

Origin of a Potential Energy Surface

The idea of a potential energy surface describing how atoms interact comes from an approximation of the Schrödinger equation made by Born and Oppenheimer. The Schrödinger equation can be written as:

$$H\psi = E\psi$$

ψ is known as a wave function. It represents the system being considered. H is the Hamiltonian or energy operator. The equation essentially consists of the Hamiltonian operator asking the system characterized by a wave function for its energy. The right hand side of the equality essentially contains the system characterized by the wave function answering “my energy is E ”. This type of equation is known as an eigen function/ eigen value equation.

For those of you familiar with first year chemistry, for the hydrogen atom, the square of the wave function or orbital describes the regions in which one can find the electron with high probability (s, p, d, and f orbitals).

Soon after scientists solved it for the hydrogen atom and approximately for other atoms, Born and Oppenheimer began to think about how it could tell us something about molecules. The bigger the system, the harder it is to solve the equation. Born and Oppenheimer proposed one simplification with the example of a hydrogen molecule, H_2 . They proposed the following scheme:

1. Fix the nuclei at some R (distance between nuclei).
2. Solve the SE for the energy of the electron configuration at that R .
3. Change the R and start again.

This scheme allows us to look at the electron energy as a function of distance between the nuclei. The resulting function of energy as a function of distance or nuclear configuration is the potential energy surface of the system. The minima of these functions represent stable configurations of the system. Saddle points represent transition states. For a one-dimensional function, it is easy to plot the function and find the lowest energy points and the barriers between minima. However, as the function increases in dimensionality, this becomes more and more difficult. In this unit, we'll consider methods to find minima and saddle points in high dimensional systems.

Minima and Saddle Points

Some of the most common methods for finding minima are the simplex and conjugate gradient algorithms. Both are well described in Numerical recipes sections 10.4 and 10.6. (<http://www.library.cornell.edu/nr/bookcpdf.html>)

The nudged elastic band method has become a staple in determining saddle points. It is described in http://theory.cm.utexas.edu/vtsttools/references/pdfs/henkelman00_9901.pdf