Solution to Problem Set 5

1.

$$\psi_n = \frac{1}{\sqrt{2^n \cdot n! \sqrt{\pi}\alpha}} H_n\left(\frac{x}{\alpha}\right) e^{-\frac{x^2}{2\alpha^2}}$$

$$\therefore \psi_1 = \frac{1}{\sqrt{2 \cdot \sqrt{\pi}\alpha}} \cdot 2\left(\frac{x}{\alpha}\right) e^{-\frac{x^2}{2\alpha^2}} = \frac{\sqrt{2}}{\alpha^{\frac{3}{2}}\pi^{\frac{1}{4}}} x e^{-\frac{x^2}{2\alpha^2}}$$

For v = 1, at the turning point $\frac{1}{2}kx_0^2 = \frac{3}{2}h\upsilon \Rightarrow x_0 = \sqrt{\frac{3h\upsilon}{k}} = \pm\sqrt{3}\alpha$

Probability = $2\int_{\sqrt{3}\alpha}^{\infty} \psi_1^2 dx$

$$= 4\frac{1}{\alpha^3\sqrt{\pi}} \int_{\sqrt{3}\alpha}^{\infty} x^2 e^{-\frac{x^2}{\alpha^2}} dx = \frac{4}{\sqrt{\pi}} \int_{\sqrt{3}}^{\infty} y^2 e^{-y^2} dy$$

$$= 1 + \sqrt{\frac{12}{\pi}} e^{-3} - Erf\left[\sqrt{3}\right] = 1 + 0.0973043 - 0.985694 = 0.1116$$

2. $\langle \psi_v | x^4 | \psi_v \rangle = \int_{-\infty}^{\infty} \psi_v x^4 \psi_v dx$

$$\psi_v = \frac{1}{\sqrt{2^v \cdot v! \sqrt{\pi}\alpha}} H_v\left(\frac{x}{\alpha}\right) e^{-\frac{x^2}{2\alpha^2}}$$

$$\therefore \int_{-\infty}^{\infty} \psi_v x^4 \psi_v dx = \frac{1}{2^v \cdot v! \sqrt{\pi}\alpha} \int_{-\infty}^{\infty} H_v^2\left(\frac{x}{\alpha}\right) e^{-\frac{x^2}{\alpha^2}} \cdot x^4 dx$$

$$= \frac{\alpha^4}{2^v \cdot v! \sqrt{\pi}} \int_{-\infty}^{\infty} e^{-y^2} \cdot H_v^2(y) \cdot y^4 dy$$

$$= \frac{\alpha^4}{2^v \cdot v! \sqrt{\pi}} \int_{-\infty}^{\infty} e^{-y^2} \cdot y^2 \cdot H_v(y) \cdot y^2 \cdot H_v(y) dy$$

$$yH_v = vH_{v-1} + \frac{1}{2}H_{v+1};\ y^2 H_v = v(v-1)H_{v-2} + \frac{2v+1}{2}H_v + \frac{1}{4}H_{v+2}$$

$$= \frac{\alpha^4}{2^v \cdot v! \sqrt{\pi}} \int_{-\infty}^{\infty} e^{-y^2} \cdot \left[v(v-1)H_{v-2} + \frac{2v+1}{2}H_v + \frac{1}{4}H_{v+2}\right] \cdot \left[v(v-1)H_{v-2} + \frac{2v+1}{2}H_v + \frac{1}{4}H_{v+2}\right] dy$$

$$= \frac{\alpha^4}{2^v \cdot v! \sqrt{\pi}} \left[v^2(v-1)^2 \cdot 2^{v-2} \cdot (v-2)! \sqrt{\pi} + \frac{(2v+1)^2}{4} \cdot 2^v \cdot v! \sqrt{\pi} + \frac{1}{16} \cdot 2^{v+2} \cdot (v+2)! \sqrt{\pi}\right]$$

$$= \frac{\alpha^4}{2^v \cdot v! \sqrt{\pi}} 2^{v-2} \cdot (v-2)! \sqrt{\pi} v(v-1)\left[v(v-1) + (2v+1)^2 + (v+2)(v+1)\right] = \frac{3\alpha^4}{4}\left[2v^2 + 2v + 1\right]$$

