PROBLEM SET SOLUTIONS

Chapter 6, *Quantum Chemistry*, 5ᵗʰ Ed., Levine

6.5 The lowest observed microwave absorption frequency of $^{12}C^{16}O$ is 115271 MHz. (a) Compute the bond distance in $^{12}C^{16}O$. (b) Predict the next two lowest microwave absorption frequencies of $^{12}C^{16}O$. (c) Predict the lowest microwave absorption frequency of $^{13}C^{16}O$. (d) For $^{12}C^{16}O$ at 25°C, calculate the ratio of the J=1 population to the J=0 population. Repeat for the J=2 to J=0 ratio. Don't forget degeneracy.

6.5 (a) ν = 115271 MHz = 115271 x 10^6 s⁻¹;

lowest transition: $J = 0 \rightarrow J = 1$

$\nu = 2(J + 1)B$, If $J = 0$: $\nu = 2 B = 115271$ MHz

$B = \nu/2 = 115271$ x 10^6 s⁻¹/2 = 57635 x 10^6 s⁻¹

$B = \underline{h}^2/(2hI)$ or $I = \underline{h}^2/(2hB)$

$I = h/(8\pi^2 B) = (6.626$ x 10^{-34} Js$)/(8\pi^2 57635$ x 10^6 s⁻¹$)$

$= 1.46$ x 10^{-46} Js^2

$= 1.46$ x 10^{-46} (kg m²/s²) (s²)

$= 1.46$ x 10^{-46} kg m² (10^3g/1kg) (10^{10}Angstroms/1m) ^{2}

$= 1.46$ x 10^{-23} g Angstroms² (6.023 x 10^{23} amu/g)

$= 8.79$ amu Angstroms²

$I = \mu\ d^2$ or $d = R_e = (I/\mu)^{1/2}$

$R_e = \{(8.79$ amu Angstroms²$)/[12$ x $16/(12 + 16)]\}^{1/2}$

$= 1.13$ Angstroms

6.5 (b) next two lowest transitions are $J = 1 \rightarrow 2$ & $J = 2 \rightarrow 3$

$\nu = 2(J + 1)B,$

$J = 1$: $\nu = 4 B = 2 (2B) = 2 (115271 \text{ MHz}) = 230542 \text{ MHz}$

$J = 2$: $\nu = 6 B = 3 (2B) = 3 (115271 \text{ MHz}) = 345813 \text{ MHz}$

6.5 (c) $^{13}C^{16}O$: $\mu_{13C16O} = 13 \times 16/(13 + 16)$

Assume $R_e(^{13}C^{16}O) = R_e(^{12}C^{16}O)$

$\nu = 2(J+1)\underline{h}/(8\pi^2\mu d^2)$

So $\nu_{13C16O}/\nu_{12C16O} = \mu_{12C16O}/\mu_{13C16O}$

$\nu_{13C16O} = \nu_{12C16O}\,\mu_{12C16O}/\mu_{13C16O}$

$= (115271 \text{ MHz}) [(12 \times 16)/(12 + 16)] [(13 + 16)/(13 \times 16)]$

$= (115271 \text{ MHz}) (348/354)$

$= 110204 \text{ MHz}$

6.5 (d) Degeneracy of level $J = (2J+1)$; $E_J = J(J+1)\underline{h}^2/(2I)$

J	2J+1	E_J	$E_J - E_0$
0	1	0	0
1	3	$2\underline{h}^2/(2I)$	$2\underline{h}^2/(2I)$
2	5	$6\underline{h}^2/(2I)$	$6\underline{h}^2/(2I)$

$N_1/N_0 = g_1/g_0 \exp[-(E_1 - E_0)/(kT)] = (3/1) \exp[-2\underline{h}^2/(2IkT)]$

$N_2/N_0 = g_2/g_0 \exp[-(E_2 - E_0)/(kT)] = (5/1) \exp[-6\underline{h}^2/(2IkT)]$

$\underline{h}^2/(2IkT)$

$= (1.055\times10^{-34}\text{Js})^2/[2(1.46 \times 10^{-46}\text{ Js}^2)(1.38\times10^{-23}\text{ JK}^{-1}) (298K)]$

$= 0.00927$

$N_1/N_0 = 3 \exp[-2(0.00927)] = 3(0.9816) = 2.945$

$N_2/N_0 = 5 \exp[-6(0.00927)] = 5(0.9458) = 4.729$

6.17 For the ground state of the hydrogenlike atom, show that

$\langle r \rangle = 3a/(2Z)$.

