

Exam 2 Solutions

1. (15 points) Consider the boron atom.
- (a) What is the ground state electron configuration for B? (If you don't remember where B is in the periodic table, ask me. I'll tell you, but it will cost you 2 points!)
Boron is element 5 in the Periodic Table: $1s^2 2s^2 2p^1$
- (b) What term symbol or symbols come from this configuration? Circle the ground state term symbol if you predict more than one.
There are two possible term symbols; the single p electron, as in the first excited configuration in Na, says it all: ${}^2P_{1/2}^o$ (the ground state—less than half-full 2p subshell) and ${}^2P_{3/2}^o$.
- (c) There is a ${}^2S_{1/2}$ state $40\,040\text{ cm}^{-1}$ above the ground state. What is its electron configuration most likely to be?
Two possibilities should come to mind: $1s^2 2s^1 2p^2$ and $1s^2 2s^2 3s^1$. The first leads to several possible states, but with the possibility that the three 2s and 2p electrons could be all spin-aligned and produce a quartet state (there's the answer to part (e)!), which would be lower in energy than any doublet state, we should reject this possibility and go for the $1s^2 2s^2 3s^1$ configuration which can *only* produce a ${}^2S_{1/2}$ state.
- (d) Would an optical transition from the ground state of part (b) to the ${}^2S_{1/2}$ state mentioned in part (c) be allowed? Why or why not?
Note that the ground state has odd parity while this one has even parity. They are both doublet states, so $\Delta S = 0$, the transition would be from a P state to an S state ($\Delta L = -1$, which is allowed), and even if $\Delta J = 0$ (from the ground $J = 1/2$ to the excited $J = 1/2$ state), that's OK, as long as $J \neq 0$. The transition is allowed.
- (e) Give any configuration of B that will lead to at least one *quartet* term.
The first configuration that can produce a quartet term is the one mentioned in part (a): $1s^2 2s^1 2p^2$.

2. (15 points) You will recall that a particle of mass m in a one-dimensional box of length L over the range $0 \leq x \leq L$ has a ground-state energy E_1 and a normalized wavefunction ψ_1 given by

$$E_1 = \frac{\hbar^2 \pi^2}{2mL^2} \quad \psi_1 = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{\pi x}{L}\right).$$

Now consider a 1-D box that has a bump in potential over its range instead of a flat potential. In particular, let the potential have the form

$$V(x) = V_0 \sin\left(\frac{\pi x}{L}\right), \quad 0 \leq x \leq L$$

where V_0 is a constant such that $|V_0| \ll E_1$. This is a situation that calls for first-order perturbation theory! Calculate the first-order energy correction to E_1 . One or more of the integrals below may be useful:

$$\int_0^\pi \sin y \, dy = 2 \quad \int_0^\pi \sin^2 y \, dy = \frac{\pi}{2} \quad \int_0^\pi \sin^3 y \, dy = \frac{4}{3}$$

The first-order energy expression is the expectation value of the perturbation Hamiltonian for the quantum state of interest. Here, the perturbation is just the potential function $V(x)$, and the wavefunction of interest is $\psi_1(x)$. We calculate

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$$E_1^{(1)} = \int \psi_1^*(x) V(x) \psi_1 dx = V_0 \left(\frac{2}{L}\right) \int_0^L \sin^3\left(\frac{\pi x}{L}\right) dx$$

Let $y = \pi x/L$ so that $dx = L/\pi dy$. This gives us

$$E_1^{(1)} = V_0 \left(\frac{2}{L}\right) \int_0^L \sin^3\left(\frac{\pi x}{L}\right) dx = V_0 \left(\frac{2}{L}\right) \frac{L}{\pi} \int_0^\pi \sin^3 y dy = V_0 \frac{24}{\pi^3} = \frac{8V_0}{3\pi}.$$

3. (15 points) The lowest three energy levels of atomic carbon have term symbols and energies as shown below:

$$\text{_____ } 43.5 \text{ cm}^{-1} \quad 3P_2$$

$$\text{_____ } 16.4 \text{ cm}^{-1} \quad 3P_1$$

$$\text{_____ } 0.0 \text{ cm}^{-1} \quad 3P_0$$

- (a) The ratio of the energy gaps between these three levels is

$$\frac{43.5 \text{ cm}^{-1} - 16.4 \text{ cm}^{-1}}{16.4 \text{ cm}^{-1} - 0.0 \text{ cm}^{-1}} = 1.65$$

What does our theoretical expression for the spin-orbit energy predict for this ratio?

