

Name:

Mid-Term Examination

Chemistry 3BB3

Winter, 2006

Except when noted otherwise, you should use the Born-Oppenheimer approximation and atomic units throughout this exam.

Part 1. Multiple Choice/Short Answer

1-2. Write expressions for each of the following operators in SI units.

Quantity	Quantum-Mechanical Operator in <u>SI units</u>
nuclear kinetic energy, \hat{T}_n	
electronic kinetic energy, \hat{T}_e	
nuclear-electron attraction energy, \hat{V}_{ne}	
nuclear-nuclear repulsion energy, \hat{V}_{nn}	
electron-electron repulsion energy, \hat{V}_{ee}	

We wrote the “electronic” Schrödinger equation for the P -atom, N -electron molecule in the Born-Oppenheimer approximation as

$$\begin{aligned} \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee} + \hat{V}_{nn} \psi_e(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_P) \\ = U_{BO}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_P) \psi_e(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_P) \end{aligned}$$

3. Using the above notation and the notation from problems 1 and 2, write the Schrödinger equation for the nuclei in the Born-Oppenheimer Approximation.

4. Let $\Psi(r_1, \sigma_1; r_2, \sigma_2; \dots; r_N, \sigma_N)$ be antisymmetric with respect to exchange of any two electronic coordinates. Show that the probability of two electrons with the same spin being at the same location is zero.

5. Which of the following statements are true.

- | | |
|-------------------------------------------|-------------------------------------------------|
| (a) A Bohr is about .5 Angstroms. | (e) A Hartree is about 2,200 cm^{-1} . |
| (b) An Angstrom is about .5 Bohr. | (f) An cm^{-1} is about 2,200 Hartree. |
| (c) A Hartree is about 27 electron volts. | (g) A Hartree is about 2,600 kJ/mol. |
| (d) An electron volt is about 27 Hartree. | (h) A kJ/mol is about 2600 Hartree. |

6. Write the radial Schrödinger Equation for the one-electron atom with atomic number Z and orbital angular momentum quantum number l in atomic units.

In particle physics experiments, one often observes “exotic” atoms, where two particles bind to each other to form a hydrogen-like atom. In problems seven and eight, let’s imagine an atom where the electron, e^- , was replaced by an antimuon, μ^+ . The antimuon has a charge of $+e$ (where e is the magnitude of the charge of the electron) and a mass that is 203 times the mass of the electron. According to the standard model of particle physics, the heaviest baryon (the proton is the lightest baryon) will have the quark configuration ttb^+ , with mass about 700,000 times that of the electron. (By contrast, the mass of the proton is 1836 times that of the electron.) This “heavy baryon,” which has not yet been observed experimentally, could be called the “top proton” (because it is similar to the normal proton, but with up and down quarks replaced by top and bottom quarks). The anti-top proton, \overline{ttb} has a charge equal to that of the electron ($-e$), and the same mass as the “top proton.” Summarizing, then, we have:

	Hydrogen Atom		Exotic “anti-top muon” hydrogen-like atom.	
particles	electron (e^-)	proton (p)	antimuon (μ^+)	anti-“top proton” \overline{ttb}
charge	$-e$	$+e$	$+e$	$-e$
mass	m_e	$1836 m_e$	$203 m_e$	$698,000 m_e$

For the purposes of questions seven and eight, ignore the effects of nuclear forces; we are only interested in the electrostatic interaction between the light particle (the electron or the antimuon) and the heavy particle (the proton or the anti-top proton).

7. Using the Born-Oppenheimer Approximation, the ground-state electrostatic energy of the exotic “anti-top muon” hydrogen-like atom is:

$$E_{\substack{\text{anti-top muon} \\ \text{exotic atom}}} = \underline{\hspace{2cm}} \text{ Hartree}$$

8. The Born-Oppenheimer approximation is

- (a) more accurate for the hydrogen atom than for the exotic “anti-top muon” hydrogen-like atom.
- (b) less accurate for the hydrogen atom than for the exotic “anti-top muon” hydrogen-like atom.