3. A. $k = 4\pi^2 \upsilon_e^2 \cdot \mu = 4\pi^2 (\overline{\upsilon_e} c)^2 \cdot \mu$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{1*35*10^{-3}}{36*6.023*10^{23}} = 1.614*10^{-27} kg$$

$$\therefore k = 4*\pi^2*(2990.9463*10^2*3*10^8)^2*1.614*10^{-27} = 513 N/m$$

B. $E_{vib} = (v+\frac{1}{2})h\upsilon_e - (v+\frac{1}{2})^2 h\upsilon_e x_e$

v = 0 ;

$$\Rightarrow \frac{E_0}{hc} = \frac{1}{2}\upsilon_e - \frac{1}{4}\upsilon_e x_e = \frac{1}{2}*2990.9463 - \frac{1}{4}*52.8186 = 1482.27 cm^{-1}$$

$$\Rightarrow E_0 = 6.626*10^{-34}*3*10^8*1482.27*10^2 = 2.947*10^{-20} J = 0.184 eV$$

v = 1 ;

$$\Rightarrow \frac{E_1}{hc} = \frac{3}{2}\upsilon_e - \frac{9}{4}\upsilon_e x_e = \frac{3}{2}*2990.9463 - \frac{9}{4}*52.8186 = 4367.58 cm^{-1}$$

$$\Rightarrow E_1 = 6.626*10^{-34}*3*10^8*4367.58*10^2 = 8.682*10^{-20} J = 0.543 eV$$

C. $$\lambda_{0\to 1} = \frac{hc}{E_1 - E_0} = \frac{6.626*10^{-34}*3*10^8}{(0.543-0.184)*1.6*10^{-19}}*10^9 = 3460.66 nm$$

D. v = 0 ;

$$\frac{1}{2}kx^2 = \frac{1}{2}h\upsilon \Rightarrow x = \sqrt{\frac{h\upsilon}{k}} = \sqrt{\frac{hc\overline{\upsilon}}{k}}$$

$$\Rightarrow x = \sqrt{\frac{6.626*10^{-34}*3*10^8*2990.9463*10^2}{513}}*10^9 = 0.011 nm$$

E. A. $k = 4*\pi^2*(877.16*10^2*3*10^8)^2*1.614*10^{-27} = 44.12 N/m$

B.

$$\frac{E_0}{hc} = \left(\frac{1}{2}\upsilon_e - \frac{1}{4}\upsilon_e x_e\right) = \frac{1}{2}*877.16 - \frac{1}{4}*16.04 = 434.57 cm^{-1}$$

$$\Rightarrow E_0 = 8.638*10^{-21} J = 0.054 eV$$

$E_1 = 1279.65 cm^{-1} = 2.544*10^{-20}$ J = 0.159 eV

C. $$\lambda_{0\to 1} = \frac{hc}{E_1 - E_0} = \frac{6.626*10^{-34}*3*10^8}{(0.159-0.054)*1.6*10^{-19}}*10^9 = 11832.14 nm$$

D. $$x = \sqrt{\frac{6.626*10^{-34}*3*10^{8}*877.16*10^{2}}{44.12}}*10^{9} = 0.0199nm$$

4. A.

$$x_a = R - \frac{m_b}{M} r \Rightarrow \dot{x}_a = \dot{R} - \frac{m_b}{M}\dot{r}$$
$$x_b = R - \frac{m_a}{M} r \Rightarrow \dot{x}_b = \dot{R} - \frac{m_a}{M}\dot{r}$$

$$T = \frac{1}{2}m_a(\dot{x}_a)^2 + \frac{1}{2}m_b(\dot{x}_b)^2$$
$$= \frac{1}{2}m_a\left(\dot{R} - \frac{m_b}{M}\dot{r}\right)^2 + \frac{1}{2}m_b\left(\dot{R} - \frac{m_a}{M}\dot{r}\right)^2$$
$$= \frac{1}{2}m_a\left(\dot{R}^2 + \frac{m_b^2}{M^2}\dot{r}^2 - 2\frac{m_b}{M}\dot{R}\dot{r}\right) + \frac{1}{2}m_b\left(\dot{R}^2 + \frac{m_a^2}{M^2}\dot{r}^2 - 2\frac{m_a}{M}\dot{R}\dot{r}\right)$$
$$= \frac{1}{2}M\dot{R}^2 + \frac{1}{2}\mu\left(\frac{m_b}{M} + \frac{m_a}{M}\right)\dot{r}^2 = \frac{1}{2}M\dot{R}^2 + \frac{1}{2}\mu\dot{r}^2$$

