

# Chemistry 3730 Fall 2002 Test 3

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, HyperChem, and their help systems. No other aids, printed or electronic, are allowed.

If you use Maple or HyperChem 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. Show the results of any significant intermediate steps when feasible. For HyperChem, you should give sufficient detail to allow replication of your results, but again I don't want a click-by-click account of your use of the software.

Time: 2 h

Total marks: 58

There is also a possibility of 3 bonus marks. Any bonus marks earned will be applied directly to your final grade.

## Useful information

Spherical polar coordinates:

$$dV = r^2 \sin \theta dr d\theta d\phi, \theta \in [0, \pi], \phi \in [0, 2\pi)$$

$$1 \text{ kcal/mol} = 4.33641 \times 10^{-2} \text{ eV}$$

Maple syntax reminders:

If you want	type
$e^x$	<code>exp(x)</code>
$ x $	<code>abs(x)</code>
$\sqrt{x}$	<code>sqrt(x)</code>
$\pi$	<code>Pi</code>

1. Calculate the first ionization energy of an arsenic atom. Report your answer in eV. [10 marks]
2. Answer **one** of the following two questions. [4 marks]
  - (a) The description of the ground state of helium as a  $1s^2$  configuration is an approximation. Explain briefly the nature of this approximation.
  - (b) What is the major difficulty in using the variational method to compute excited state wavefunctions?

3. We saw in class that the following are all wavefunctions corresponding to the triplet state of helium in the  $1s^1 2s^1$  electronic configuration:

$$\psi_1 = \phi_1(1,2) \alpha(1) \alpha(2),$$

$$\psi_0 = \phi_1(1,2) \frac{1}{\sqrt{2}} [\alpha(1) \beta(2) + \alpha(2) \beta(1)]$$

$$\psi_{-1} = \phi_1(1,2) \beta(1) \beta(2);$$

$$\text{where } \phi_1(1,2) = \frac{1}{\sqrt{2}} [1s(1) 2s(2) - 1s(2) 2s(1)].$$

There is also a singlet wavefunction:

$$\psi_{\text{singlet}} = \frac{1}{2} [1s(1) 2s(2) + 1s(2) 2s(1)] [\alpha(1) \beta(2) - \alpha(2) \beta(1)].$$

- (a) Either show directly that  $\psi_1$  is orthogonal to  $\psi_0$ , or provide an argument to this effect based on fundamental quantum mechanical principles. [4 marks]
- (b) Since all three of the triplet wavefunctions have the same energy, any linear combination of the three is also a solution to Schrödinger's equation with the same energy. If, in a particular experiment, we do nothing to select among these three possibilities (i.e. if the experiment doesn't create a special axis in space relative to which  $S_z$  has a meaning), then excitation to the triplet state will in general produce a mixture of the three. Suppose that in a particular experiment, we have created the superposition state

$$\Psi_{11(-1)} = N(\psi_1 + \psi_0 - \psi_{-1}),$$

where  $N$  is a normalization factor. Determine the value of  $N$ . [4 marks]

- (c) Is  $\Psi_{11(-1)}$  an eigenfunction of  $\hat{S}^2$ ? If so, what is the eigenvalue? If not, demonstrate that it isn't. [4 marks]
- (d) Is  $\Psi_{11(-1)}$  an eigenfunction of  $\hat{S}_z$ ? If so, what is the eigenvalue? If not, demonstrate that it isn't. [4 marks]

**Bonus question:** Construct a normalized wavefunction which has the same energy as  $\Psi_{11(-1)}$  but is orthogonal to it. [1 bonus mark]

4. Estimate the ground-state energy of a particle of mass  $m$  subjected to a potential  $V(x) = A|x|$  using the variational wavefunction  $\phi(x) = e^{-bx^2}$ . [18 marks]

Hints: The variational wavefunction only makes sense if  $b > 0$ , and Maple will need to be given this information. The equation you need to solve has multiple solutions, but only one is physically sensible. (The correct solution will stand out.) You will have to substitute the desired solution into your variational energy. The best way to do this is to use `subs()`. The command

$$\text{subs}(u=\text{value}, \text{expression});$$

replaces the variable  $u$  by  $\text{value}$  wherever it appears in  $\text{expression}$  (which can be the name of a variable). After making the substitution, you should tell Maple that  $a$ ,  $m$  and  $\hbar$  are all positive quantities and then use `simplify()`.

**Bonus question:** Use the variational method to obtain an estimate for the energy of the first excited state. [2 bonus marks]

5. Calculate the expectation value of the kinetic energy for a **hydrogen** atom in the  $2p_0$  state. In spherical polar coordinates and atomic units, the normalized  $2p_0$  hydrogenic wavefunction is

$$\psi_{2p_0} = \sqrt{\frac{Z^5}{32\pi}} r e^{-Zr/2} \cos \theta$$

and the kinetic energy operator is

$$\hat{K} = -\frac{1}{2r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{2r^2} \hat{L}^2.$$

What are the units of your answer? [10 marks]

Hints: Start by setting up the calculation on paper. Do as many simplifications as you can by hand. When you're ready to start typing integrals into Maple, start from the inside out. For example, if there's a derivative inside an integral, start by typing the expression of which you want to take the derivative, then add the `diff()` function and its parentheses, then add the `int()` function and its parentheses.