9-21. $E_{0r} = \dfrac{\hbar^2}{2I}$ (Equation 9-14) where $I = \dfrac{1}{2}mr_0^2$ for a symmetric molecule.

$$E_{0r} = \frac{\hbar^2}{mr_0^2} = \frac{(\hbar c)^2}{mc^2 r_0^2} = \frac{(197.3eV \cdot nm)^2}{(16uc)^2 (931.5\times10^6 eV/uc^2)(0.121nm)^2} = 1.78\times10^{-4}eV$$

9-22. For Co: $f = 6.42\times10^{13}Hz$ (See Example 9-6)

$E_V = (v + 1/2)hf$ (Equation 9-20)

(a) $E_1 - E_0 = 3hf/2 - hf/2 = hf$

$$= (4.14\times10^{-15}eV \cdot s)(6.42\times10^{13}Hz)$$

$$= 0.27eV$$

(b) $\dfrac{n_1}{n_0} = e^{-(E_1 - E_0)/kT}$ (from Equation 8-2)

$$0.01 = e^{-(0.27)/(8.62\times10^{-5})T}$$

$$\ln(0.01) = -(0.27eV)/(8.62\times10^{-5}eV/K)T$$

$$T = \frac{-(0.27eV)}{\ln(0.01)(8.62\times10^{-5}eV/K)}$$

$$T = 680K$$

9-23. For LiH: $f = 4.22\times10^{13}Hz$ (from Table 9-7)

(a) $E_V = (v+1/2)hf = E_0 = hf/2 = (4.14\times10^{-15}eV \cdot s)(4.22\times10^{13}Hz)/2$

$$E_0 = 0.087eV$$

(b) $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$ (Equation 9-17)

$$\mu = \frac{(7.0160u)(1.0078u)}{(7.0160u) + (1.0078u)} = 0.8812u$$

(c) $f = \dfrac{1}{2\pi}\sqrt{\dfrac{K}{\mu}}$ (Equation 9-21)

$$K = (2\pi f)^2 \mu = (2\pi)^2 \left(4.22\times10^{13}\,Hz\right)(0.8812)\left(1.66\times10^{-27}\,kg/u\right)$$

$$K = 117\,N/m$$

(d) $E_n = n^2h^2/8mr_0^2 \rightarrow r_0^2 = n^2h^2/8mE_n$

$$r_0 \approx h/\left(8mE_0\right)^{1/2}$$

$$r_0 \approx \frac{6.63\times10^{-34}\,J\cdot s}{\left[8(0.8812u)\left(1.66\times10^{-27}\,kg/u\right)(0.087eV)\left(1.60\times10^{-19}\,J/eV\right)\right]^{1/2}}$$

$$r_0 \approx 5.19\times10^{-11}\,m = 0.052nm$$

9-25. (a) $\mu = \dfrac{m_1m_2}{m_1+m_2} = \dfrac{(39.1u)(35.45u)}{39.1u+35.45u} = 18.6u$

(b) $E_{0r} = \dfrac{\hbar^2}{2I}$ (Equation 9-14) $I = \mu r_0^2$

$$E_{0r} = \frac{\hbar^2}{2\mu r_0^2} = \frac{(\hbar c)^2}{2\mu c^2 r_0^2} \rightarrow r_0^2 = \frac{(\hbar c)^2}{2\mu c^2 E_V}$$

$$\therefore r_0 = \frac{\hbar c}{\left(2\mu c^2 E_V\right)^{1/2}} = \frac{197.3eV\cdot nm}{\left[2\left(10.6uc^2\right)\left(931.5\times10^6\,eV/uc^2\right)\left(1.43\times10^{-5}\,eV\right)\right]^{1/2}}$$

$$r_0 = 0.280nm$$

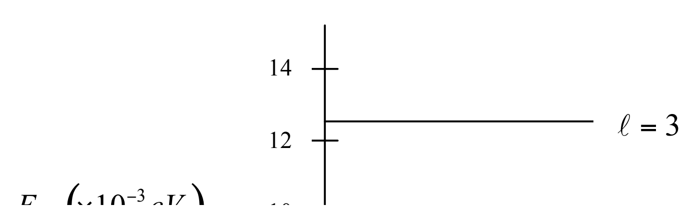
9-27. $E_{0r} = \hbar^2/2I$ Treating the *Br* atom as fixed,

