I The Born Oppenheimer model of the hydrogen molecule ion

Introduction

The complete time dependent Schrodinger equation (TISE) for H_2^+ is too difficult to solve. Born and Oppenheimer (BOpp) introduced an important simplification; an approximate solution for the ground state energy of this ion can then be found with a variational method.

In this account, a flow chart shows the order of processes that begins with a classical hamiltonian and ends with a variational solution to the BOpp model. I will expand these steps in the following notes and end the essay with an explanation of how the solution contributes to our understanding of binding.

The flow chart

The **classical hamiltonian** (total energy) for the two protons (subscripts 1 and 2) and the electron (no subscript) is given in box 1 of the flowchart. The protons have mass M each, and the electron has mass m; p and r are momenta and position vectors of the point particles. V is the electrostatic energy of the system,

$$V(r_1, r_2, r) = (e^2/4\pi\varepsilon_0)(|r_1 - r_2|^{-1} - |r_1 - r|^{-1} - |r_2 - r|^{-1})$$

The complete time independent Schrodinger equation is formed by replacing the classical hamiltonian with a hamiltonian operator **H** according to the rule:

$$p_x \rightarrow (h/2\pi i)\partial/\partial x \text{ etc}$$

The result is shown in box 2. The complete TISE is

$$\mathbf{H}\ \psi(r_1, r_2, r) = E_{tot}\ \psi(r_1, r_2, r)$$

where ψ is the wave function of the three body problem and E_{tot} is the total energy of the system.

The complete model cannot be solved exactly, so approximations must be found. This leads us into box 3.

Born and Oppenheimer argued that each proton is almost 2000 times more massive than the electron, and so should (classically) move slower than the electron - they are effectively stationary.
The operator analogue of this is just to cross out the proton momentum operators from the TISE (roughly speaking, $M \rightarrow \infty$ in the denominators).

Proton positions r_1 and r_2 will still appear in the electron potential term but since they commute with the electron kinetic energy operator, they act like ordinary numbers. In