9.1: Potential Energy and the Hamiltonian

The first task of applying quantum mechanics to a problem is writing the Hamiltonian. This requires deriving an expression for potential energy. Consider as an example, the simplest diatomic molecule, H_2^+.

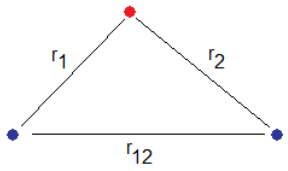

Figure 9.1.1

In the above diagram, the blue dots indicate protons and the red dot, an electron. There will be attractive forces between the electron and protons 1 and 2 (separated by r_1 and r_2 respectively) and a repulsive force between the two protons, separate by a distance r_{12}. In atomic units, the Hamiltonian can be written

$$\hat{H} = \hat{T}_1 + \hat{T}_2 + \hat{T}_e - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_{12}}$$

where T_1, T_2 and T_e indicate the kinetic energies of protons 1 and 2 and the electron, respectively. As was the case in the helium atom, the H_2^+ molecule involves a three body problem which cannot be solved analytically. As such, an approximation must be made in order to proceed.