$\psi_{n/m} = \psi_{100} = R_{1s}(r)\, Y_0^0(\theta, \phi)$

Table 6.1: $R_{1s}(r) = 2\,(Z/a)^{3/2}\, \exp[-Zr/a]$

Spherical harmonics are normalized:

$\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta\, Y_l^{m*}(\theta, \phi)\, Y_l^m(\theta, \phi) = 1$

$\langle r \rangle = \langle \psi_{100} | r | \psi_{100} \rangle$

$\qquad = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta\, Y_0^{0*}(\theta, \phi)\, Y_0^0(\theta, \phi)$

$\qquad\qquad \times \int_0^{\infty} dr\, r^2\, R_{1s}*(r)\, R_{1s}(r)\, r$

$\qquad = (1) \int_0^{\infty} dr\, r^2\, 4\,(Z/a)^3 \exp[-2Zr/a]\, r$

$\qquad = 4\,(Z/a)^3 \int_0^{\infty} dr\, r^3 \exp[-2Zr/a]$

$\qquad = 4\,(Z/a)^3\, 3!/(2Z/a)^4$

$\qquad = 3a/(2Z)$

6.17 (not part of the question)

Note that the expectation value of r is NOT the most probable value of r. The most probable value is obtained from the maximum in the plot of aR^2r^2, and occurs at $r = a$ for R_{1s}:

$\partial\,(aR^2r^2)/\,\partial r = a\,4\,(Z/a)^3\,\partial\,(r^2\exp\,[-2Zr/a])/\,\partial r$

$\qquad = a\,4\,(Z/a)^3\,\{-(2Z/a)\,r^2\exp\,[-2Zr/a] + 2r\exp\,[-2Zr/a]\}$

$\qquad = a\,4\,(Z/a)^3\,(2r)\,\exp\,[-2Zr/a]\,(-Zr/a + 1)$

$\qquad = 0$ if $(-Zr/a + 1) = 0$,

Or $r = a/Z$ (Z=1 for H)

6.6 Find $\langle r \rangle$ for the 2p0 state of the hydrogen atom.

$R_{2p}(r) = 1/(2\sqrt{6}) \{(Z/a)^{5/2} r \exp [-Zr/(2a)]\}$

$\langle r \rangle = \langle \psi_{210} | r | \psi_{210} \rangle$

$\quad = \int_0^{2\pi} d\phi \int_0^{\pi} \sin \theta \, d\theta \, Y_1^{0*}(\theta, \phi) \, Y_1^{0}(\theta, \phi)$

$\qquad \times \int_0^{\infty} dr \, r^2 \, R_{2p}^*(r) \, R_{2p}(r) \, r$

$\quad = \int_0^{\infty} dr \, r^3 (1/24) (Z/a)^5 \, r^2 \exp [-Zr/a]$

$\quad = (1/24) (Z/a)^5 \int_0^{\infty} dr \, r^5 \exp [-Zr/a]$

$\quad = (1/24) (Z/a)^5 (5!)/(Z/a)^6$

$\quad = 5a/Z$

6.30 For the hydrogen atom ground state: (a) Find <V>; (b) Use the results of (a) and problem 6.29 to find <T>; then find <T>/<V>; (c) use <T> to calculate the root mean square speed $<v^2>^{1/2}$ of the electron; then find the numerical value of $<v^2>^{1/2}/c$, where c is the speed of light.

6.30 (a) $<V> = <\psi_{100}|V|\psi_{100}>$

$= \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta \, Y_0^{0*}(\theta, \phi) \, Y_0^0(\theta, \phi)$

$\quad\quad x \int_0^{\infty} dr \, r^2 \, 4 \, (Z/a)^3 \exp[-2Zr/a] \, [-Z(e')^2/r]$

$= 4 (Z/a)^3 [-Z(e')^2] \int_0^{\infty} dr \, r \exp[-2Zr/a]$

$= 4 (Z/a)^3 [-Z(e')^2] [1!/(2Z/a)^2]$

$= -Z^2(e')^2/a, \, Z = 1$

$= -(e')^2/a$

6.30 (b) From 6.29; $<T> + <V> = E$

$E_N = -(Z^2/N^2) [(e')^2/(2a)]; Z=1, N=1, E = -(e')^2/(2a)$

$<T> = E - <V>$

$\quad\quad = -(e')^2/(2a) - [-(e')^2/a]$

$\quad\quad = (e')^2/(2a)$

$<T>/<V> = [(e')^2/(2a)] [-a/[(e')^2] = -1/2$

6.30 (c) $<T> = <m_e v^2/2> = (m_e/2) <v^2> = (e')^2/(2a)$

Root mean square speed $= <v^2>^{1/2}$

$\quad\quad = [(2/m_e) <T>]^{1/2}$

$\quad\quad = \{(2/m_e) [(e')^2/(2a)]\}^{1/2}$

$\quad\quad = \{(e')^2/(m_e a)\}^{1/2}; \quad\quad a = \hbar^2/[\mu (e')^2], \mu \sim m_e$