Usually the form of the wave function for a hydrogen-like atom is a rather complicated function of r , θ , and ϕ . However, for certain special values of the principle quantum number, n , and orbital angular momentum quantum number, l , the wave function takes a simple form. In problems 9 and 10, we will consider the lowest-energy g -orbital.

9. For the one-electron atom with atomic number Z , the lowest-energy g orbital is proportional to

$$\psi_{\text{lowest energy } g \text{ orbital}} r, \theta, \phi \propto$$

10. The energy of the lowest-energy g orbital is (in atomic units):

$$E_{\text{lowest energy } g \text{ orbital}} = \text{Hartree}$$

- 11-12. For each of the following orbitals, write the appropriate eigenvalue. (If the orbital is not an eigenvalue of the operator in question, write “not an eigenvalue” (or something similar) to indicate this.)

$$\begin{array}{ll} \hat{L}^2 \psi_{2p_x} \mathbf{r} = & \psi_{2p_x} \mathbf{r} \\ \hat{L}^2 \psi_{3d_{3z^2-r^2}} \mathbf{r} = & \psi_{3d_{3z^2-r^2}} \mathbf{r} \\ \hat{L}_z \psi_{2p_x} \mathbf{r} = & \psi_{2p_x} \mathbf{r} \\ \hat{L}_z \psi_{3d_{3z^2-r^2}} \mathbf{r} = & \psi_{3d_{3z^2-r^2}} \mathbf{r} \end{array}$$

- 13-14. The following statements pertain to the restricted-Hartree-Fock method (RHF) and the unrestricted Hartree-Fock method (UHF). Which of the following statements are true?

- The Hartree-Fock method includes the effects of electron correlation.
- The RHF wave function is usually chosen to be an eigenfunction of \hat{S}^2 and \hat{L}^2 .
- The UHF wave function is usually chosen to be an eigenfunction of \hat{S}^2 and \hat{L}^2 .
- In an RHF wave function, α -spin electrons and β -spin electrons occupy the same “spatial” orbitals.
- In an UHF wave function, α -spin electrons and β -spin electrons occupy the same “spatial” orbitals.
- The UHF wave function is higher in energy than the RHF wave function.
- The RHF wave function is higher in energy than the UHF wave function.
- The RHF energy is greater than the exact energy.
- The UHF energy is greater than the exact energy.

15. Below, sketch the 1s, 2s, and 3s orbitals in the Hydrogen atom.

As a very primitive model of the Helium atom, we computed the energy of the atom when we neglected the electron-electron repulsion entirely, obtaining an energy of -4 Hartree.

16. Neglecting electron-electron repulsion, what is the energy of the Neon atom? (Write your answer in Hartree units.)

17. The answer in question 16 is

- (a) less than the exact ground-state energy of the Neon atom.
- (b) greater than the exact ground-state energy of the Neon atom.

18. Write an appropriate Slater determinant (include all the rows and all the columns) for a 3S state with the $1s^2 2s^1 5s^1$ electron configuration. Remember to include the appropriate normalization constant for orthogonal and normalized orbitals.

