations without a priori assumptions.

- Dramatically increases the predictive power of MD.

Introducing Quantum Mechanics

Difference from Newtonian Mechanics

Newtons 2. law (N2L) links the dynamics of an object to the sum of forces acting on it.

$$\sum \mathbf{F}(\mathbf{r}) = m\mathbf{a}$$
$$\frac{\partial \mathbf{p}}{\partial t} = -\nabla V(\mathbf{r})$$

Assuming we live on a scale where all forces are *conservative*, the dynamics arise due to impulses generated by potentials.

The Schrödinger equation (SE) links the dynamics of a quantum system to the time evolution of it's *wave function*, a quantity once squared represents the probability density of the system's constituent particles.

$$i\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t} = \frac{1}{2m}\mathbf{P}^2\psi(\mathbf{r},t) + \mathbf{V}(\mathbf{r})\psi(\mathbf{r},t) \equiv \mathbf{H}\psi(\mathbf{r},t)$$

The time evolution of the wave function is in turn governed by the interplay between potential and kinetic energy just as in the Newtonian case.
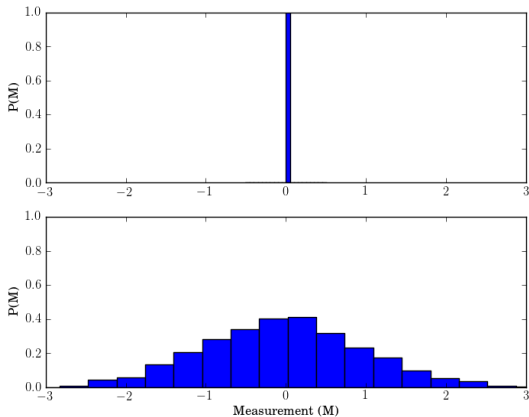
N2L can be deduced from the SL by taking the expectation value in the distribution given by the solution

$$-\langle\nabla\mathbf{V}\rangle_\psi = \left\langle\frac{\partial\mathbf{P}}{\partial t}\right\rangle_\psi$$

Imagine having a series of *identical* experiments.

- **Classical scale:** Every measurement yields the same result $\mathbf{m}_{\mathrm{CL}}$.

- **Quantum scale:** Every measurement $\mathbf{m}_{\mathrm{QM}}$ can in theory be different, however, under the restriction that
  $\langle \mathbf{m}_{\mathrm{QM}} \rangle = \mathbf{m}_{\mathrm{CL}}$

Challenges

The electrons

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- ... which implies interference with other electrons...

- ... which in turn implies that the solutions are not separable into single particle solutions.

The system needs to be treated as one unified entity; the electrons are *entangled*.

Crucial in order to describe chemical reactions and molecular structures.

This implies that all the single particle equations become coupled, which is reason why quantum mechanics scales badly in comparison to classical calculations.

The initial conditions

Solving the initial $t = t_0$ problem is **non-trivial**. The wave function at the initial time is found by solving the *time-independent SE* for a given potential and a set of boundary conditions.

$$\mathbf{H}\psi(\mathbf{r}, t_0) = E\psi(\mathbf{r}, t_0).$$

Quantization of energy, etc. arise due to the boundary conditions.

Time evolution

Time evolution in quantum mechanics is a field of it's own, involving obscenely heavy calculations due to entanglement.
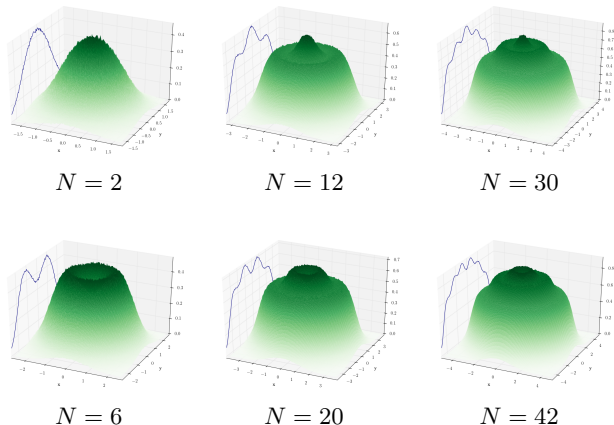
Hence it's avoided.

Figure 1: Densities for two-dimensional quantum dots.

When the electron density is lowered, we approach a limit where the quantum and classical solutions are reconciled. We *un-entangle* the system.
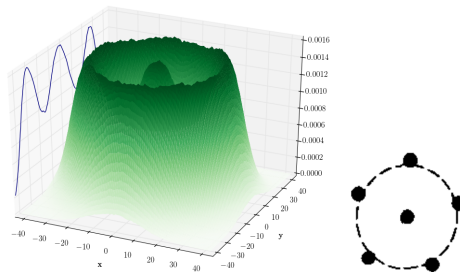
Figure 2: Density for a 6-particle two-dimensional quantum dot compared
to the classical theoretical configuration taken from F. Bolton,
U. Rössler. *Superlattices and microstructures* **13**, 139 (1993).

Parameterizing Potentials using Quantum Mechanics

Connecting the scales

How do we connect a molecular dynamics scenario of particle interactions to the quantum scale?