$\quad\quad = \{(e')^2/(m_e \hbar^2/[m_e (e')^2])\}^{1/2}$

$\quad\quad = \{(e')^4/\hbar^2\}^{1/2}$

$\quad\quad = (e')^2/\hbar; \quad\quad\quad\quad\quad\quad e' = e/\text{SQRT}(4\pi \varepsilon_0)$

$$= \{1.602 \times 10^{-19} \, C / SQRT \, (4\pi \, 8.854 \times 10^{-12})\}^2$$

$$/(1.055 \times 10^{-34} \, Js); \quad \text{Units: } C^2/(Js) = m \, s^{-1}$$

$$= 2.188 \times 10^6 \, m \, s^{-1}$$

$$<v^2>^{1/2}/c = 2.188 \times 10^6 \, m \, s^{-1}/ \, 3.000 \times 10^8 \, m \, s^{-1}$$

$$= 1/137$$

6.34 State which of the three operators L^2, L_z, and the hydrogen atom Hamiltonian each of the following functions is an eigenfunction of: (a) $2p_z$, (b) $2p_x$, (c) $2p_1$.

6.34 (a) $\psi_{2pz} = \psi_{2p0} = R_{21}(r)\ Y_1^0\ (\theta, \phi)$

$L^2\ Y_l^m\ (\theta, \phi) = l\ (l + 1)\ Y_l^m\ (\theta, \phi)$

$L_z\ Y_l^m\ (\theta, \phi) = m\underline{h}\ Y_l^m\ (\theta, \phi)$

$H\ \psi_{nlm} = E_n\ \psi_{nlm}$

$L^2\ R_{21}(r)\ Y_1^0\ (\theta, \phi) = R_{21}(r)\ L^2\ Y_1^0\ (\theta, \phi)$

$\qquad\qquad = R_{21}(r)\ [1(1+1)\ \underline{h}^2]\ Y_1^0\ (\theta, \phi)$

$\qquad\qquad = 2\ \underline{h}^2\ R_{21}(r)\ Y_1^0\ (\theta, \phi),\ \text{Yes eigenfunction}$

$L_z\ R_{21}(r)\ Y_1^0\ (\theta, \phi) = R_{21}(r)\ (0\ \underline{h})\ Y_1^0\ (\theta, \phi)$

$\qquad\qquad = (0\ \underline{h})\ R_{21}(r)\ Y_1^0\ (\theta, \phi),\ \text{Yes eigenfunction}$

$H\ R_{21}(r)\ Y_1^0\ (\theta, \phi) = E_2\ R_{21}(r)\ Y_1^0\ (\theta, \phi),\ \text{Yes eigenfunction}$

6.34 (b) $\psi_{2px} = (\psi_{2p-1} + \psi_{2p1})/\sqrt{2}$

$L^2\ (\psi_{2p-1} + \psi_{2p1})/\sqrt{2} = (L^2\psi_{2p-1} + L^2\psi_{2p1})/\sqrt{2}$

$\qquad = (2\underline{h}^2\psi_{2p-1} + 2\underline{h}^2\psi_{2p1})/\sqrt{2}$

$\qquad = 2\underline{h}^2\ (\psi_{2p-1} + \psi_{2p1})/\sqrt{2},\ \text{Yes eigenfunction}$

$L_z(\psi_{2p-1} + \psi_{2p1})/\sqrt{2} = (L_z\psi_{2p-1} + L_z\psi_{2p1})/\sqrt{2}$

$\qquad = (-\underline{h}\ \psi_{2p-1} + \underline{h}\ \psi_{2p1})/\sqrt{2},\ \text{No not eigenfunction}$

$H\ (\psi_{2p-1} + \psi_{2p1})/\sqrt{2} = (H\psi_{2p-1} + H\psi_{2p1})/\sqrt{2}$

$\qquad = (E_2\ \psi_{2p-1} + E_2\ \psi_{2p1})/\sqrt{2}$

$\qquad = E_2(\psi_{2p-1} + \psi_{2p1})/\sqrt{2},\ \text{Yes eigenfunction}$

6.34 (c) $L^2\ \psi_{2p1} = 2\underline{h}^2\psi_{2p1}$, Yes eigenfunction

$L_z \, \psi_{2p1} = \underline{h} \, \psi_{2p1}$, Yes eigenfunction

$H \, \psi_{2p1} = E_2\psi_{2p1}$, Yes eigenfunction