Homework H32 Solution

1. Write down the Born–Oppenheimer wavefunction $\psi_{tot}(\vec{r}, \vec{R}_A, \vec{R}_B)$ for $H_2{}^+$ when the molecule is in the "ground electronic, ground vibrational, and 1st excited rotational state." Use the MO basis for the electronic part. $\vec{r}$ is the coordinate of the electron, and $\vec{R}_n$ with n=A or B are the two coordinates of the H^+ nuclei. So for example, the distance from the electron to nucleus A is $r_{1A} = |\vec{r} - \vec{R}_A|$, and the distance between the two nuclei is $R = |\vec{R}_B - \vec{R}_A|$ etc.

Use actual written-out functions for $\psi_0(r_{1A}, r_{1B}, spin)$, $\chi_m(R)$ and $Y_{JM_J}(\theta, \phi)$.

Except for the spin parts α and β, your function should be spelled out in terms of simple known function like Gaussians, exponentials, cosines, etc. Neglect normalization. Don't forget about the spin wavefunction You can leave the constants undefined, like k in $1s_A(r_{1A}) \sim e^{-kr_{1A}}$ and ω in $e^{-m\omega R^2/2\hbar}$

Solution: Using the Born–Oppenheimer approximation, we solve the electronic Schroedinger equation at fixed nuclear distances, and then solve for the nuclear part using the electronic energy as a function of R: the electronic energy becomes the nuclear potential energy, or the "glue" that holds the nuclei together. Thus we get a total wavefunction which in the simplest approximation is a product of electronic, vibrational and rotational states.

For one electron in the $H_2{}^+$ molecule, the MO basis is formed out of a linear combination of the atomic orbitals. For the ground electronic state, we consider the bonding orbital σ, while the spin can be either α, or β.

$$\psi_0 \sim [1s_A(r_{1A}) + 1s_B(r_{1B})] * (\alpha \; or \; \beta)$$

Thus

$$\psi_0 \sim [e^{-kr_{1A}} + e^{-kr_{1B}}]\alpha$$

OR

$$\psi_0 \sim [e^{-kr_{1A}} + e^{-kr_{1B}}]\beta$$

Now the ground state electronic potential energy $E_0(R)$ depends on R: it goes to zero if the molecule dissociates, reaches a minim at $R=R_{eq}$, and blows up if R gets small due to nuclear repulsion. Near the minimum, we can expand it in a Taylor series $E(R) = E_{min}+k/2 \cdot (R-R_{eq})^2$. Thus the ground vibrational state is approximately the ground state of a harmonic oscillator with $\omega=\sqrt{(k/m)}$. Remember that it is the vibration of the molecule around its center of mass, which is determined by the nuclear coordinates, so m is the reduced mass of the nuclei. So, ignoring normalization,

$$\chi_0(R) \sim e^{-m\omega(R-R_{eq})^2/2\hbar}$$

For the 1st excited rotational state, we have $J = 1, M_J = 0$ as one of three choices. So,

$$Y_{10} \sim \cos\theta$$

Thus the total Born – Oppenheimer wavefunction, neglecting normalization, is

$$\psi_{tot} = [e^{-kr_{1A}} + e^{-kr_{1B}}]\alpha \cdot e^{-m\omega(R-R_{eq})^2/2\hbar} \cdot \cos\theta$$

OR

$$\psi_{tot} = [e^{-kr_{1A}} + e^{-kr_{1B}}]\beta \cdot e^{-m\omega(R-R_{eq})^2/2\hbar} \cdot \cos\theta$$

This wavefunction depends on 5 coordinates: the electron distance from nucleus A, the electron distance from nucleus B, the spin angle, the distance between the two nuclei, and the angle the internuclear axis makes with the z axis. In general it depends on 6 coordinates: the φ angle would show up for the $M_J=\pm 1$ components.

How come only 6 coordinates? An electron and two nuclei have a total of 9 x,y and z coordinates! The reason is that we are neglecting the overall 'translational' motion of the molecule in space. What would the wavefunction for translation be, if the mass of the whole molecule is 2 atomic units, and it is in a box of size 1 mm by 1 mm by 1 mm? Think about that for the final exam.