Figure 2. Newton and Schrödinger's cat. Previously, classical physics and quantum chemistry belonged to rivalling worlds. The Nobel Laureates in Chemistry 2013 have opened a gate between those worlds and have brought about a flourishing collaboration.
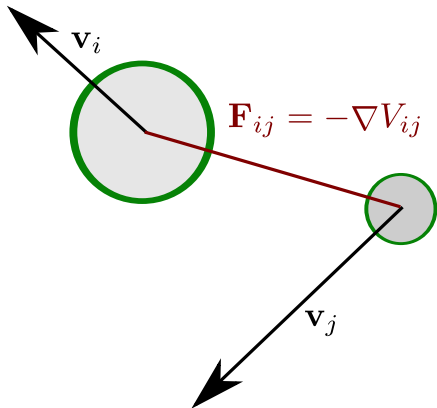
$$E_{ij} = \tfrac{1}{2}\left(m_i|\mathbf{v}_i|^2 + m_j|\mathbf{v}_j|^2\right) + \boxed{V_{ij}}$$

Let's freeze the dynamics as in the previous image and do some super advanced physics.

What is potential energy?

Well, it's what can be transferred into kinetic energy!

So, any energy sources that are **not** part of the MD kinetic energy is MD potential energy.

Since the electrons are not modeled in MD, kinetic energy of electrons count as potential energy in this case.

In other words: It is the total energy in quantum mechanics which corresponds to the potential in molecular dynamics.

The basic idea

Given a snapshot of some MD calculation, e.g. two molecules at a distance r_{ij}, the total quantum mechanical energy is obtained by solving the time-independent SL within this geometry

$$\mathbf{H}(r_{ij})\psi(\mathbf{r}_e) = E(r_{ij})\psi(\mathbf{r}_e,)$$
$$\mathbf{H}(r_{ij})\psi(\mathbf{r}_e) = V_{ij}\psi(\mathbf{r}_e,)$$
$$\mathbf{F}_{ij} = -\nabla_{r_{ij}} E(r_{ij}).$$

The force is obtained by calculating the gradient of this energy.

Setting up H

The Hamiltonian is set up by building a potential consisting of

- Core-core Coulomb interaction.

- Electron-core Coulomb interaction.

- Electron-electron Coulomb interaction.

Benefits: One potential to rule them all.

Calculating the gradient...

Multiplying the time independent SE with the gradient on both sides reveals a new eigenvalue problem:

$$\mathbf{H}(r_{ij})\psi(\mathbf{r}_e) = E(r_{ij})\psi(\mathbf{r}_e),$$

$$-\nabla_{r_{ij}}\mathbf{H}(r_{ij})\psi(\mathbf{r}_e) = -\nabla_{r_{ij}}E(r_{ij})\psi(\mathbf{r}_e),$$

$$\left(-\nabla_{\mathbf{r_{ij}}}\mathbf{H}\right)\psi(\mathbf{r}_e) = \mathbf{F}_{ij}\psi(\mathbf{r}_e).$$
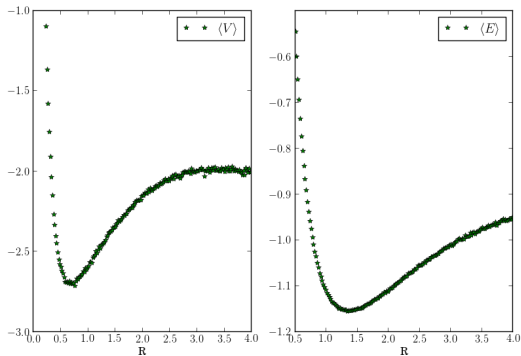
Calculating the gradient...

Or we can simply calculate the energy for a series of r_{ij} beforehand, and then simply perform numerical derivatives on these values.
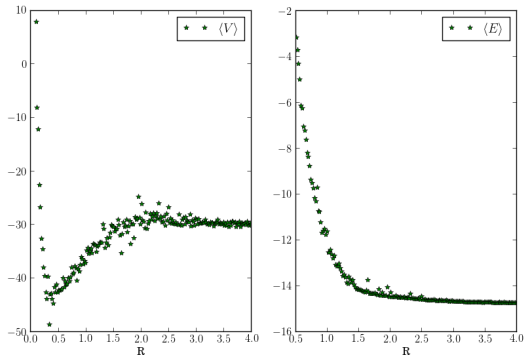
Examples!

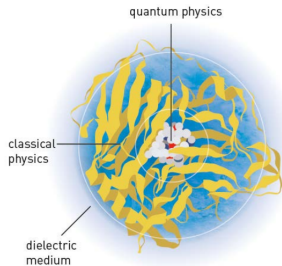The below figure shows calculations for H_2

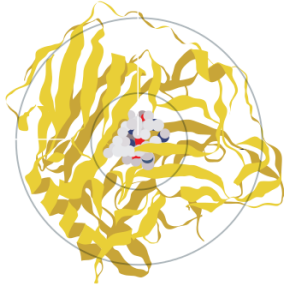Studying the same calculations applied to Li_2 we see something interesting...

Can this explain why di-litium isn't found in the universe?

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went to multiscale modeling!

"Apply the power where it's needed."

Sophisticated methods exist for performing quantum mechanical computation of a large number of atoms, such as *density functional theory* (DFT).

This method revolves around computing $\psi(\mathbf{r})^2$ instead of the wave function, which takes care of a "bunch of problems" and eases the computational scaling.

In addition, it takes the most difficult interactions due to entanglement and stores them in an *unknown potential* which is often modeled using the free electron gas.

Questions?

$$V_{\text{LJ}}(r_{ij}\,;\,\sigma,\,\epsilon) = 4\epsilon \left(\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6} \right)$$