Chemistry 4000/5000/7001, Fall 2012, Assignment 2 Solutions

1. (a) $\mathrm{J\,s}$

   (b) Since E is in J, ω has units of $\mathrm{J/J\,s} = \mathrm{s^{-1}}$. Frequency is normally thought of as a number of events per unit time, so these are appropriate units. In this case, the frequency is actually measuring the angle traversed (in radians) per unit time.

2. (a)

$$\begin{aligned} E_1 &= \frac{h^2}{8mL^2} \\ &= \frac{(6.626\,069\,57 \times 10^{-34}\,\mathrm{J\,s})^2}{8(9.109\,382\,9 \times 10^{-31}\,\mathrm{kg})(1 \times 10^{-9}\,\mathrm{m})^2} \\ &= 6 \times 10^{-20}\,\mathrm{J} \end{aligned}$$

   (b)

$$\begin{aligned} \frac{1}{2}mv^2 &= 6 \times 10^{-20}\,\mathrm{J} \\ \therefore v^2 &= \frac{2(6 \times 10^{-20}\,\mathrm{J})}{9.109\,382\,9 \times 10^{-31}\,\mathrm{kg}} = 1 \times 10^{11}\,\mathrm{m^2\,s^{-2}} \\ \therefore v &= 4 \times 10^{5}\,\mathrm{m\,s^{-1}} \end{aligned}$$

   (c)

$$\begin{aligned} p &= mv \\ &= (9.109\,382\,9 \times 10^{-31}\,\mathrm{kg})(4 \times 10^{5}\,\mathrm{m\,s^{-1}}) \\ &= 3 \times 10^{-25}\,\mathrm{kg\,m\,s^{-1}} \end{aligned}$$

3. (a) From the NIST web site, we find

$$\begin{aligned}
m(^1\mathrm{H}) &= 1.007\,825\,032\,07\,\mathrm{u} \\
m(^{19}\mathrm{F}) &= 18.998\,403\,22\,\mathrm{u} \\
\therefore \frac{1}{\mu} &= \frac{1}{m(^1\mathrm{H})} + \frac{1}{m(^{19}\mathrm{F})} \\
&= \frac{1}{1.007\,825\,032\,07} + \frac{1}{18.998\,403\,22\,\mathrm{u}} \\
&= 0.992\,223\,5724 + 0.052\,636\,003\,\mathrm{u}^{-1} \\
&= 1.044\,871\,726\,\mathrm{u}^{-1} \\
\therefore \mu &= 0.957\,055\,278\,\mathrm{u} \\
&\equiv 0.957\,055\,278\,\mathrm{g\,mol}^{-1} \\
&\equiv \frac{0.957\,055\,278\,\mathrm{g\,mol}^{-1}}{(1000\,\mathrm{g\,kg}^{-1})(6.022\,141\,29 \times 10^{23}\,\mathrm{mol}^{-1})} \\
&= 1.589\,227\,538 \times 10^{-27}\,\mathrm{kg}
\end{aligned}$$

(b)

$$\begin{aligned}
\omega_0 &= \sqrt{k/\mu} \\
&= \sqrt{\frac{965.7\,\mathrm{N/m}}{1.589\,227\,538 \times 10^{-27}\,\mathrm{kg}}} \\
&= 7.795 \times 10^{14}\,\mathrm{s}^{-1}
\end{aligned}$$

4. $N = 12$ so cyclobutane has $3N - 6 = 30$ normal modes.

Bonus: A bending mode would involve little or no change in the bond lengths. In questions like this, I'm in favor of rapid methods since the normal-mode motions don't depend much on the method used. (The frequencies do, however.) I therefore did a PM3 semi-empirical calculation, starting with a geometry optimization. Using this computational method, I find a number of modes that look to me like bending modes: $1410\,\mathrm{cm}^{-1}$, $1260\,\mathrm{cm}^{-1}$, $1107\,\mathrm{cm}^{-1}$, $1039\,\mathrm{cm}^{-1}$, $981\,\mathrm{cm}^{-1}$, $846\,\mathrm{cm}^{-1}$ and $801\,\mathrm{cm}^{-1}$.

5. There are at least two ways to tackle this problem:

(a)

$$\begin{aligned}\frac{\partial \Phi}{\partial t} &= -\frac{i}{\hbar}\hat{H}\Phi \\ &= -\frac{i}{\hbar}\hat{H}\left(\Psi_1 + \Psi_2\right) \\ &= -\frac{i}{\hbar}\left(\hat{H}\Psi_1 + \hat{H}\Psi_2\right) \\ &= -\frac{i}{\hbar}\left[\hat{H}\left(\psi_1 e^{-i\omega t}\right) + \hat{H}\left(\psi_2 e^{-i\omega t}\right)\right],\end{aligned}$$

taking $\omega_1 = \omega_2 = \omega$.

$$\begin{aligned}\therefore \frac{\partial \Phi}{\partial t} &= -\frac{i}{\hbar}\left[e^{-i\omega t}\left(\hat{H}\psi_1 + \hat{H}\psi_2\right)\right] \\ &= e^{-i\omega t}\left(E\psi_1 + E\psi_2\right),\end{aligned}$$

taking, again, $E_1 = E_2 = E$.

$$\therefore \frac{\partial \Phi}{\partial t} = -\frac{iE}{\hbar}e^{-i\omega t}\left(\psi_1 + \psi_2\right).$$

The only time dependence on the right-hand side is in the common rotation term $e^{-i\omega t}$. The spatial part of the wavefunction factors out. Thus, this is solution has no interesting time dependence (i.e. no wave propagation).

(b) The other option is to simply calculate the probability density.

$$\begin{aligned}\Phi(x,t) &= \Psi_1(x,t) + \Psi_2(x,t) \\ &= e^{-i\omega t}\psi_1(x) + e^{-i\omega t}\psi_2(x) \\ &= e^{-i\omega t}\left[\psi_1(x) + \psi_2(x)\right]\end{aligned}$$

with a common ω since the two solutions correspond to the same energy.

$$\therefore \left|\Phi^*\Phi\right| = \left|\psi_1 + \psi_2\right|^2,$$

which is time independent. The probability density is therefore stationary.