

Atomic & Molecular Physics Solutions to Problem Sheet 2224.4
Issued Thursday 6 March 2008, due Thursday 13 March 2008

1. For a diatomic molecule to exhibit a rotation spectrum it must possess an electric dipole moment on which the applied electric field can exert a torque. Homonuclear molecules typically have an equal probability of finding the electrons more closely associated with each nucleus (no separation of charge), i.e. no dipole moment, unlike heteronuclear molecules. Purely rotational transitions typically occur in the microwave region of the spectrum.

The frequencies of purely rotational transitions from $J \rightarrow J'$ are $E(J) - E(J')$, which for $J' = J - 1$ is $E = 2BJ$, where B is the rotational constant. A graph of frequency against J (the higher rotational quantum number) should therefore be a straight line, as in figure 1 below.

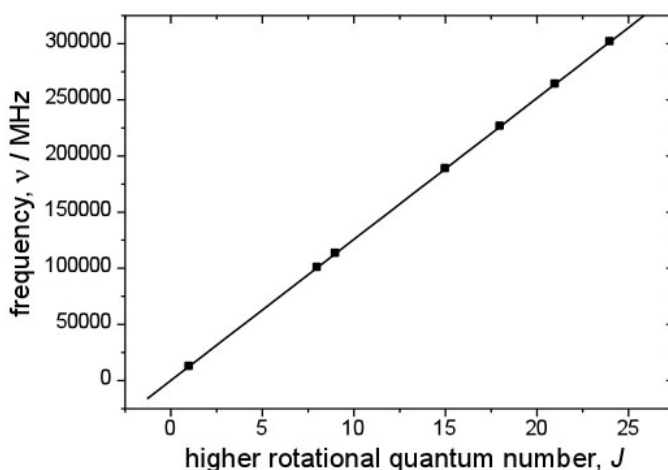


Figure 1: graph of transition frequency against higher rotational quantum number, J

For the right graph [4]

The gradient of the graph is $2B = 12566$ MHz, giving the rotational constant

$$\underline{B = 6283 \text{ MHz}}$$

[1]

The rotational constant is related to the bond length through the moment of inertia:

$$B = \frac{\hbar^2}{2I_e}$$

(in energy units, where

$$I_e = \mu R_e^2$$

with μ the reduced mass which is:

$$\mu_{\text{RbF}} = \left(\frac{1}{85} + \frac{1}{19} \right)^{-1} \times 1.66 \times 10^{-27} \text{ kg} = 2.59 \times 10^{-26} \text{ kg}$$

In frequency units (Hertz) we have that:

$$\frac{B}{h} = \bar{B} = \frac{1}{2\pi} \frac{\hbar}{2\mu R_e^2}$$

giving for the bond length:

$$R_e = \sqrt{\frac{1}{2\pi} \frac{\hbar}{2\mu \bar{B}}}$$

Inserting values:

$$R_e = \sqrt{\frac{1}{2\pi} \frac{1.054 \times 10^{-34}}{2 \times 2.59 \times 10^{-26} \times 6.283 \times 10^9}} = 2.27 \times 10^{-10} \text{ m}$$

[2]

2. The wavefunctions and electron distributions are shown in figure 2

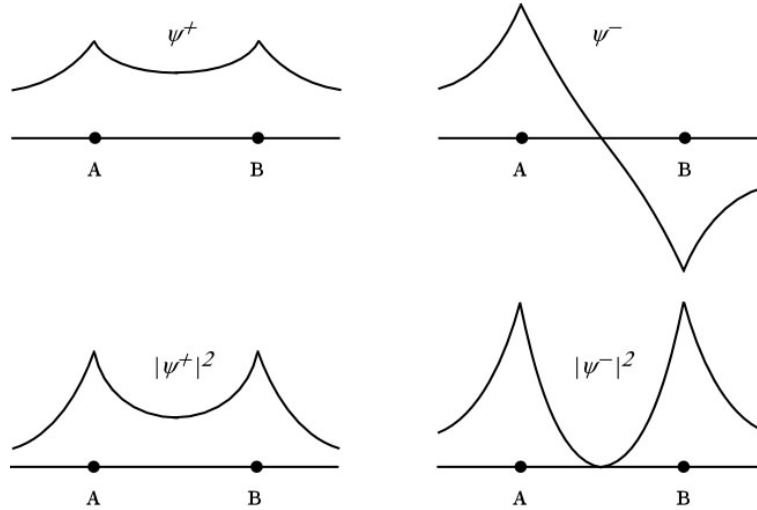


Figure 2: Wavefunctions and electron distributions for H_2^+

[2]

