3.012 Bonding-Structure: Recitation 5 (Solutions)

1 Hydrogen Molecular Ion $\mathbf{H_2^+}$

Solution I

(a) Hamiltonian (1 electron + 2 protons): $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_a} - \frac{e^2}{4\pi\epsilon_0 r_b}$ (where m is the electron mass)

In atomic units: $\underline{\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b}}$

(b) Internuclear repulsion: $V_{N-N} = \frac{(+e)(+e)}{4\pi\epsilon_0 R}$

In atomic units: $\underline{V_{N-N} = \frac{1}{R}}$

(c) When R goes to $+\infty$ bohr, the H_2^+ ion dissociates into a proton and a hydrogen atom. The ground-state electronic energy is thus equal to that of a hydrogen atom (the electron does not feel the electrostatic potential of the second proton):

$\underline{E_{ele,1}(R = \infty) = -13.6058/1^2 \text{ eV} = -1/2 \text{ Ha}}$.

(d) $E_{\alpha,\beta}$ can be expressed as:

$$E_{\alpha,\beta} = \frac{\langle\psi_{\alpha,\beta}|\hat{H}|\psi_{\alpha,\beta}\rangle}{\langle\psi_{\alpha,\beta}|\psi_{\alpha,\beta}\rangle} = \frac{\{\alpha\langle\psi_{1s}(r_a)| + \beta\langle\psi_{1s}(r_b)|\}\hat{H}\{\alpha|\psi_{1s}(r_a)\rangle + \beta|\psi_{1s}(r_b)\rangle\}}{\{\alpha\langle\psi_{1s}(r_a)| + \beta\langle\psi_{1s}(r_b)|\}\{\alpha|\psi_{1s}(r_a)\rangle + \beta|\psi_{1s}(r_b)\rangle\}} \tag{1}$$

Expanding the expression of $E_{\alpha,\beta}$ and using the definitions of the coefficients H_{aa}, H_{ab} and S_{ab}, wee obtain: $\underline{E_{\alpha,\beta} = \frac{(\alpha^2+\beta^2)H_{aa}+2\alpha\beta H_{ab}}{\alpha^2+\beta^2+2\alpha\beta S_{ab}}}$

Erratum: note that the parameters α, β are assumed to be real. This should have been specified in the question.

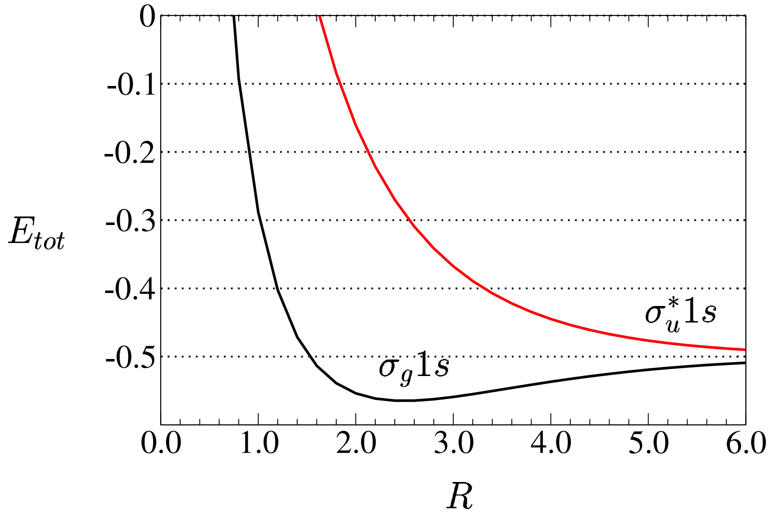
(e) When $\alpha = \beta$ (bonding molecular orbital, constructive interference between the 1s orbitals centered on each proton), $E_{\alpha,\beta}$ becomes: $E_{ele,1} = E_{\alpha,\alpha} = \frac{2\alpha}{2\alpha}\frac{H_{aa}+H_{ab}}{1+S_{ab}}$. Thus, $\underline{E_{ele,1} = \frac{H_{aa}+H_{ab}}{1+S_{ab}}}$.

(f) Similarly, $\underline{E_{ele,2} = E_{\alpha,-\alpha} = \frac{H_{aa}-H_{ab}}{1-S_{ab}}}$ (antibonding molecular orbital).