We use our expression for the spin-orbit energy, noting that the ratio we are asked to calculate means that the constants in that expression will cancel and that all three states have the same L and S quantum numbers, but different J quantum numbers. This gives us

$$\frac{2(2+1) - 1(1+1)}{1(1+1) - 0(0+1)} = \frac{6-2}{2-0} = \frac{4}{2} = 2$$

which is close to the experimental value 1.65.

- (b) There are many other 3P states of C, but the lowest-energy 3P levels of odd parity have the energies shown below:

$$\text{_____ } 60,393.52 \text{ cm}^{-1} \quad 3P_2^o$$

$$\text{_____ } 60,353.00 \text{ cm}^{-1} \quad 3P_1^o$$

$$\text{_____ } 60,333.80 \text{ cm}^{-1} \quad 3P_0^o$$

What configuration leads to these levels?

The ground state configuration is $1s^2 2s^2 2p^2$, which has even parity. We want an odd parity configuration, and the first excitation that can give us that is $1s^2 2s^2 2p^1 3s^1$. (The $1s^2 2s^1 2p^3$ configuration is a reasonable possibility of odd parity that can produce $^3P^o$ states and was given full credit if you chose it.)

- (c) Imagine a sample of atomic C produced in such a way that all three 3P levels of part (a) were substantially populated. How many distinct absorption transitions would such a sample exhibit to the levels of part (b)?

The ΔJ selection rule is in command here. The 3P_0 state can go only to $J = 1$ (because $J = 0$ to $J = 0$ is forbidden), but 3P_1 can go to $J = 0, 1$, or 2 , while 3P_2 can go to $J = 2$ or 1 . There are six transitions in all.

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4. (15 points) Use atomic orbitals to construct a trial wavefunction that can correctly serve as an approximation for the exact wavefunction in each of the following possibilities. Use symbols such as “1” and “2” to represent electrons, symbols such as “1s” to represent one-electron wavefunctions, “A” and “B” to represent nuclei, and the usual α and β symbols for spin wavefunctions.

(a) The ground state of He.

We have two identical spin-1/2 electrons occupying the same atomic orbital, 1s, so the wavefunction must be made antisymmetric through the spin part:

$$\psi = 1s(1)1s(2) \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

(b) A triplet excited state of He based on the configuration $1s^1 2s^1$.

Triplet states have symmetric spin functions, so the spatial part has to be antisymmetric. There are three possibilities; any one of them is acceptable:

$$\psi = \frac{1}{\sqrt{2}} [1s(1)2s(2) - 1s(2)2s(1)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

$$\psi = \frac{1}{\sqrt{2}} [1s(1)2s(2) - 1s(2)2s(1)] \alpha(1)\alpha(2)$$

$$\psi = \frac{1}{\sqrt{2}} [1s(1)2s(2) - 1s(2)2s(1)] \beta(1)\beta(2)$$

(c) An *unbound* state of H_2 that correctly dissociates to two $1s^1$ hydrogen atoms.

This is the triplet state of H_2 , called Ψ_4 on page 512 in the text, built from the MO configuration $1\sigma_g^1 1\sigma_u^{*1}$. We can write the antisymmetric spatial part in terms of these MOs (with any of the three symmetric spin parts) as

$$\psi = \frac{1}{\sqrt{2}} [1\sigma_g(1)1\sigma_u^*(2) - 1\sigma_g(2)1\sigma_u^*(1)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

$$\psi = \frac{1}{\sqrt{2}} [1\sigma_g(1)1\sigma_u^*(2) - 1\sigma_g(2)1\sigma_u^*(1)] \alpha(1)\alpha(2)$$

$$\psi = \frac{1}{\sqrt{2}} [1\sigma_g(1)1\sigma_u^*(2) - 1\sigma_g(2)1\sigma_u^*(1)] \beta(1)\beta(2)$$

and we can then write the MOs in terms of atomic orbitals:

$$1\sigma_g = \frac{1s_A + 1s_B}{\sqrt{2(1+S)}} \equiv \frac{A+B}{\sqrt{2(1+S)}}$$

$$1\sigma_u^* = \frac{1s_A - 1s_B}{\sqrt{2(1-S)}} \equiv \frac{A-B}{\sqrt{2(1-S)}}$$

