Chemistry 3730 Fall 2002 Test 2 Solutions

1.

$$\begin{aligned}
\langle Y_{5(-3)}|\hat{L}_x^2+\hat{L}_y^2|Y_{5(-3)}\rangle &= \langle Y_{5(-3)}|\hat{L}^2-\hat{L}_z^2|Y_{5(-3)}\rangle \\
&= \langle Y_{5(-3)}|\hat{L}^2|Y_{5(-3)}\rangle - \langle Y_{5(-3)}|\hat{L}_z^2|Y_{5(-3)}\rangle \\
&= 5(5+1)\hbar^2\langle Y_{5(-3)}|Y_{5(-3)}\rangle - (-3\hbar)\langle Y_{5(-3)}|\hat{L}_z|Y_{5(-3)}\rangle \\
&= 30\hbar^2 - (-3\hbar)^2\langle Y_{5(-3)}|Y_{5(-3)}\rangle \\
&= 30\hbar^2 - 9\hbar^2 = 21\hbar^2
\end{aligned}$$

This is the expectation value of $L_x^2+L_y^2$ for a rotating system for which the angular part of the wavefunction is a spherical harmonic corresponding to the quantum number $\ell=5$, $m_\ell=-3$.

2. First, define the wavefunction:

```
> psi2 := x -> (alpha/(4*Pi))^(1/4)*(2*alpha*x^2-1)
  *exp(-alpha*x^2/2);
```

$$\psi 2 := x \to \frac{1}{4}\,4^{(3/4)}\,(\frac{\alpha}{\pi})^{(1/4)}\,(2\,\alpha x^2-1)\,e^{(-1/2\,\alpha x^2)}$$

```
assume(alpha>0);
```

I'm going to do the calculation in a couple of steps. First, I'm going to calculate the expectation value of K:

```
> avg_K:=-hbar^2/(2*mu)*int(psi2(x)*diff(psi2(x),x$2),
  x=-infinity..infinity);
```

$$avg\_K := \frac{5\,hbar^2\,\alpha\tilde{}}{4\,\mu}$$

Now the expectation value of V:

```
> avg_V:=k/2*int(psi2(x)^2*x^2,x=-infinity..infinity);
```

$$avg\_V := \frac{5\,k}{4\,\alpha\tilde{}}$$

The expectation value of the Lagrangian is therefore

$$\begin{aligned}
\langle L \rangle &= \frac{5\hbar^2\alpha}{4\mu} - \frac{5k}{4\alpha} \\
&= \frac{5\hbar^2}{4\mu}\frac{\sqrt{\mu k}}{\hbar} - \frac{5k}{4}\frac{\hbar}{\sqrt{\mu k}} \\
&= \frac{5}{4}\hbar\sqrt{\frac{k}{\mu}} - \frac{5}{4}\hbar\sqrt{\frac{k}{\mu}} = 0.
\end{aligned}$$

3. (a) This problem is a perturbation on the harmonic oscillator problem. The perturbation is

```
> H1 := x -> A*cos(u*x);
```

$$H1 := x \to A\cos(u\,x)$$

The ground-state wavefunction is

```
> psi00 := x -> (alpha/Pi)^(1/4)*exp(-alpha*x^2/2);
```

$$\psi 00 := x \to (\frac{\alpha}{\pi})^{(1/4)}\, e^{(-1/2\,\alpha\, x^2)}$$

Notation: The first 0 represents the fact that this is a solution to the zero-order problem. The second 0 indicates the ground state of the harmonic oscillator.
The energy correction is

```
> E10 := int(psi00(x)*H1(x)*psi00(x),x=-infinity..infinity);
```

$$E10 := e^{(-\frac{u^2}{4\alpha\tilde{}})}\,A$$

The approximate energy of the ground state is therefore

$$E_0 = E_0^{(0)} + E_0^{(1)} = \frac{1}{2}\hbar\omega + Ae^{-u^2/(4\alpha)}.$$

(b) To calculate the coefficients of the expansion, we need the ground-state energies:

```
> E0 := n -> hbar*omega*(n+1/2);
```

$$E0 := n \to hbar\, \omega\, (n + \frac{1}{2})$$

The coefficient c_{01} is calculated as follows:

```
> psi01 := x -> (4*alpha^3/Pi)^(1/4)*x*exp(-alpha*x^2/2);
```

$$\psi 01 := x \to 4^{(1/4)}\, (\frac{\alpha^3}{\pi})^{(1/4)}\, x\, e^{(-1/2\, \alpha\, x^2)}$$

```
> c01 := int(psi01(x)*H1(x)*psi00(x),x=-infinity..infinity)/(E0(0)-E0(1));
```

