II The Born Oppenheimer model of the hydrogen molecule ion

Introduction

H_2^+ is the simplest of all molecules, just two protons sharing a single electron. But even so, an exact solution of the quantum equations is difficult to find, and the situation is even more acute with larger molecules. The Born Oppenheimer (BOpp) approach is to replace the complete time dependent Schrodinger equation (TISE) with a simplified model. Further approximations are needed to solve even this simplified model.

In this account, the complete time independent Schrodinger equation for H_2^+ is derived from the classical hamiltonian, the Born Oppenheimer model is introduced and a method for obtaining approximate solutions is explained.

The classical hydrogen molecule ion

In the classical ion, the total energy is given by the hamiltonian,

$$H_{\mathrm{cl}} = (1/2M)(p_1^2 + p_2^2) + (1/2m)p^2 + V(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}),$$

where

p_1, p_2, p are momenta of proton 1, proton 2 and the electron ($p_1^2 = p_{1x}^2 + p_{1y}^2 + p_{1z}^2$, etc),

M and m are proton and electron masses,

$\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}$ are position vectors of the two protons and the electron ($\boldsymbol{r}_1 = x_1\mathbf{i} + y_1\mathbf{j} + z_1\mathbf{k}$, etc) - see Figure 1 - and

$V(\boldsymbol{r}_1, \boldsymbol{r}_2, \mathbf{r}) = (e^2/4\pi\varepsilon_0)(|\boldsymbol{r}_1 - \boldsymbol{r}_2|^{-1} - |\boldsymbol{r}_1 - \boldsymbol{r}|^{-1} - |\boldsymbol{r}_2 - \boldsymbol{r}|^{-1})$ is the electrostatic energy of the system.

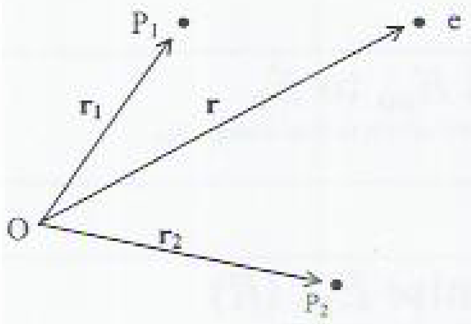

Figure 1
Classical H_2^+ molecule showing positions vectors of protons P_1 and P_2 and electron e