(and if you left out the overlap integral, S , I didn't deduct any points) so that the final list of possibilities is

$$\psi = \frac{1}{\sqrt{2(1+S)(1-S)}} [B(1)A(2) - B(2)A(1)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

$$\psi = \frac{1}{\sqrt{2(1+S)(1-S)}} [B(1)A(2) - B(2)A(1)] \alpha(1)\alpha(2)$$

$$\psi = \frac{1}{\sqrt{2(1+S)(1-S)}} [B(1)A(2) - B(2)A(1)] \beta(1)\beta(2)$$

Note that the spatial part is purely covalent, but antibonding (due to the minus sign).

5. (10 points) In the last homework, we learned that the $1s^1 2p^1 \ ^1P_1^0 \rightarrow 1s^2 \ ^1S_0$ transition in He, at 584.33 Å, has a radiative lifetime, τ_{rad} , of 6.0×10^{-10} s. The transition between the corresponding two levels in the highly-ionized two electron ion Ne^{+8} has a radiative lifetime of only 1.12×10^{-13} s. If you look back through the

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expressions that relate τ_{rad} to atomic transition properties, you'll find that only two such properties have changed on going from He to Ne^{+8} . Tell me *which two* they are, *how* they change (i.e., get bigger, get smaller, get much bigger, don't change very much, etc.), *why* they change the way you say they do, and *which one must dominate* in order to explain the decrease in τ_{rad} on going from He to Ne^{+8} .

The two quantities that must change are the transition frequency ν_{12} and the transition dipole moment p_{12} . Everything else is either a constant or a degeneracy factor g that is the same because the nature of the states in both atoms is the same. The frequency must increase significantly, because Ne^{+8} has a much larger nuclear charge ($Z = 10$ for Ne, $Z = 2$ for He) and atomic energies decrease dramatically (like Z^2) as Z increases, as do the energy separations between them and thus their transition frequencies. (In fact, the observed wavelength for this transition in Ne^{+8} happens to be 13.46 \AA , in the x-ray region of the spectrum. The frequency increases by a factor of $584.33 \text{ \AA}/13.46 \text{ \AA} = 43.4$.) The transition dipole moment is probably *smaller* for Ne^{+8} than for He simply because Ne^{+8} is a smaller atom! The dominant factor, however, must be the frequency change, since it enters the expression for τ_{rad} as ν^3 . In fact, now that I've told you the transition wavelength, and pulling the He value for p_{12} from the last homework, $5.95 \times 10^{-30} \text{ C m}$, we can find p_{12} for Ne^{+8} . We write

$$\tau_{\text{rad}} \propto \frac{\lambda^3}{p_{12}^2} \quad \text{so} \quad \frac{6.0 \times 10^{-10} \text{ s}}{1.12 \times 10^{-13} \text{ s}} = \frac{(584.33 \text{ \AA})^3}{(5.95 \times 10^{-30} \text{ C m})^2} \frac{p_{12}^2}{(13.43 \text{ \AA})^3}$$

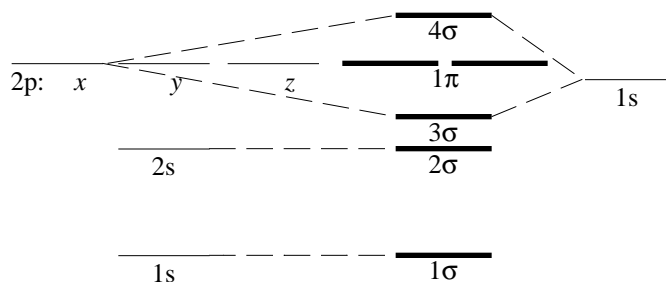
and solve to find p_{12} for Ne^{+8} is $1.5 \times 10^{-30} \text{ C m}$, which is smaller, as expected, but not by as great a factor as the wavelength decrease (or frequency increase).