B. $$\psi(y) \approx e^{-\frac{y^2}{2}};$$
$$\therefore \frac{d^2}{dx^2}\psi(y) \approx e^{-\frac{y^2}{2}}\left(y^2+1\right)$$
Applying this to the Schrodinger equation, we get
$$e^{-\frac{y^2}{2}}\left(\alpha^2\beta+1\right) \Rightarrow e^{-\frac{y^2}{2}} = 0 \text{ for large y.}$$
Thus, ψ(y) is an approximate solution of the Schrodinger equation.

C.

$$\psi(y) = \phi(y)e^{-\frac{y^2}{2}}$$
$$\Rightarrow \psi' = e^{-\frac{y^2}{2}}(\phi' - y\phi)$$
$$\Rightarrow \psi'' = e^{-\frac{y^2}{2}}\left(\phi'' - 2y\phi' + (y^2-1)\phi\right)$$

$$\therefore \psi'' + (\alpha^2\beta - y^2)\psi = e^{-\frac{y^2}{2}}\left(\phi'' - 2y\phi' + (y^2-1)\phi + \left(\alpha^2\beta - y^2\right)\phi\right)$$
$$\Rightarrow e^{-\frac{y^2}{2}}\left(\phi'' - 2y\phi' + (\alpha^2\beta - 1)\phi\right) = 0$$
$$\Rightarrow \phi'' - 2y\phi' + (\alpha^2\beta - 1)\phi = 0$$

Problems from Levine :

4.11.

$$\psi_1 = c_1 x e^{-\frac{\alpha x^2}{2}}$$

$$\therefore \int_{-\infty}^{\infty} \psi_1^2 dx = 1 \Rightarrow \int_{0}^{\infty} \psi_1^2 dx = 0.5$$

$$\Rightarrow \int_0^{\infty} c_1^2 x^2 e^{-\alpha x^2} dx = 0.5 \Rightarrow c_1^2 \left[\frac{1}{4}\sqrt{\frac{\pi}{\alpha^3}} \right] = 0.5 \Rightarrow c_1 = \left(\frac{4\alpha^3}{\pi} \right)^{\frac{1}{4}}$$

$$\psi_2 = c_0 (1 - 2\alpha x^2) e^{-\frac{\alpha x^2}{2}}$$

$$\Rightarrow c_0^2 \int_0^{\infty} \left(1 + 4\alpha^2 x^4 - 4\alpha x^2\right) e^{-\alpha x^2} dx = 0.5$$

$$\Rightarrow c_0^2 \left[\frac{1}{2}\sqrt{\frac{\pi}{\alpha}} + 4\alpha^2 \cdot \frac{3}{8}\sqrt{\frac{\pi}{\alpha^5}} - 4\alpha \cdot \frac{1}{4}\sqrt{\frac{\pi}{\alpha^3}} \right] = 0.5$$

$$\Rightarrow c_0^2 \sqrt{\frac{\pi}{\alpha}} \left[\frac{1}{2} + \frac{3}{2} - 1 \right] = 0.5$$

$$\Rightarrow c_0 = \left(\frac{\alpha}{4\pi} \right)^{\frac{1}{4}}$$

4.16. $$\psi_1 = \left(\frac{4\alpha^3}{\pi} \right)^{\frac{1}{4}} x e^{-\frac{\alpha x^2}{2}}$$

$$\frac{d\psi_1}{dx} = 0 \Rightarrow \left(\frac{4\alpha^3}{\pi} \right)^{\frac{1}{4}} \left[e^{-\frac{\alpha x^2}{2}} \left(1 - \alpha x^2\right) \right] = 0$$

$$\Rightarrow 1 - \alpha x^2 = 0 \Rightarrow x = \pm \alpha^{-\frac{1}{2}}$$

4.25. a.

