

Homework H30 Solution

1. For 2 e⁻ in the ground state (e.g. $\frac{1}{\sqrt{2}}|\sigma\rangle_1|\sigma\rangle_2\{|\alpha_1\rangle|\beta_2\rangle - |\alpha_2\rangle|\beta_1\rangle\}$) or 1st excited state (e.g. $\frac{1}{\sqrt{2}}\{|\sigma\rangle_1|\sigma^*\rangle_2 - |\sigma^*\rangle_1|\sigma\rangle_2\}|\alpha_1\rangle|\alpha_2\rangle$) show again that $\langle\psi_0|\hat{H}|\psi_1\rangle = 0$.

Solution:

This is similar to what we saw in H26, but we must write out the full Hamiltonian

$$\hat{H} \equiv \hat{h}_1 + \hat{h}_2 + \hat{V}_{12}$$

which gives

$$\begin{aligned} \langle\psi_0|\hat{H}|\psi_1\rangle &= \langle\psi_0|\hat{h}_1 + \hat{h}_2 + \hat{V}_{12}|\psi_1\rangle \\ &= \{\langle\beta_2|\langle\alpha_1| - \langle\beta_1|\langle\alpha_2|\}_2\langle\sigma|_1\langle\sigma|\frac{1}{\sqrt{2}}(\hat{h}_1 + \hat{h}_2 + \hat{V}_{12})\frac{1}{\sqrt{2}}\{|\sigma\rangle_1|\sigma^*\rangle_2 - |\sigma^*\rangle_1|\sigma\rangle_2\}|\alpha_1\rangle|\alpha_2\rangle \\ &= \frac{1}{2}\{\langle\beta_2|\langle\alpha_1| - \langle\beta_1|\langle\alpha_2|\}\{|\alpha_1\rangle|\alpha_2\rangle\}_2\langle\sigma|_1\langle\sigma|(\hat{h}_1 + \hat{h}_2 + \hat{V}_{12})\{|\sigma\rangle_1|\sigma^*\rangle_2 - |\sigma^*\rangle_1|\sigma\rangle_2\} \end{aligned}$$

At this point, it would be necessary to obtain the 6 terms arising from the 3 parts of the Hamiltonian and the spatial wavefunctions if the spin part of the wavefunction was nonzero. However, dealing with the spin part in bold we have

$$\{\langle\beta_2|\langle\alpha_1| - \langle\beta_1|\langle\alpha_2|\}\{|\alpha_1\rangle|\alpha_2\rangle\} = \langle\beta|\alpha\rangle_2\langle\alpha|\alpha\rangle_1 - \langle\beta|\alpha\rangle_1\langle\alpha|\alpha\rangle_2 = 0 - 0 = 0$$

which indicates that $\langle\psi_0|\hat{H}|\psi_1\rangle = 0$. In fact, it will *always* equal zero for the functions given and any Hamiltonian operator or operator in general, as long as said operator is either independent of spin. Or only the S_z operator appears in it.

2.

Solution:

- a. The calculation yields 6 normal modes. This is the number of normal modes expected since the number of vibrational degrees of freedom for a nonlinear molecule of N atoms is 3N – 6. The “-6” portion of the formula is due to 3 degrees of freedom each for translational and rotational motion leaving 3N – 6 due to vibrational motion.
- b. ~599 : wagging bend
 ~1814: scissoring bend
 ~1814: scissoring bend
 ~3779: symmetric stretch
 ~3983: asymmetric stretch
 ~3983: asymmetric stretch
- c. One pair around 1814 cm⁻¹ and the other around 3983 cm⁻¹. Note that the normal modes are similar but not identical in their motion. This is easier to see if just viewing the vectors describing the motion.

- d. The Hartree-Fock method does not solve the Schrödinger equation exactly but rather provides an approximation for a wavefunction, this is an inherent characteristic of the method. Perhaps a larger basis set will provide more accurate results, since this would be an improvement on how accurately we are employing our method. For example, a 6-31+G* basis set used for the same computation yields 1305, 1885, 1885, 3235, 3355, 3355 cm^{-1} as the frequencies of the six normal modes. Most of these frequencies are still roughly as accurate as the 6-31G calculation with the exception of the two asymmetric stretches, which are now very accurate (3343 cm^{-1} experimental).