$$I = m_H r_0^2 = (1.0078u)\left(1.66\times10^{-27}\,kg/u\right)(0.141nm)^2$$

$$E_{0r} = \frac{\left(1.055\times10^{-34}\,J\cdot s\right)^2}{2(1.0078u)\left(1.66\times10^{-27}\,kg/u\right)(0.141nm)^2\left(10^{-9}\,m/nm\right)^2}$$

$$= 1.67\times10^{-22}\,J = 1.04\times10^{-3}\,eV$$

$E_\ell = \ell(\ell+1)E_{0r}$ for $\ell = 0, 1, 2, \cdots$ (Equation 9-13)



The four lowest states have energies:

$E_0 = 0$

$E_1 = 2E_{0r} = 2.08\times10^{-3}\,eV$

$E_2 = 6E_{0r} = 6.27\times10^{-3}\,eV$

$E_3 = 12E_{0r} = 12.5\times10^{-3}\,eV$

9-29. $E_{0r} = \dfrac{\hbar^2}{2I}$ where $I = \mu r_0^2$ (Equation 9-14)

For $K^{35}Cl$: $\mu = \dfrac{(39.102u)(34.969u)}{39.102u + 34.969u} = 18.46u$

For $K^{37}Cl$: $\mu = \dfrac{(39.102u)(34.966u)}{39.102u + 34.966u} = 19.00u$

$r_0 = 0.267nm$ for KCl.

$$E_{0r}\left(K^{35}Cl\right) = \frac{\left(1.055\times10^{-34}\,J\cdot s\right)^2}{2\left(18.46u\right)\left(1.66\times10^{-27}\,kg/u\right)\left(0.267\times10^{-9}\,m\right)^2}$$

$$= 2.55\times10^{-24}\,J = 1.59\times10^{-5}\,eV$$

$$E_{0r}\left(K^{37}Cl\right) = \frac{\left(1.055\times10^{-34}\,J\cdot s\right)^2}{2\left(19.00u\right)\left(1.66\times10^{-27}\,kg/u\right)\left(0.267\times10^{-9}\,m\right)^2}$$

$$= 2.48\times10^{-24}\,J = 1.55\times10^{-5}\,eV$$

$\Delta E_{0r} = 0.04\times10^{-5}\,eV$

9-33. $\dfrac{A_{21}}{B_{21}u(f)} = e^{hf/kT} - 1$ (Equation 9-42)

For the Hα line $\lambda = 656.1 nm$

At $T = 300K$, $\frac{hf}{kT} = \frac{hc}{\lambda kT} = \frac{1240 eV\cdot nm}{(656.1 nm)(8.62\times10^{-5} eV/K)(300K)} = 73.1$

$e^{hf/kT} - 1 = e^{73.1} - 1 \approx 5.5\times10^{31}$

Spontaneous emission is more probable by a very large factor!

9-34. $\frac{n(E_1)}{n(E_0)} = \frac{e^{-E_1/kT}}{e^{-E_0/kT}}$ i.e., the ratio of the Boltzmann factors.

For O_2: $f = 4.74\times10^{13} Hz$ and

$$E_0 = hf/2 = (4.14\times10^{-15} eV\cdot s)(4.74\times10^{13} Hz)/2 = 0.0981 eV$$

$$E_1 = 3hf/2 = 0.294 eV$$

At 273K, $kT = (8.62\times10^{-5} eV/K)(273K) = 0.0235 eV$

$$\frac{n(E_1)}{n(E_0)} = \frac{e^{-0.0294/0.0235}}{e^{-0.0981/0.0235}} = \frac{e^{-12.5}}{e^{-4.17}} = 2.4\times10^{-4}$$

Thus, about 2 of every 10,000 molecules are in the E_1 state.