(e) From the preceding, $E_{tot,1}(R) = E_{ele,1}(R) + V_{N-N}(R) = \frac{H_{aa}+H_{ab}}{1+S_{ab}} + 1/R$
$E_{tot,2}(R) = E_{ele,2}(R) + V_{N-N}(R) = \frac{H_{aa}-H_{ab}}{1-S_{ab}} + 1/R$

R	H_{aa}	H_{ab}	S_{ab}	$E_{tot,1}$	$E_{tot,2}$
0.	-1.5	-1.5	1.	$+\infty$	$+\infty$
1.	-1.229	-1.164	0.858	-0.288	-0.545
1.2	-1.167	-1.066	0.807	-0.402	-0.310
1.4	-1.110	-0.968	0.752	-0.471	-0.140
1.6	-1.058	-0.873	0.697	-0.513	-0.013
1.8	-1.013	-0.783	0.641	-0.539	-0.084
2.	-0.972	-0.699	0.586	-0.553	-0.160
2.2	-0.936	-0.621	0.533	-0.5611	-0.221
2.4	-0.905	-0.549	0.482	-0.5644	-0.269
2.6	-0.876	-0.484	0.434	-0.5637	-0.309
2.8	-0.852	-0.426	0.389	-0.562	-0.341
3.	-0.830	-0.373	0.348	-0.559	-0.367
$+\infty$	-0.5	0.	0.	-0.5	-0.5

(h) The bonding (resp. antibonding) orbital is conventionally labeled $\sigma_g 1s$ (resp. $\sigma_u^* 1s$).



The approximate equilibrium distance (lowest Born-Oppenheimer energy) is $\underline{R_e = 2.4 \text{ bohr}}$.

(i) Equilibrium dissociation energy:
$\underline{D_e = E_{tot,1}(+\infty) - E_{tot,1}(R_e) = -0.5 - (-0.5644) \text{ Ha} = 0.0644 \text{ Ha}}$.

Thus D_e is smaller by one order of magnitude than the Born-Oppenheimer energy $E_{tot,1}(R_e)$, the nuclear-repulsion energy $V_{N-N}(R_e)$ (and the electronic energy $E_{ele,1}(R_e)$). As a consequence, it is often said that bonding is the result of a "subtle balance" between the electronic and the nuclear-repulsion contributions (small relative errors in the determination of $V_{N-N}(R_e)$ and $E_{ele,1}(R_e)$ can result in large errors in the equilibrium properties).

(j) From the curve of $E_{tot,1}$, one can obtain the second derivative of the $\sigma_g 1s$ Born-Oppenheimer energy: $\frac{d^2 E_{tot,1}}{dR^2}(R_e)$. The vibrational frequency ν of H_2^+ is then given by:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{d^2 E_{tot,1}/dR^2(R_e)}{\mu_{H_2^+}}} \tag{2}$$

where $\mu_{H_2^+}=m(\text{H})/2$ is the reduced mass of the molecular ion (Cf. Engel, Reid 18.6).

2 H_2^+: Orbital Energies

Solution II

The Born-Oppenheimer (BO) energies corresponding to the $\sigma_g 1s$ bonding orbital and to the $\sigma_u^* 1s$ antibonding orbital of H_2^+, obtained from the LCAO method are shown together with the energies of the exact orbitals, obtained by solving the stationary Schrödinger equation. The energy reference is chosen to be $-1/2$ Ha $= -13.6058$ eV. Hence, all the BO energies converge to 0 eV as R goes to $+\infty$ Å (dissociated H_2^+ molecular ion). Refer to Problem I (c).

As expected, the exact ground-state energy is always below the LCAO ground-state energy. The differences between the exact energies and their LCAO counterparts become smaller as R increases. This observation results from the fact that the LCAO trial wavefunctions (linear combination of two hydrogen $1s$ orbitals centered on each nucleus) provide a better representation of the exact orbitals ($1s$ orbital of hydrogen) as the internuclear distance increases. In contrast, as R goes to 0 Å, the LCAO trial set is unable to reproduce the exact ground-state orbital ($1s$ orbital of helium). Due to these discrepancies, the LCAO equilibrium internuclear distance is found to overestimate the exact equilibrium distance by approximately 30 % ($R_e^{LCAO} \approx 1.3$ Å, $R_e^{exact} \approx 1.0$ Å).