III The Born Oppenheimer model of the hydrogen molecule ion

Quantum mechanics is necessary to explain the stability of atoms and molecules. After the hydrogen atom the next simplest system is the hydrogen molecule ion, H_2^+, which consists of two protons and one electron, together forming (in the ground state) a bound system. Relative to the energy of a separated hydrogen atom and a proton the binding energy of H_2^+ is about 2.8 electron volts. In a nutshell, the quantum explanation of the binding of H_2^+ is that there is a solution to the time-independent Schroedinger equation (TISE) (for the H_2^+ system) for which the electron is "shared" between the protons so that at close separation the two repel one another but at larger separation they attract. This results in a minimum in the effective proton-proton potential and hence in a stable configuration. A rigorous analysis must examine the lowest energy eigenvalue of the Hamiltonian operator for the H_2^+ system.

The classical Hamiltonian for the H_2^+ system is

$$H_{\mathrm{cl}} = \left[\frac{|p_1|^2}{2M} + \frac{|p_2|^2}{2M}\right] + \left[\frac{e^2}{4\pi\varepsilon_0 |r_1 - r_2|}\right] + \left[\frac{|p|^2}{2m}\right] - \frac{e^2}{4\pi\varepsilon_0}\left[\frac{1}{|r - r_1|} + \frac{1}{|r - r_2|}\right]$$

The first term is the kinetic energy of the two protons, each of mass M. The second term is the potential energy (of repulsion) between the two, located at r_1 r_2. The third term is the electron's kinetic energy and the fourth is its potential energy (of attraction) with the two protons. The electron's location is r.

A full solution to the TISE with operators representing the momenta and positions of both protons and the electron would be difficult. The Born-Oppenheimer approximation uses the fact that the proton mass M is about 2000 times the electron mass m. Then taking the limit $M \to \infty$ eliminates the first term in H_{cl} leaving only the proton variables r_1 and r_2.

The second term becomes just a constant depending on $|r_1 - r_2|$, which may be subtracted from the Hamiltonian and added later. Then the usual procedure gives for the remaining electron Hamiltonian the operator.

$$\tilde{H}_{\mathrm{cl}} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{e^2}{4\pi\varepsilon_0}\left[\frac{1}{|r - r_1|} + \frac{1}{|r - r_2|}\right]$$

Finding the lowest energy eigenstate of this operator is still difficult. In the Course we used the variational method to estimate this energy by minimizing $E_t = (\psi_t, \tilde{H}_{\mathrm{cl}}\psi_t)/(\psi_t, \psi_t)$, where the trial function ψ_t was built from the hydrogen atom ground state function $\psi_0(r)$ as follows:

$$\psi_t(r) = A\psi_0(r - r_1) + B\psi_0(r - r_2)$$