# Problem M04Q.1

The Hamiltonian for this problem is

$$H = -\frac{\hbar^2}{2m_e}(\nabla_{r_1}^2 + \nabla_{r_2}^2) - \frac{\hbar^2}{2m_p}(\nabla_{R_1}^2 + \nabla_{R_2}^2) + \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{|r_1 - r_2|} + \frac{1}{|R_1 - R_2|} - \sum_{i,j=1}^{2}\frac{1}{|r_i - R_j|}\right),$$

where $r_1, r_2$ are the positions of the electrons and $R_1, R_2$ are the positions of the protons.

Since $m_p \gg m_e$, we make the Born-Oppenheimer approximation

$$H_{\text{electronic}}(R_1, R_2) = -\frac{\hbar^2}{2m_e}(\nabla_{r_1}^2 + \nabla_{r_2}^2) + \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{|r_1 - r_2|} - \sum_{i,j=1}^{2}\frac{1}{|r_i - R_j|}\right),$$

with the positions $R_1, R_2$ treated as fixed parameters. The nuclear degrees of freedom separate into translational, rotational, and vibrational degrees of freedom.

We will work in a frame with zero center-of-mass velocity. We denote rotational angular momentum by $\mathbf{N}$, and index vibrational degree of freedom by a quantum number $v$.

Since we ignore fine structure, we have Hund's case (b) coupling of $\mathbf{N}$ and $\mathbf{S}$ to total angular momentum $\mathbf{J}$, with well-defined quantum number $m_J$.

(a) The ground state electronic wavefunction is the bonding molecular orbital adiabatically connected to the symmetric combination of atomic $1s$ orbitals around each proton. The electronic wavefunction is symmetric under exchange, and so the electron spins must occupy the singlet state $\mathbf{S} = 0$. Hence the ground rovibronic state is $X^1\Sigma_{0,g}^+(J = 0, v = 0)$.

Since we are ignoring hyperfine structure, the proton spins contribute a fourfold degeneracy of the ground state.

(b) We assume the question is asking about the lowest *electronic* excited state (the rotational and vibrational energy scales are much smaller).

The next-highest electronic state is the LUMO antibonding orbital, but this is not bound. This state is adiabatically connected to the *antisymmetric* combination of the $1s$ atomic orbitals. The HOMO-LUMO gap is determined by Coloumb and exchange terms originating from the Coloumb repulsion of the electrons.

The lowest-lying *bound* electronic excited state is adiabatically connected to the symmetrized combination of the $1s$ and $2p$ atomic orbitals. The lowest-lying rovibronic state within this electronic manifold can be described by the $B'^1\Sigma_u^+(J = 0, v = 0)$ term symbol.

(c) The $X^1\Sigma \to B'^1\Sigma$ gap is well-approximated by the $1s \to 2p$ transition energy in atomic hydrogen, of order

$$\left(\frac{1}{1^2} - \frac{1}{2^2}\right)\text{Ry}_\infty \sim 10 \text{ eV}.$$

The HOMO-LUMO gap is roughly twice the binding energy of the $H_2$ molecule.