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	M_L					
M_S	5	4	3	2	1	0
$3/2$			$ \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha $	$ \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_{-1}}\alpha $	$ \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_{-2}}\alpha $ $ \psi_{3d_2}\alpha \quad \psi_{3d_0}\alpha \quad \psi_{3d_{-1}}\alpha $	$ \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha \quad \psi_{3d_{-1}}\alpha $ $ \psi_{3d_2}\alpha \quad \psi_{3d_0}\alpha \quad \psi_{3d_{-2}}\alpha $
$1/2$	$ \psi_{3d_2}\alpha \quad \psi_{3d_2}\beta \quad \psi_{3d_1}\alpha $	$ \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta $ $ \psi_{3d_2}\alpha \quad \psi_{3d_2}\beta \quad \psi_{3d_0}\alpha $	$ \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\beta $ $ \psi_{3d_2}\alpha \quad \psi_{3d_1}\beta \quad \psi_{3d_0}\alpha $ $ \psi_{3d_2}\beta \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha $ $ \psi_{3d_2}\alpha \quad \psi_{3d_2}\beta \quad \psi_{3d_{-1}}\alpha $	$ \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_{-1}}\beta $ $ \psi_{3d_2}\alpha \quad \psi_{3d_1}\beta \quad \psi_{3d_{-1}}\alpha $ $ \psi_{3d_2}\beta \quad \psi_{3d_1}\alpha \quad \psi_{3d_{-1}}\alpha $ $ \psi_{3d_2}\alpha \quad \psi_{3d_2}\beta \quad \psi_{3d_{-2}}\alpha $ $ \psi_{3d_2}\alpha \quad \psi_{3d_0}\alpha \quad \psi_{3d_0}\beta $ $ \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta \quad \psi_{3d_0}\alpha $	$ \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_{-2}}\beta $ $ \psi_{3d_2}\alpha \quad \psi_{3d_1}\beta \quad \psi_{3d_{-2}}\alpha $ $ \psi_{3d_2}\beta \quad \psi_{3d_1}\alpha \quad \psi_{3d_{-2}}\alpha $ $ \psi_{3d_2}\alpha \quad \psi_{3d_0}\alpha \quad \psi_{3d_{-1}}\beta $ $ \psi_{3d_2}\alpha \quad \psi_{3d_0}\beta \quad \psi_{3d_{-1}}\alpha $ $ \psi_{3d_2}\beta \quad \psi_{3d_0}\alpha \quad \psi_{3d_{-1}}\alpha $ $ \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta \quad \psi_{3d_{-1}}\alpha $ $ \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha \quad \psi_{3d_0}\beta $	$ \psi_{3d_2}\alpha \quad \psi_{3d_0}\alpha \quad \psi_{3d_{-1}}\beta $ $ \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha \quad \psi_{3d_{-1}}\beta $ $ \psi_{3d_2}\alpha \quad \psi_{3d_{-1}}\alpha \quad \psi_{3d_{-2}}\beta $ $ \psi_{3d_2}\alpha \quad \psi_{3d_{-1}}\alpha \quad \psi_{3d_{-2}}\beta $

19. List all the terms associated with the ground state electron configuration of Vanadium, $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$. (You do not need to show the possible values of J here.)

20. What is the term symbol for the ground state term of the Cobalt atom, which has electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$?

21. What are the possible values of M_j in the ground state of the Cobalt atom?

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22. We are interested in the $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3 4p^1$ excited state of the Manganese atom. What are the possible terms?

For each of the following, write the eigenvalue. (If there is no eigenvalue, write “no eigenvalue”; if there are multiple eigenvalues possible, write all the possibilities.) Here, the wave functions are denoted either by (a) a Slater determinant or (b) a term symbol. In each case, it is up to you to decipher the relevant quantum numbers.

23.

$$\begin{aligned} \hat{L}^2 \begin{vmatrix} \psi_{3d_2} \alpha & \psi_{3d_1} \alpha & \psi_{3d_0} \alpha \end{vmatrix} &= \begin{vmatrix} \psi_{3d_2} \alpha & \psi_{3d_1} \alpha & \psi_{3d_0} \alpha \end{vmatrix} \\ \hat{L}_z \begin{vmatrix} \psi_{3d_2} \alpha & \psi_{3d_1} \alpha & \psi_{3d_0} \alpha \end{vmatrix} &= \begin{vmatrix} \psi_{3d_2} \alpha & \psi_{3d_1} \alpha & \psi_{3d_0} \alpha \end{vmatrix} \\ \hat{L}^2 \begin{vmatrix} \psi_{3d_2} \alpha & \psi_{3d_1} \alpha & \psi_{3d_1} \beta \end{vmatrix} &= \begin{vmatrix} \psi_{3d_2} \alpha & \psi_{3d_1} \alpha & \psi_{3d_1} \beta \end{vmatrix} \\ \hat{L}_z \begin{vmatrix} \psi_{3d_2} \alpha & \psi_{3d_1} \alpha & \psi_{3d_1} \beta \end{vmatrix} &= \begin{vmatrix} \psi_{3d_2} \alpha & \psi_{3d_1} \alpha & \psi_{3d_1} \beta \end{vmatrix} \end{aligned}$$