To find the electronic energies we must evaluate:

$$\begin{aligned} \langle \psi_{\pm} | \hat{H}_{el} | \psi_{\pm} \rangle &= \langle \psi_{\pm} | E_{\pm}(R) | \psi_{\pm} \rangle \\ &= E_{\pm} \langle \psi_{\pm} | \psi_{\pm} \rangle \end{aligned}$$

and so the energy of the ψ_{\pm} states is:

$$\begin{aligned} E_{\pm}(R) &= \frac{\int \psi_{\pm}^* \hat{H}_{el} \psi_{\pm} d\tau}{\int \psi_{\pm}^* \psi_{\pm} d\tau} \\ &= \frac{A_{\pm}}{N_{\pm}} \\ &= \frac{\text{expectation value of } \hat{H}_{el}}{\text{normalization constant}} \end{aligned}$$

Then the normalization term is:

$$\begin{aligned}
 N_{\pm} &= \frac{1}{2} \int [\Phi_{1s}^*(r_A) \pm \Phi_{1s}^*(r_B)] [\Phi_{1s}(r_A) \pm \Phi_{1s}(r_B)] d\tau \\
 &= \frac{1}{2} \left[1 + 1 \pm 2 \int \Phi_{1s}^*(r_A) \Phi_{1s}(r_B) d\tau \right] \\
 &= 1 \pm I(R),
 \end{aligned}$$

since:

$$\int \Phi_{1s}^*(r_{A,B}) \Phi_{1s}(r_{A,B}) d\tau = 1$$

and

$$I(R) = \int \Phi_{1s}^*(r_B) \Phi_{1s}(r_A) d\tau = \int \Phi_{1s}(r_B) \Phi_{1s}^*(r_A) d\tau$$

$I(R)$ is the **overlap** between $\Phi_{1s}(r_A)$ and $\Phi_{1s}(r_B)$. It is non-zero since they are **not orthogonal** as they are centered on different origins. [2]

Now for the expectation values, A_{\pm} . We use the electronic Hamiltonian:

$$\hat{H}_{el} = -\frac{1}{2} \nabla_r^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$

First we recall from the treatment of atomic hydrogen that:

$$\left[-\frac{1}{2} \nabla_r^2 - \frac{1}{r_A} \right] \Phi_{1s}(r_A) = E_{1s} \Phi_{1s}(r_A)$$

and

$$\left[-\frac{1}{2} \nabla_r^2 - \frac{1}{r_B} \right] \Phi_{1s}(r_B) = E_{1s} \Phi_{1s}(r_B),$$

where E_{1s} is ground state energy of H atom.

We want:

$$\begin{aligned}
 A_{\pm} &= \int \frac{1}{\sqrt{2}} [\Phi_{1s}^*(r_A) \pm \Phi_{1s}^*(r_B)] \\
 &\quad \times \hat{H}_{el} \frac{1}{\sqrt{2}} [\Phi_{1s}(r_A) \pm \Phi_{1s}(r_B)] d\tau.
 \end{aligned}$$

that we will re-write as:

$$A_{\pm} = \langle \hat{H}_{el} \rangle = \frac{1}{2} [H_{AA} + H_{BB}] \pm H_{AB}$$

where

$$\begin{aligned}
 H_{AA} &= \int \Phi_{1s}^*(r_A) \hat{H}_{el} \Phi_{1s}(r_A) d\tau \\
 &= E_{1s} \quad (\text{Energy of H atom}) \\
 &+ \frac{1}{R} \int \Phi_{1s}(r_A) \Phi_{1s}(r_A) d\tau \quad (\text{internuclear repulsion}) \\
 &- \int \Phi_{1s}^*(r_A) \frac{1}{r_B} \Phi_{1s}(r_A) d\tau \quad (\text{Coulomb Integral}) \\
 &= E_{1s} + \frac{1}{R} - J(R)
 \end{aligned}$$

where $J(R)$ is due to the interaction with the other atom, B. There is a similar term H_{BB} from the other atom, B:

$$H_{BB} = E_{1s} + \frac{1}{R} - J(R)$$

[2]

Also:

$$H_{AB} = H_{BA} = \int \Phi_{1s}^*(r_A) \hat{H}_{el} \Phi_{1s}(r_B) d\tau$$

and

$$H_{AB} = \pm \left[\left(E_{1s} + \frac{1}{R} \right) I(R) - \underbrace{\int \Phi_{1s}^*(r_A) \frac{1}{r_A} \Phi_{1s}(r_B) d\tau}_{\text{'K' exchange integral}} \right].$$

So

$$H_{AB} = \pm \left(E_{1s} + \frac{1}{R} \right) I(R) \mp K(R).$$

[2]

Putting these results together, the electronic energy is:

$$\begin{aligned}
 E_{\pm} &= A_{\pm} / N_{\pm} \\
 &= \frac{\left(E_{1s} + \frac{1}{R} \right) - J \pm \left(E_{1s} + \frac{1}{R} \right) I \mp K}{1 \pm I} \\
 &= \underbrace{E_{1s} + \frac{1}{R}}_{\text{H atom + Coulomb repulsion}} + \frac{-J \mp K}{1 \pm I}.
 \end{aligned}$$

[1]

Note: The numbers in square brackets are intended to show the approximate credit for each part of the working, although as this question is bookwork all students should be getting 10 marks.