6. (15 points) Below are ionization energies of various atomic orbitals of H and C:

H 1s: 13.6 eV C 1s: 296 eV 2s: 19.4 eV 2p: 10.7 eV

- (a) Use these data to construct an MO diagram for CH. Make sure you order all your molecular orbitals in increasing energy and give each an appropriate name, but don't try to draw your diagram exactly to scale.

Here it is. Qualitatively, it's the same figure that was on the Assignment 6 solution handout regarding problem 6.1's question about OH!



- (b) Which species, CH^+ , CH, and/or CH^- , would you predict to have a *singlet* ground electronic state, and why?

Count electrons: CH^+ has 6, CH has 7, and CH^- has 8. For CH^+ , we have the ground-state configuration $1\sigma^2 2\sigma^2 3\sigma^3$, which is a singlet. CH is a doublet (one 1π electron), and CH^- would be a triplet (two 1π electrons, one in each 1π , spin aligned).

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7. (15 points) Here are some questions that need only short, but succinct, answers.
- (a) The radial distribution function for one of the $n = 3$ hydrogen atom orbitals is zero at $r = 0$ and at $r = \infty$, but nowhere else. What value (or values) must the l and m quantum numbers have for this orbital?
- If $n = 3$, the wavefunction itself must have $n - 1 = 2$ nodes in all. The radial distribution function displays only the radial (spherical) nodes, and this one has none. That means all the nodes are planar ones, and since the number of planar nodes equals l , this must be an $l = 2$ orbital. We don't have any way of knowing m , so m could be $+2$, $+1$, 0 , -1 , or -2 .
- (b) What is the magnitude of the *total* angular momentum for a He atom in a 3P_2 state? (A symbolic expression will do—no need for a calculated value.)
- $J = 2$ in this state, so the answer is $\sqrt{J(J+1)} \hbar = \sqrt{6} \hbar$.
- (c) Can an electron trapped by a harmonic oscillator potential absorb light and make a transition from the ground to the first excited state of the oscillator? (Obviously, a simple “yes” or “no” answer isn't good enough here! Explain how you arrived at your answer, and—big hint!—note that a sufficient answer would address symmetry issues only!)
- If the transition dipole moment p_{12} isn't zero by symmetry, then the transition is possible. Let's call the oscillator coordinate x . The ground state wavefunction for the harmonic oscillator is an *even* function of x , but the first excited state wavefunction is an *odd* function (one node right at $x = 0$). But that's OK—the dipole operator, $-ex$, is also an odd function of x . Thus, the integrand is a function of overall even \times odd \times odd = even symmetry. The integral doesn't vanish by symmetry (the integrand would have to be odd for the integral to vanish) and the transition is allowed.
- (d) The lowest energy H_2^+ molecular orbital of σ_g symmetry correlates to a $1s$ atomic orbital in the united atom limit. To which atomic orbital does the lowest energy σ_u^* orbital correlate in this limit?
- The σ_u^* orbital has a node in the middle of the bond (let's let the bond lie along the z axis) as a plane perpendicular to the bond. As the nuclei approach the UA limit, this node is preserved, and the σ_u^* orbital becomes the $2p_z$ atomic orbital.
- (e) What He atom ground-state energy is predicted if the term in the full Hamiltonian representing electron-electron repulsion is ignored? (Express your energy in terms of the H atom ground-state energy, -13.6 eV.)
- Neglecting this term is the “independent electron” approximation: the only terms left in the Hamiltonian are those that describe the ground state of the He^+ ion twice, once for each of the two electrons. The energy predicted here is thus twice the energy of a He^+ ground state, and since the energies of one-electron atoms of nuclear charge Ze are Z^2 times the energy of a hydrogen ground-state atom, the final answer is $2Z^2E_1 = 2(2^2)(-13.6 \text{ eV}) = -108.8 \text{ eV}$.