Similarly, at 77K, $\frac{n(E_1)}{n(E_0)} = 1.4\times10^{-13}$

9-35. $E = \ell(\ell+1)E_{0r}$ for $\ell = 0, 1, 2, \cdots$ (Equation 9-13)

Where $E_{0r} = \frac{\hbar^2}{2I}$ and $I = \mu r_0^2$ with $\mu = m/2$

$$E_{0r} = \frac{(1.055\times10^{-34} J\cdot s)^2}{2(18.99u)(1.66\times10^{-27} kg/u)(0.14\times10^{-9} m)^2} = 1.80\times10^{-23} J = 1.12\times10^{-4} eV$$

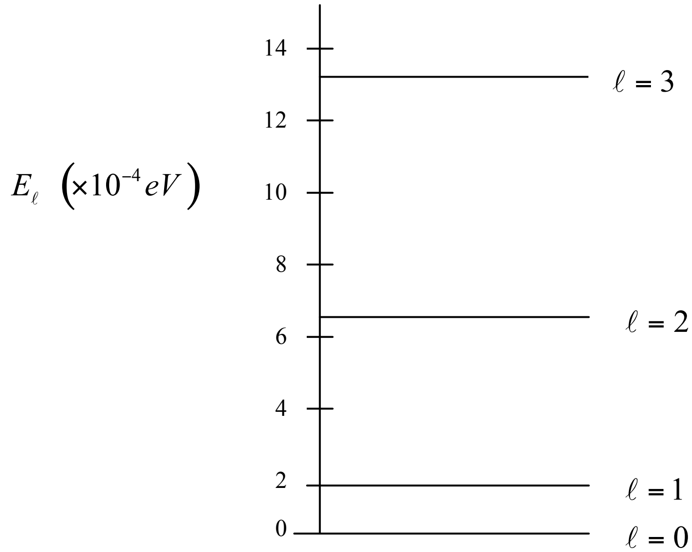
(a) $E_0 = 0$

$E_1 = 2E_{0r} = 2.24\times10^{-4} eV$ $\qquad E_1 - E_0 = 2.24\times10^{-4} eV$

(Problem 9-35 continued)

$$E_2 = 6E_{0r} = 6.72\times10^{-4}eV \qquad E_2 - E_1 = 4.48\times10^{-4}eV$$

$$E_3 = 12E_{0r} = 13.4\times10^{-4}eV \qquad E_3 - E_2 = 6.72\times10^{-4}eV$$



(b) $\Delta\ell \pm 1 \qquad \Delta E = hc/\lambda \rightarrow \lambda = hc/\Delta E$

For $E_1 - E_0 : \lambda = \dfrac{1240eV\cdot nm}{2.24\times10^4 eV} = 5.54\times10^6 nm = 5.54nm$

For $E_2 - E_1 : \lambda = \dfrac{1240eV\cdot nm}{4.48\times10^4 eV} = 2.77\times10^6 nm = 2.77nm$

For $E_3 - E_2 : \lambda = \dfrac{1240eV\cdot nm}{6.72\times10^4 eV} = 1.85\times10^6 nm = 1.85nm$

9-36. (a) $10MW = 10^7 J/s \rightarrow E = (10^7 J/s)(1.5\times10^{-9}s) = 1.5\times10^{-2}J$

(b) For ruby laser: $\lambda = 694.3nm$, so the energy/photon is:

$E = hc/\lambda = 1240eV\cdot nm/694.3nm = 1.786eV$

Number of photons = $\dfrac{(1.5\times10^{-2}J)}{(1.786eV)(1.60\times10^{-19}J/eV)} = 5.23\times10^6$

9-37. $4mW = 4\times10^{-3}J/s$

$$E = hc/\lambda = \frac{1240eV\cdot nm}{632.8nm} = 1.960eV \;\; per \;\; photon$$

$$\text{Number of photons} = \frac{4\times10^{-3}J/s}{(1.960eV)(1.60\times10^{-19}J/eV)} = 1.28\times10^{16}/s$$

9-39. (a)

$$\frac{n(E_2)}{n(E_1)} = \frac{e^{-E_2/kT}}{e^{-E_1/kT}} = e^{(E_2-E_1)/kT} \qquad E_2 - E_1 = hc/\lambda = 1240eV\cdot nm/420nm = 2.95eV$$

$$\text{At } T = 297K, \quad kT = (8.61\times10^{-5}eV/K)(297K) = 0.0256eV$$

$$n(E_2) = n(E_1)e^{-2.95/0.0256} = 2.5\times10^{21}e^{-115} = 2\times10^{-29} \approx 0$$

(b) Energy emitted = $(1.8\times10^{21})(2.95eV/photon) = 5.31\times10^{21}eV = 850J$