

Chemistry 3730 Fall 2002 Final Examination

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. Hand-held calculators are allowed. You may use Maple, HyperChem, and their help systems. No other aids, printed or electronic, are allowed.

Read the instructions for each section carefully. If you are asked to answer only a limited number of questions, make sure to make it clear (by crossing out any aborted work which you don't want marked) which question(s) I should mark. Otherwise, I will mark the first answer(s) I see. **I will not mark more than the required number of questions from any given section.**

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: 3 h

Total marks: 110

Useful information

$$h = 6.6260688 \times 10^{-34} \text{ J/Hz}$$
$$\hbar = 1.05457160 \times 10^{-34} \text{ J s}$$
$$m_e = 9.1093819 \times 10^{-31} \text{ kg}$$

Particle in a box:

$$\Psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$
$$E_n = \frac{n^2 h^2}{8mL^2}$$

Spherical polar coordinates:

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

Maple syntax reminders:

If you want	type
e^x	<code>exp(x)</code>
\sqrt{x}	<code>sqrt(x)</code>
z^*	<code>conjugate(z)</code>
i	<code>I</code>
π	<code>Pi</code>

1 Answer all questions in this section.

Value of this section: 66 marks

1. Explain briefly the physical basis of the Born-Oppenheimer approximation. Why is this approximation needed in quantum chemical calculations? [4 marks]
2. Calculate the probability that a particle in a box of length L occupies the interval $\frac{L}{8} \leq x \leq \frac{3L}{8}$ as a function of the quantum number n . How does this probability behave as $n \rightarrow \infty$? Why? [8 marks]
3. The real spherical harmonics $Y_{1,x}$ and $Y_{1,y}$ are defined by

$$Y_{1,x} = \frac{1}{\sqrt{2}}(Y_{11} - Y_{1(-1)}),$$
$$Y_{1,y} = \frac{1}{i\sqrt{2}}(Y_{11} + Y_{1(-1)}).$$

- (a) Evaluate $\langle Y_{1,x} | \hat{L}^2 | Y_{1,x} \rangle$. [4 marks]
 - (b) Are $Y_{1,x}$ and $Y_{1,y}$ orthogonal? [4 marks]
4. Consider an electron in a one-dimensional box of length 1 nm which is subjected to the additional potential energy

$$V(x) = \begin{cases} 3 \times 10^{-20} \text{ J} & \text{for } 0 < x < 0.3 \text{ nm,} \\ 0 & \text{for } 0.3 \text{ nm} < x < 1 \text{ nm.} \end{cases}$$

This problem will be solved numerically. Enter the numerical values of any required constants into your Maple session as you go. I strongly suggest that you use SI units in all calculations. Give all answers to four significant figures.

- (a) Calculate the energy of the ground state using first-order perturbation theory. [7 marks]
Hints: Set up the integral on paper before you start. In this and subsequent parts of this question, you can divide any integral involving $V(x)$ into two parts, one of which is zero.
- (b) Calculate the ground-state wavefunction by first-order perturbation theory, stopping at the first nonzero correction. Normalize the wavefunction. [6 marks]

- (c) Calculate the energy by the variational method using the variational wavefunction

$$\phi = \psi_1 + a_2\psi_2,$$

i.e. use the particle-in-a-box wavefunctions ψ_1 and ψ_2 as basis functions. [16 marks]

Maple hint: The `subs()` function can be used to substitute values into expressions without redefining any variables. The syntax is

```
subs(u=value, expression);
```

where `u` is the Maple variable whose value you want to substitute into `expression`.

- (d) Normalize the variational wavefunction. [4 marks]
- (e) For this problem, which method gives the best result, perturbation theory or the variational method? Do you expect this to be generally true? Discuss briefly. [4 marks]
- (f) Sketch the two approximate wavefunctions. Discuss any features which seem noteworthy. [4 marks]

Maple hint: To plot more than one function together in Maple, enclose the list of functions in square brackets. For instance

```
plot([f(x), g(x)], x=-1..1);
```

plots the functions $f(x)$ and $g(x)$ on one graph over the interval $[-1, 1]$.

- (g) Discuss briefly the advantages and disadvantages of the perturbation and variational methods for solving quantum mechanical problems. [5 marks]

2 Answer *one* question from this section.

Value of this section: 4 marks

Extra answers will not be marked.

1. In one sentence, explain what an STO-4G basis set is. How many basis functions would an STO-4G basis set have for a carbon atom? [4 marks]
2. Explain briefly what polarization functions are and why they are needed in certain quantum chemical calculations. [4 marks]

3 Answer two questions from this section.

Value of this section: 40 marks

Extra answers will not be marked.

- Prove that Hermitian operators have real eigenvalues. Why is this important? [6 marks]
 - Explain what an expectation value is in relation to the measurement of physical observables. [2 marks]
 - Calculate the expectation value of r for a hydrogenic atom in the $2p_1$ state:

$$\Psi_{2p_1}(r, \theta, \phi) = \frac{Z^{5/2}}{8\sqrt{\pi}} r e^{-Zr/2} \sin \theta e^{i\phi}$$

(in atomic units). Clearly state the units of your answer. How does your answer depend on Z ? Does this make sense? [12 marks]

Maple hints: Maple will need to know that Z is a positive number. You can set this calculation up on paper and do some simplifications ahead of time or, if you're really careful, you can do the calculation directly in Maple. If you choose the latter course, spend a moment looking over the Maple syntax help on p 1 of this exam before you start.

- Calculate the dissociation energy of an OH radical. Briefly justify the methods used. [20 marks]

Hints: Lewis diagrams can be used to figure out the appropriate spin multiplicities for the various species involved in this calculation. In HyperChem's Build menu, choose "Explicit Hydrogens" before "Model Build" to avoid problems with HyperChem's built-in valence rules. It's probably a good idea to save the result of your calculation for OH once it is complete to avoid having to start over if something goes wrong in subsequent steps.

To create a ghost atom, select the atom, choose "Name Selection" from the "Select" menu. Name the selected atom "ghost-atoms". Unselect the atom and enable the ghost atoms option in the advanced options dialog of the *ab initio* setup window.

- What problem are Slater determinants intended to address? [2 marks]
 - Write down a single Slater determinant for a $1s^1 2s^1$ state of a helium atom in which the two electrons have opposite spin. Expand your Slater determinant to give an explicit expression for the wavefunction. [4 marks]
 - Write down the electronic Hamiltonian of a helium atom in atomic units. [2 marks]
 - Determine the energy corresponding to your single Slater determinant. Express the answer in terms of the hydrogenic orbital energies ϵ_{1s} and ϵ_{2s} , the Coulomb integral $J_{(1s)(2s)}$, and the exchange integral $K_{(1s)(2s)}$. Does this state correspond to a singlet or a triplet state? Discuss briefly. [12 marks]