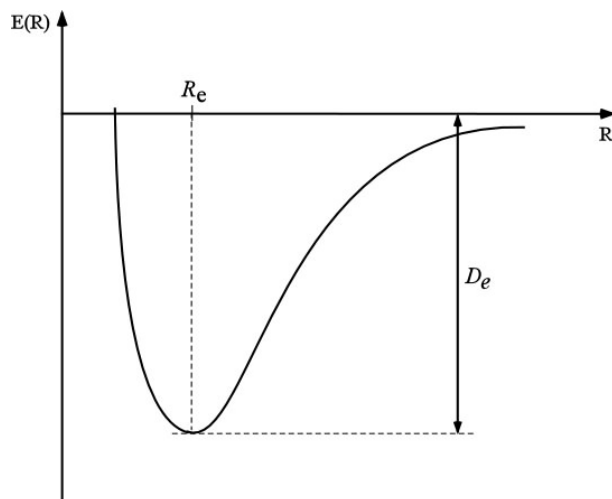


Figure 3: The Morse potential

3. The Morse potential, V_{Morse} is sketched in figure 3 below:

For the right sketch, with D_e and R_e marked correctly:

[3]

If we expand the Morse potential:

$$V_{\text{Morse}} = D_e \left(e^{-2\alpha(R-R_e)} - 2e^{-\alpha(R-R_e)} \right)$$

for small displacements from equilibrium, i.e. $\alpha(R - R_e) \ll 1$, we find:

$$V_{\text{Morse}} \approx D_e \left(1 - 2\alpha(R - R_e) + \frac{1}{2}(-2\alpha(R - R_e))^2 - 2D_e + 2\alpha(R - R_e) - \frac{1}{2}2(\alpha(R - R_e))^2 \right)$$

or:

$$V_{\text{Morse}} \approx D_e \left(-1 + \alpha^2(R - R_e)^2 \right) = D_e \left(-1 + \frac{1}{2}k(R - R_e)^2 \right)$$

i.e. the Morse potential is approximately harmonic for small displacements with spring constant, $k = 2\alpha^2 D_e$.

[2]

The molecular state terms $^1\Sigma_g$ and $^3\Sigma_u$ tell us:

- $\Sigma \rightarrow$ the projection of the electronic angular momentum onto the molecular axis is 0, i.e. $L_z = 0$.
- the superscripts 1 and 3 give the spin multiplicity, i.e. there is a singlet and triplet term with net spin $S = 0, 1$
- the subscript gives the symmetry with respect to exchange of nuclear labels: u (ungerade) odd with respect to exchange, g (gerade) even with respect to exchange.

[1]

From the given parameters and the above expression for the spring constant, we have:

$$D_e = 240 \text{ cm}^{-1} = 4.77 \times 10^{-21} \text{ J}$$

and so:

$$k = 2 \times 240 \text{ cm}^{-1} = 4.77 \times 10^{-21} \times (0.720 \times 10^{10})^2 = \underline{0.494 \text{ Nm}^{-1}}.$$

The vibrational frequency is related to the spring constant as $\omega = \sqrt{\frac{k}{\mu}}$, with μ the reduced mass. For $^{133}\text{Cs}_2$ the reduced mass is $\mu = \frac{1}{2}m_{\text{Cs}} = \frac{1}{2} \times 133 \times 1.67 \times 10^{-27} \text{ kg} = 1.11 \times 10^{-25} \text{ kg}$. This gives a vibrational frequency:

$$\omega = \sqrt{\frac{0.494}{1.11 \times 10^{-25}}} = 2.11 \times 10^{12} \text{ rad s}^{-1}$$

or:

$$\tilde{\nu} = \frac{1}{100} \frac{1}{2\pi} \frac{\omega}{c} = 11.2 \text{ cm}^{-1}$$

[2]

From the given equilibrium bond length and that $I_e = \mu R_e^2$, we get that:

$$I_e = 1.11 \times 10^{-25} \times (6.496 \times 10^{-10})^2 = \underline{4.68 \times 10^{-44} \text{ kg}}$$

Since we know that the rotational constant $B = \frac{\hbar^2}{2I_e}$ we calculate:

$$B = \frac{(1.054 \times 10^{-34})^2}{2 \times 4.68 \times 10^{-44}} = 4.69 \times 10^{24} \text{ J}$$

or in wavenumbers:

$$\tilde{B} = \frac{1}{100} \frac{B}{hc} = \frac{1}{100} \frac{4.69 \times 10^{24}}{6.626 \times 10^{-34} \times 2.998 \times 10^8} = \underline{5.97 \times 10^{-3} \text{ cm}^{-1}}$$

[2]