

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

1. Explain briefly why heteronuclear diatomic molecules have a rotational spectrum, but homonuclear molecules do not. In which region of the spectrum do transitions that arise from purely rotational transitions occur?

The data in the table below¹ is taken from the rotational spectrum of $^{85}\text{Rb}^{19}\text{F}$.

transition $J \rightarrow J'$	frequency ν / MHz
1 \rightarrow 0	12,574
8 \rightarrow 7	100,667
9 \rightarrow 8	113,246
15 \rightarrow 14	188,673
18 \rightarrow 17	226,351
21 \rightarrow 20	263,998
24 \rightarrow 23	301,607

Table 1: Spectroscopic data for $^{85}\text{Rb}^{19}\text{F}$

By plotting a suitable graph determine the rotational constant of $^{85}\text{Rb}^{19}\text{F}$ and the equilibrium bond length. [10]

2. According to the Linear Combination of Atomic Orbitals theory the hydrogen molecular ion H_2^+ electronic ground state wavefunction can be constructed from symmetric and anti-symmetric combinations of hydrogen atom ground state wavefunctions Φ_{1s} centred on the nuclei, i.e. $\psi_{\pm} = \frac{1}{\sqrt{2}} (\Phi_{1s}(\underline{r}_A) \pm \Phi_{1s}(\underline{r}_B))$

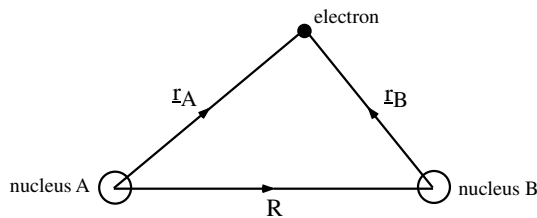


Figure 1: the hydrogen molecular ion

Sketch the form of the wavefunctions ψ_{\pm} and the electron distributions $|\psi_{\pm}|^2$.

Derive expressions for the energies E_{\pm} associated with the wavefunctions ψ_{\pm} in terms of the ground state energy of the hydrogen atom, E_{1s} , an overlap integral, $I = \int \Phi_{1s}^*(\underline{r}_B) \Phi_{1s}(\underline{r}_A) d\tau$, a Coulomb repulsion $\frac{1}{R}$ between the nuclei, a Coulomb integral, $J = \int \Phi_{1s}^*(\underline{r}_A) \frac{1}{r_B} \Phi_{1s}(\underline{r}_A) d\tau$ and an exchange integral, $K = \int \Phi_{1s}^*(\underline{r}_A) \frac{1}{r_A} \Phi_{1s}(\underline{r}_B) d\tau$, where $\underline{r}_{A,B}$ and \underline{R} are defined in figure 1. [10]

TURN OVER FOR QUESTION 3

¹Data taken from NIST diatomic spectra database

3. For many covalent diatomic molecules the effective potential in which the nuclei move is well described by the Morse potential:

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

Sketch the form of the Morse potential, marking on your sketch the equilibrium bond length, R_e , and the depth of the potential well at equilibrium, D_e .

By expanding V_{Morse} as a power series in $(R - R_e)$, show that for small displacements from equilibrium the Morse potential is approximately harmonic, that is

$$V_{\text{Morse}} \approx \frac{1}{2}k(R - R_e)^2.$$

where k is the spring constant of the bond, and find an expression for k in terms of D_e and α .

The homonuclear dimer Cs_2 can be made by photoassociation of laser-cooled caesium (^{133}Cs) atoms in the $6^2s_{\frac{1}{2}}$ ground states, leading to the molecular states $^1\Sigma_g$ and $^3\Sigma_u$. What can you deduce about the electronic angular momenta and symmetry of the molecular wavefunction from these symbols?

For the $^3\Sigma_u$ molecular state the parameters of the Morse potential² are: $D_e = 240 \text{ cm}^{-1}$, $\alpha = 0.720 \text{ \AA}^{-1}$, and $R_e = 6.496 \text{ \AA}$

Calculate the spring constant of the bond, and hence the vibrational frequency (in wavenumbers) of the molecule near the bottom of the potential well. Calculate also the moment of inertia of the molecule, and hence the rotational constant B (in wavenumbers). [10]

²L. S. Butcher, D. N. Stacey, C. J. Foot & K. Burnett, *Phil. Trans. R. Soc. London A*, **357** 1421-1439 (1999)