3.012 Bonding-Structure: Recitation 5

1   Hydrogen Molecular Ion H_2^+

Recall

- *Born-Oppenheimer approximation:*

  i) ions are fixed

  ii) $E_{tot} = E_{ele} + V_{N-N}$ ($E_{total} = E_{electronic\,ground\,state} + V_{nuclear\,repulsion}$)

- *International System units, atomic units:*

Quantity	Symbol	Atomic Units	S.I. Units
Hartree	Ha	1 a.u. (of energy)	4.36×10^{-18} J ($= 27.2$ eV)
electron charge	e	1 a.u. (of charge)	1.60×10^{-19} C
electron mass	m_e	1 a.u. (of mass)	9.11×10^{-31} kg
Bohr Radius	a_0	1 a.u. (of length)	0.529×10^{-10} m
permittivity of free space	ϵ_0	$\frac{1}{4\pi}$ a.u.	8.85×10^{-12} $C^2.N^{-1}.m^{-2}$
Planck's constant	$\hbar$	1 a.u.	1.054×10^{-34} J.s

Problem I

(a) Write the Hamiltonian $\hat{H}$ (Born-Oppenheimer approximation) corresponding to H_2^+ in atomic units (Cf. Figure 1).

(b) Write the nuclear-repulsion term $V_{N-N}(R)$ in atomic units.

(c) When $R = +\infty$ bohr, the H_2^+ ion dissociates into a proton and a hydrogen atom. What is the corresponding ground-state electronic energy $E_{ele,1}(R = \infty)$?

We wish to find approximate eigenfunctions and eigenenergies for H_2^+ without solving the complex Schrödinger equation. To this end, we employ the variational method. We
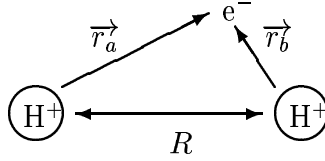
Figure 1: H_2^+ molecular ion

select the trial wavefunctions as linear combinations of two normalized $1s$ orbitals centered on each proton H^+: $\psi_{\alpha,\beta} = \alpha\psi_{1s}(r_a) + \beta\psi_{1s}(r_b)$ (α and β are the variational parameters).

(d) Calculate $E_{\alpha,\beta}$, the expectation value for the total energy of an electron in the state $\psi_{\alpha,\beta}$. Show that it can be written as:

$$E_{\alpha,\beta} = \frac{(\alpha^2 + \beta^2)H_{aa} + 2\alpha\beta H_{ab}}{\alpha^2 + \beta^2 + 2\alpha\beta S_{ab}} \tag{1}$$

where $\begin{cases} H_{aa} = \langle\psi_{1s}(r_a)|\hat{H}|\psi_{1s}(r_a)\rangle = \langle\psi_{1s}(r_b)|\hat{H}|\psi_{1s}(r_b)\rangle \\ H_{ab} = \langle\psi_{1s}(r_a)|\hat{H}|\psi_{1s}(r_b)\rangle = \langle\psi_{1s}(r_b)|\hat{H}|\psi_{1s}(r_a)\rangle \\ S_{ab} = \langle\psi_{1s}(r_a)|\psi_{1s}(r_b)\rangle = \langle\psi_{1s}(r_b)|\psi_{1s}(r_a)\rangle \end{cases}$

(e) We now admit that $E_{\alpha,\beta}$ reaches its minimal value when $\alpha = \beta$ (bonding molecular orbital, constructive interference between the $1s$ orbitals centered on each proton).
Calculate the corresponding energy $E_{ele,1}$.

(f) The higher-energy molecular orbital corresponds to a destructive interference between the $1s$ orbitals centered on each proton: $\alpha = -\beta$.
Calculate the corresponding energy $E_{ele,2}$.

(g) The values of the coefficients H_{aa}, H_{ab} and S_{ab} as a function of the internuclear distance R can be calculated using Mathematica (Figure 2). The results (in atomic units) are presented below:

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R	H_{aa}	H_{ab}	S_{ab}	$E_{tot,1}$	$E_{tot,2}$
0.	-1.5	-1.5	1.	—	—
0.2	-1.478	-1.479	0.993	3.516	5.164
0.4	-1.427	-1.425	0.974	1.054	2.430
0.6	-1.363	-1.350	0.943	0.270	1.427
0.8	-1.295	-1.261	0.904	-0.092	0.887
1.	-1.229	-1.164	0.858	—	—
1.2	-1.167	-1.066	0.807	—	—
1.4	-1.110	-0.968	0.752	—	—
1.6	-1.058	-0.873	0.697	—	—
1.8	-1.013	-0.783	0.641	—	—
2.	-0.972	-0.699	0.586	—	—
2.2	-0.936	-0.621	0.533	—	—
2.4	-0.905	-0.549	0.482	—	—
2.6	-0.876	-0.484	0.434	—	—
2.8	-0.852	-0.426	0.389	—	—
3.	-0.830	-0.373	0.348	—	—
4.	-0.749	-0.186	0.189	-0.536	-0.444
5.	-0.699	-0.088	0.096	-0.519	-0.476
6.	-0.666	-0.040	0.047	-0.509	-0.490
$+\infty$	-0.5	0.	0.	—	—

Calculate the approximate Born-Oppenheimer energy (bonding energy), $E_{tot,1}(R) = E_{ele,1}(R) + V_{N-N}(R)$. Calculate the antibonding energy $E_{tot,2}(R) = E_{ele,2}(R) + V_{N-N}(R)$.

(h) Plot $E_{tot,1}(R)$ and $E_{tot,2}(R)$. What is the approximate equilibrium internuclear distance R_e?

(i) The difference between $E_{tot,1}(R = +\infty)$ and $E_{tot,1}(R = R_e)$ is called the equilibrium dissociation energy D_e. Calculate the equilibrium dissociation energy? How does it compare with the values of the Born-Oppenheimer energy and of the nuclear-repulsion energy at the equilibrium internuclear distance?

(j) Based on the Born-Oppenheimer energies, provide a method to calculate the vibrational frequency of H_2^+.

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rb[r_, θ_, R_] := ((r*Sin[θ])^2 + (R-r*Cos[θ])^2)^0.5;
V[r_] := -1/r;
ψ[r_] := π^-0.5*Exp[-r];
ddψ[r_] := (1-2/r)*ψ[r];
For[i = 0, i < 31,
  R := i*0.2;
  Haa = NIntegrate[
     ψ[r] * (-0.5*ddψ[r] + (V[r] +V[rb[r, θ, R]]) *ψ[r]) *r^2*Sin[θ], {r, 0, ∞}, {θ, 0, π}, {φ, 0, 2π}];
  Hab = NIntegrate[ψ[rb[r, θ, R]] * (-0.5*ddψ[r] + (V[r] +V[rb[r, θ, R]]) *ψ[r]) *r^2*Sin[θ],
     {r, 0, ∞}, {θ, 0, π}, {φ, 0, 2π}];
  Sab = NIntegrate[ψ[rb[r, θ, R]] *ψ[r] *r^2*Sin[θ], {r, 0, ∞}, {θ, 0, π}, {φ, 0, 2π}];
  Print[R, " ", Haa, " ", Hab, " ", Sab]
  ; i++]
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Figure 2: Mathematica notebook to calculate H_{aa}, H_{ab} and S_{ab}

2 H_2^+: Orbital Energies

Problem II

What is the meaning of the following graph?