$$\upsilon_{light} = \frac{1}{h}\left[\left(v_2 + \frac{1}{2}\right) h\upsilon_e - \left(v_2 + \frac{1}{2}\right)^2 h\upsilon_e x_e - \left(v_1 + \frac{1}{2}\right) h\upsilon_e + \left(v_1 + \frac{1}{2}\right)^2 h\upsilon_e x_e \right]$$

$$= \left[(v_2 - v_1)\upsilon_e - \left(v_2^2 - v_1^2 + v_2 - v_1\right)\upsilon_e x_e \right]$$

For $v_2 = v_1 + 1$,

$$\upsilon_{light} = \upsilon_e - \left((v_1 + 1)^2 - v_1^2 + (v_1 + 1) - v_1\right)\upsilon_e x_e = \upsilon_e - 2\upsilon_e x_e (v_1 + 1)$$

b. For $0 \rightarrow v_2$,

$$\upsilon_{light} = \left((v_2 - v_1)\upsilon_e - \left(v_2^2 - v_1^2 + v_2 - v_1\right)\upsilon_e x_e\right) = \upsilon_e\left(v_2 - x_e\left(v_2^2 + v_2\right)\right)$$
$$= \upsilon_e v_2\left(1 - x_e\left(v_2 + 1\right)\right)$$

4.26.a. $\overline{\upsilon} = \frac{E_{vib}}{hc} = \frac{\upsilon_e}{c}\left(v + \frac{1}{2}\right) - \frac{\upsilon_e x_e}{c}\left(v + \frac{1}{2}\right)^2$

$$2885.98 = \frac{\upsilon_e}{c} - \frac{2\upsilon_e x_e}{c} \qquad (1)$$

$$5667.98 = \frac{2\upsilon_e}{c} - \frac{6\upsilon_e x_e}{c} \qquad (2)$$

From (1) and (2), we get

$$\frac{2\upsilon_e x_e}{c} = 103.98 \Rightarrow \frac{\upsilon_e x_e}{c} = 51.99cm^{-1}$$

Therefore, $\frac{\upsilon_e}{c} = 2885.98 + (2 * 51.99) = 2989.96cm^{-1}$

b. $\overline{\upsilon}_{0\rightarrow 3} = \frac{3\upsilon_e}{c} - \frac{12\upsilon_e x_e}{c} = (3 * 2989.96) - (12 * 51.99) = 8346cm^{-1}$

4.27.a. T = 298 K ; $\overline{\upsilon}$ = 1359cm^{-1} ; kT = 1.381*10^{-23} * 298 = 4.11538*10^{-21} J ;

$E_1 - E_0 = hc\overline{\upsilon} = 6.626 * 10^{-34} * 3 * 10^8 * 1359 * 10^2 = 2.7 * 10^{-20} J$

$$\therefore \frac{N_1}{N_0} = \exp\left(-\frac{2.7 * 10^{-20}}{4.11538 * 10^{-21}}\right) = 1.41 * 10^{-3}$$

For T = 473 K ; ; kT = 1.381*10^{-23} * 473 = 6.53213*10^{-21} J ;

$$\therefore \frac{N_1}{N_0} = \exp\left(-\frac{2.7 * 10^{-20}}{6.53213 * 10^{-21}}\right) = 0.01599$$

b. $\overline{\upsilon}$ = 381cm^{-1} ;

$E_1 - E_0 = hc\overline{\upsilon} = 6.626 * 10^{-34} * 3 * 10^8 * 381 * 10^2 = 7.573518 * 10^{-21} J$

T = 298 K ;

$$\therefore \frac{N_1}{N_0} = \exp\left(-\frac{7.573518 * 10^{-21}}{4.11538 * 10^{-21}}\right) = 0.1588$$

T = 473 K ;

$$\therefore \frac{N_1}{N_0} = \exp\left(-\frac{7.573518 * 10^{-21}}{6.53213 * 10^{-21}}\right) = 0.3137$$