$$c01 := 0$$

We proceed similarly for c_{02}. (I use cut-and-paste a lot when I do this kind of work in Maple.)

```
> psi02 := x -> (alpha/(4*Pi))^(1/4)*(2*alpha*x^2-1)*exp(-alpha*x^2/2);
```

$$\psi 02 := x \to \frac{1}{4}\, 4^{(3/4)}\, (\frac{\alpha}{\pi})^{(1/4)}\, (2\, \alpha\, x^2 - 1)\, e^{(-1/2\, \alpha\, x^2)}$$

```
> c02 := int(psi02(x)*H1(x)*psi00(x),x=-infinity..infinity)/(E0(0)-E0(2));
```

$$c02 := -\frac{1}{2}\, \frac{\frac{1}{2}\sqrt{2}\, e^{(-\frac{u^2}{4\tilde{\alpha}})}\, A\, (1 - \frac{u^2}{2\, \tilde{\alpha}}) - \frac{1}{2}\sqrt{2}\, e^{(-\frac{u^2}{4\tilde{\alpha}})}\, A}{hbar\, \omega}$$

```
> c02:=simplify(c02);
```

$$c02 := \frac{1}{8}\, \frac{\sqrt{2}\, e^{(-\frac{u^2}{4\tilde{\alpha}})}\, A\, u^2}{\tilde{\alpha}\, hbar\, \omega}$$

This is our first nonzero correction, so we can stop here. The unnormalized wavefunction is therefore

```
> psi_u := x -> psi00(x) + c02*psi02(x);
```

$$psi\_u := x \to \psi 00(x) + c02\, \psi 02(x)$$

The normalization factor is

```
> N := 1/sqrt(int(psi_u(x)^2,x=-infinity..infinity));
```

$$N := \frac{8}{\sqrt{\frac{\sqrt{\frac{\tilde{\alpha}}{\pi}}\sqrt{\pi}\,(64\,\tilde{\alpha}^2\, hbar^2\,\omega^2 + A^2\,u^4\,\sqrt{4}\,e^{(-\frac{u^2}{2\tilde{\alpha}})})}{\tilde{\alpha}^{(5/2)}\, hbar^2\,\omega^2}}}$$

```
> N := simplify(N);
```

$$N := \frac{4\sqrt{2}\,\tilde{\alpha}}{\sqrt{\frac{32\,\tilde{\alpha}^2\, hbar^2\,\omega^2 + A^2\,u^4\,e^{(-\frac{u^2}{2\tilde{\alpha}})}}{hbar^2\,\omega^2}}}$$

The normalized wavefunction is therefore

```
> psi10 := x -> N*psi_u(x);
```

$$\psi 10 := x \to N\,\mathrm{psi\_u}(x)$$

4. The lines in the spectrum are spaced by $2B$. It follows that

$$B = \frac{1}{2}\left(0.528\,687\,80\,\mathrm{cm}^{-1}\right) = 0.264\,343\,9\,\mathrm{cm}^{-1} \equiv 26.434\,39\,\mathrm{m}^{-1}.$$

We also know that

$$\begin{aligned} B &= \frac{h}{8\pi^2 Ic}, \\ \therefore I &= \frac{h}{8\pi^2 Bc} \\ &= \frac{6.626\,068\,8\times 10^{-34}\,\mathrm{J/Hz}}{8\pi^2(26.434\,39\,\mathrm{m}^{-1})(2.997\,924\,58\times 10^{8}\,\mathrm{m/s})} \\ &= 1.058\,952\times 10^{-45}\,\mathrm{kg\,m}^2. \end{aligned}$$

We also know that $I = \mu r^2$. To go any further, we need to calculate μ:

$$\begin{aligned} m_{\mathrm{Au}} &= \frac{196.966\,552\times 10^{-3}\,\mathrm{kg/mol}}{6.022\,142\,0\times 10^{23}\,\mathrm{mol}^{-1}} \\ &= 3.270\,706\times 10^{-25}\,\mathrm{kg}. \\ m_{\mathrm{F}} &= \frac{18.998\,403\,20\times 10^{-3}\,\mathrm{kg/mol}}{6.022\,142\,0\times 10^{23}\,\mathrm{mol}^{-1}} \\ &= 3.154\,758\times 10^{-26}\,\mathrm{kg}. \end{aligned}$$

$$
\begin{aligned}
\therefore \mu &= \left(\frac{1}{m_{\mathrm{Au}}} + \frac{1}{m_{\mathrm{F}}}\right)^{-1} \\
&= 2.877\,235 \times 10^{-26}\,\mathrm{kg}. \\
\therefore r^2 &= \frac{I}{\mu} = 3.680\,450 \times 10^{20}\,\mathrm{m}^2. \\
\therefore r &= 1.918\,45\,\text{Å}.
\end{aligned}
$$