Chemistry 3730 Fall 2002 Test 2

Write all your answers in the booklets provided. You are entitled to *one* $8\frac{1}{2} \times 11$-inch piece of paper containing any information you want. (Some data is also given at the end of this test paper.) Hand-held calculators are allowed. You may use Maple and its help system. No other aids, printed or electronic, are allowed.

If you use Maple to solve a problem, it is *your responsibility* to make it clear what you are doing. I expect to see the mathematical expressions evaluated using Maple, but *not* the Maple commands used to evaluate them.

Time: 2 h

Total marks: 54

Useful information

Harmonic oscillator wavefunctions:

n	$\psi_n(x)$
0	$\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$
1	$\left(\frac{4\alpha^3}{\pi}\right)^{1/4} x e^{-\alpha x^2/2}$
2	$\left(\frac{\alpha}{4\pi}\right)^{1/4} (2\alpha x^2 - 1) e^{-\alpha x^2/2}$
3	$\left(\frac{\alpha^3}{9\pi}\right)^{1/4} (2\alpha x^3 - 3x) e^{-\alpha x^2/2}$
4	$\left(\frac{\alpha}{576\pi}\right)^{1/4} (4\alpha^2 x^4 - 12\alpha x^2 + 3) e^{-\alpha x^2/2}$

$\alpha = \sqrt{\mu k}/\hbar$.

Harmonic oscillator energy: $E_n = \hbar\omega\left(n + \frac{1}{2}\right)$

Maple syntax reminders:

If you want	type
e^x	`exp(x)`
$\sqrt{x}$	`sqrt(x)`
π	`Pi`

Fundamental constants:

$$\begin{aligned} c &= 2.997\,924\,58 \times 10^8\,\mathrm{m/s} \\ h &= 6.626\,068\,8 \times 10^{-34}\,\mathrm{J/Hz} \\ N_A &= 6.022\,142\,0 \times 10^{23}\,\mathrm{mol}^{-1} \end{aligned}$$

1. Evaluate the following symbolically: $\langle Y_{5(-3)} | \hat{L}_x^2 + \hat{L}_y^2 | Y_{5(-3)} \rangle$. Provide a physical interpretation for the result. [10 marks]

2. The Lagrangian, a quantity which arises in classical mechanics, is defined by $L = K - V$ where K is the kinetic energy and V is the potential energy. Calculate the expectation value of the Lagrangian for a harmonic oscillator in its second excited state. Simplify your answer as much as possible using the definition of α. [10 marks]

   Hints: Maple will need to know that α is a positive quantity. Once you have done the required bits of calculus in Maple, it will probably be easier to simplify your expression by hand.

3. (a) Calculate an approximation to the ground-state energy of a quantum mechanical system consisting of two particles bound by the following potential:

$$V(x) = \frac{1}{2}kx^2 + A\cos(ux)$$

where A is small. [10 marks]

(b) Obtain an approximate normalized wavefunction for the ground state. Carry your analysis up to the first nonzero correction to the zero-order wavefunction. [14 marks]

Maple hints: Maple will need to know that $\alpha > 0$. You are strongly encouraged to apply the `simplify()` function to your results to get something that you can easily write down. It would also make sense in this problem to show the pieces that go into your answer (insofar as this is possible) rather than to try to write down one big expression with everything substituted in.

4. Metal fluorides are generally fairly easy to make due to the very high electronegativity of fluorine. However, gold (I) fluoride has only been made very recently by a group at the University of British Columbia.[1] They were able to make $^{197}Au^{19}F$ in the gas phase and to study its rotational spectrum by microwave spectroscopy. The spacing between the rotational lines is $0.528\,687\,80\,cm^{-1}$.[2] The masses of ^{19}F and of ^{197}Au are, respectively, 18.998 403 20 and 196.966 552 amu. Calculate the bond length in AuF. [10 marks]

[1] C.J. Evans and M.C.L. Gerry, J. Am. Chem. Soc. **122**, 1560 (2000).

[2] This is actually not quite true: Because real molecules aren't rigid rotors, it is necessary to do some analysis on the real line spacings to calculate what the spacing would be if the molecule were truly rigid. This calculated value is what I am giving you to work with.