9.2: The Born-Oppenheimer Approximation

The **Born-Oppenheimer approximation** (Born & Oppenheimer, 1927) is made in order to simplify the problem in the case of a molecule. This approximation is based on the relative masses (and therefore the relative speeds) of the heavy nuclei compared to the light electron. It says that if the nuclei move (such as due to molecular vibration) that the electron(s) will react to a change in the potential energy field instantaneously. As such, the internuclear distance (r_{12}) can be fixed, and the wave function for the electron optimized. If the nuclear coordinates are fixed, the Hamiltonian becomes

$$\hat{H} = \hat{T}_e - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_{12}}$$

and the value of $\frac{1}{r_{12}}$ becomes a constant.

There are many cases where the Born-Oppenheimer approximation breaks down, such as Renner-Teller interactions and Jahn-Teller interactions which involve strong coupling between vibrational motion of a molecule and the electronic state. For the purposes of this text, we will stick to examples where the Born-Oppenheimer approximation is reasonable.

The Born-Oppenheimer approximation makes it possible to calculate a number of properties for molecules. Below is an example of a potential energy surface of O_2 calculated using molecular modeling software at the HF/6-31G(d) level of theory. Basically, the program optimizes the wavefunctions describing the molecular orbitals based on a fixed internuclear separation. After populating the resultant orbitals with electrons, a total molecular energy is generated. After repeating this process at several different internuclear separation values, the curve can be constructed.

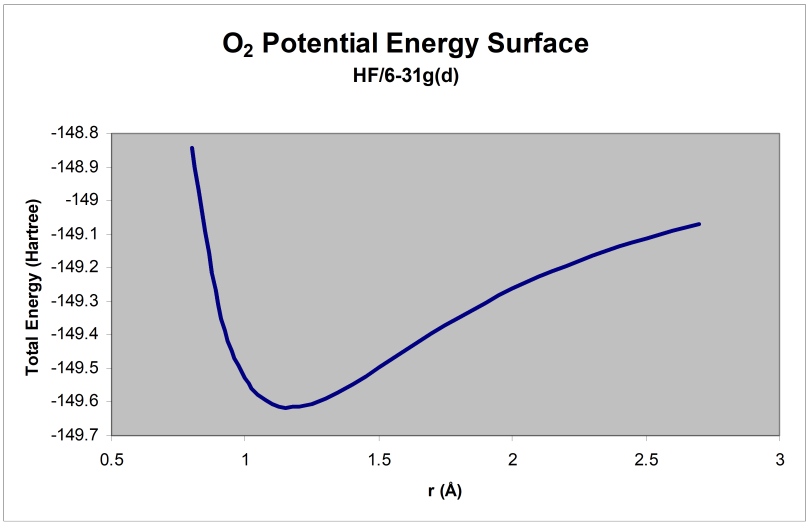

Figure 9.2.1

Such calculations are based entirely on the electronic structure of the molecule. As such, some insight into the nature of molecular orbitals and their wavefunctions is needed to proceed.