24.

$$\begin{aligned} \hat{S}^2 \begin{vmatrix} \psi_{3d_2} \alpha & \psi_{3d_1} \alpha & \psi_{3d_0} \alpha \end{vmatrix} &= \begin{vmatrix} \psi_{3d_2} \alpha & \psi_{3d_1} \alpha & \psi_{3d_0} \alpha \end{vmatrix} \\ \hat{S}_z \begin{vmatrix} \psi_{3d_2} \alpha & \psi_{3d_1} \alpha & \psi_{3d_0} \alpha \end{vmatrix} &= \begin{vmatrix} \psi_{3d_2} \alpha & \psi_{3d_1} \alpha & \psi_{3d_0} \alpha \end{vmatrix} \\ \hat{S}^2 \begin{vmatrix} \psi_{3d_2} \alpha & \psi_{3d_1} \alpha & \psi_{3d_1} \beta \end{vmatrix} &= \begin{vmatrix} \psi_{3d_2} \alpha & \psi_{3d_1} \alpha & \psi_{3d_1} \beta \end{vmatrix} \\ \hat{S}_z \begin{vmatrix} \psi_{3d_2} \alpha & \psi_{3d_1} \alpha & \psi_{3d_1} \beta \end{vmatrix} &= \begin{vmatrix} \psi_{3d_2} \alpha & \psi_{3d_1} \alpha & \psi_{3d_1} \beta \end{vmatrix} \end{aligned}$$

25.

$$\begin{aligned} \hat{J}^2 \begin{vmatrix} \psi_{3d_2} \alpha & \psi_{3d_1} \alpha & \psi_{3d_0} \alpha \end{vmatrix} &= \begin{vmatrix} \psi_{3d_2} \alpha & \psi_{3d_1} \alpha & \psi_{3d_0} \alpha \end{vmatrix} \\ \hat{J}_z \begin{vmatrix} \psi_{3d_2} \alpha & \psi_{3d_1} \alpha & \psi_{3d_0} \alpha \end{vmatrix} &= \begin{vmatrix} \psi_{3d_2} \alpha & \psi_{3d_1} \alpha & \psi_{3d_0} \alpha \end{vmatrix} \\ \hat{J}^2 \begin{vmatrix} \psi_{3d_2} \alpha & \psi_{3d_1} \alpha & \psi_{3d_1} \beta \end{vmatrix} &= \begin{vmatrix} \psi_{3d_2} \alpha & \psi_{3d_1} \alpha & \psi_{3d_1} \beta \end{vmatrix} \\ \hat{J}_z \begin{vmatrix} \psi_{3d_2} \alpha & \psi_{3d_1} \alpha & \psi_{3d_1} \beta \end{vmatrix} &= \begin{vmatrix} \psi_{3d_2} \alpha & \psi_{3d_1} \alpha & \psi_{3d_1} \beta \end{vmatrix} \end{aligned}$$

Part 2. Closed-Book Derivation

The following results may be helpful for this problem.

$$[\hat{S}_x, \hat{S}_y] = i\hbar \hat{S}_z$$

$$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z$$

$$[\hat{S}_y, \hat{S}_z] = i\hbar \hat{S}_x$$

$$[\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x$$

$$[\hat{S}_z, \hat{S}_x] = i\hbar \hat{S}_y$$

$$[\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y$$

You may also need commutator identities (e.g., formulae for $[\hat{A}, \hat{B}\hat{C}]$, $[\hat{A}\hat{B}, \hat{C}]$, $[\hat{A}, \hat{B} + \hat{C}]$, $[\hat{A} + \hat{B}, \hat{C}]$) and commutator relationships for angular momentum operators.

1a. Show that $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ and \hat{J}_z commute. (5 pts.)

1b. Show that \hat{J}^2 and \hat{S}_z do not commute. (5 pts.)

Though a lot of quantum chemists think that they are off their rockers, inorganic chemists are constantly talking about the role of *d*-orbitals in the binding of the sulfur atom.

- 2a. Determine the term symbols for the $1s^2 2s^2 2p^6 3s^2 3p^3 4d^1$ excited state of the sulfur atom? Write the terms in order of increasing energy. (That is, list the lowest energy term first, followed by the term with the second-lowest energy, etc.) Assume that Hund's rules work (6 pts.)**

2b. What values of J are associated with the ground state? (2 pts.)

2c. Write a Slater determinant that is associated with the lowest-energy term. (2 pts.)

Bonus: The term symbols for the $1s^2 2s^2 2p^1 3p^1$ excited state of the Carbon atom are $^1S, ^3S, ^1P, ^3P, ^1D, ^3D$. This is one of the cases where Hund's rules do not give the expected results. What is the ground state term? (3 pts.)

3a. Use the Hellmann-Feynman Theorem to show that (5 pts.)

$$\left\langle \psi_{n,l,m} \left| -\frac{\nabla^2}{2} \right| \psi_{n,l,m} \right\rangle = \frac{Z^2}{2n^2}.$$

3b. Using the fact that

$$\langle \psi_{n,l,m} | r^2 | \psi_{n,l,m} \rangle = \frac{n^2}{2Z^2} [5n^2 - l(l+1) + 1]$$

show that the Heisenberg uncertainty principle for the position and momentum is satisfied. I.e., show that

$$\left[\sqrt{\langle \psi_{n,l,m} | \hat{\mathbf{p}} \cdot \hat{\mathbf{p}} | \psi_{n,l,m} \rangle - \langle \psi_{n,l,m} | \mathbf{p} | \psi_{n,l,m} \rangle \cdot \langle \psi_{n,l,m} | \mathbf{p} | \psi_{n,l,m} \rangle} \right. \\ \left. \times \sqrt{\langle \psi_{n,l,m} | \mathbf{r} \cdot \mathbf{r} | \psi_{n,l,m} \rangle - \langle \psi_{n,l,m} | \mathbf{r} | \psi_{n,l,m} \rangle \cdot \langle \psi_{n,l,m} | \mathbf{r} | \psi_{n,l,m} \rangle} \right] \geq \frac{\hbar}{2}$$

for every possible value of n and l . (5 pts.)

Part 3. “Thinking” Problem

In this problem we will learn about approximating the energy of atoms and ions using the energy of other atoms and ions.

Suppose that we can decompose a Hamiltonian into two pieces, one of which depends only on the first M coordinates, and the other of which depends only on the second $N - M$ coordinates,

$$\hat{H}_{total} = \hat{H}^A(\mathbf{r}_1, \dots, \mathbf{r}_M) + \hat{H}^B(\mathbf{r}_{M+1}, \dots, \mathbf{r}_N)$$

Suppose, furthermore, that we know the eigenvalues and eigenvectors for the Hamiltonians of the two “pieces,”

$$\hat{H}^A(\mathbf{r}_1, \dots, \mathbf{r}_M) \Psi_k^A(\mathbf{r}_1, \dots, \mathbf{r}_M) = E_k^A \Psi_k^A(\mathbf{r}_1, \dots, \mathbf{r}_M)$$

$$\hat{H}^B(\mathbf{r}_{M+1}, \dots, \mathbf{r}_N) \Psi_l^B(\mathbf{r}_{M+1}, \dots, \mathbf{r}_N) = E_l^B \Psi_l^B(\mathbf{r}_{M+1}, \dots, \mathbf{r}_N)$$

1. Show that the eigenfunctions of \hat{H}_{total} can be written as the product of the eigenfunctions of the two pieces, and that the eigenvalues of \hat{H}_{total} are the sums of the eigenvalues of the two pieces. That is,

$$\Psi_{total}(\mathbf{r}_1, \dots, \mathbf{r}_N) = \Psi_k^A(\mathbf{r}_1, \dots, \mathbf{r}_M) \Psi_l^B(\mathbf{r}_{M+1}, \dots, \mathbf{r}_N)$$
$$E_{total} = E_k^A + E_l^B$$