

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. *Show the dependence on the fundamental physical constants, $\hbar, m_e, e, \epsilon_0$, etc..*

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}	

3. When we wrote the molecular Schrodinger equation using terms like those in the table, we were making several approximations. List two of the approximations.

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

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

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

5. Let $\Psi(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; \dots; \mathbf{r}_N, \sigma_N)$ 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.

6. High-resolution spectra are often resolved to about $.1 \text{ cm}^{-1}$. In order to accurately model such spectra, one needs to solve the Schrödinger equation with an accuracy of about

- | | | |
|--------------------|-----------------------|-----------------------|
| (a) 10^6 Hartree | (c) 1 Hartree | (e) 10^{-6} Hartree |
| (b) 10^3 Hartree | (d) 10^{-3} Hartree | |

7. Write the radial Schrödinger equation for the Hydrogen atom in atomic units, showing the dependence on the angular momentum quantum number, l .

8. The “g factor” for an electron is approximately

- | | | |
|---------|-----------|-----------------|
| (a) 1.0 | (c) 2.0 | (e) $\ln(2)$ |
| (b) 0.5 | (d) π | (f) $\ln \hbar$ |

Name:

9. Below, sketch the 1s, 2s, and 3s orbitals in the Hydrogen atom.
10. Write an appropriate Slater determinant for the $1s^2 2s^2 2p^1$ electron configuration. You can write either the first two rows, or the first two columns of the Slater determinant. (You do not have to write *all* the rows and columns!) Remember to include the appropriate normalization constant for orthogonal and normalized orbitals.
11. Suppose the Slater determinant in problem 10 is the solution to the unrestricted Hartree-Fock method for this state. Which of the following statements are true:
- (a) This Slater determinant has a lower energy than any other Slater determinant of orbitals for this system.
 - (b) This Slater determinant has a higher energy than any other Slater determinant of orbitals for this system.
 - (c) The 2s alpha-spin and the 2s beta-spin orbitals are the same.
 - (d) The 2s alpha-spin and the 2s beta-spin orbitals are different.
 - (e) This Slater determinant is an eigenfunction of \hat{S}^2 .
 - (f) This Slater determinant is not an eigenfunction of \hat{S}^2 .

The ionization potential is defined as “the amount of energy it takes to remove one electron from a system.” The second ionization potential is defined as “the amount of energy it takes to remove the second electron from the system.” (For a neutral molecule, the second ionization potential is the amount of energy it takes to remove an electron from the cation; for a cation, the second ionization potential is the amount of energy it takes to remove an electron from the dication; etc..) The energy of the Lithium cation, Li^+ , is -7.279903 Hartree.

12. What is the first ionization potential of the Lithium cation?

13. What is the second ionization potential of the Lithium cation?

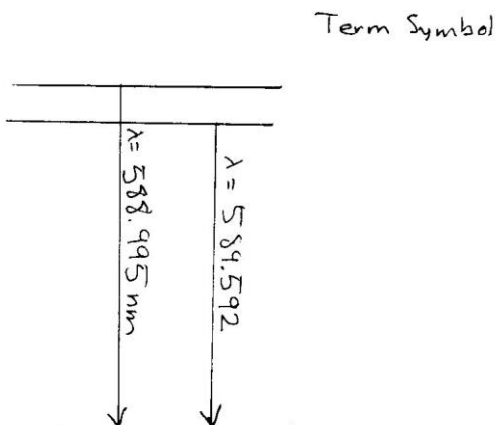
Suppose you are given the following information about the probability of observing an electron in the Helium cation (with atomic number equal to two).

- very close to the nucleus, the probability of observing an electron is proportional to r^2 .
- very far from the nucleus, the probability of observing an electron decays as e^{-r} .

14. The electron in He^+ is in what type of orbital.

15. What is the energy of this state of He^+ ?

16. Back when I pretended to be a physicist, I would often calibrate a spectrometer using the emission from the sodium “D” line (where “D” stands for “doublet” in typically confused physics parlance). The sodium “D” line corresponds to the $1s^2 2s^2 2p^6 3p^1 \rightarrow 1s^2 2s^2 2p^6 3s^1$ transition. Use term symbols to label the each state on the energy level diagram.



17. Some physicists think that the speed of light, c , might not be exactly constant, but instead might be decreasing slightly. If these physicists are correct, then a few billion years from now the speed of light will be significantly smaller than it is now and the separation between the two lines in the Sodium doublet will be
- smaller than it is today.
 - larger than it is today.

- 18,19. 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.)

$$\begin{aligned}
 \hat{L}^2 \begin{vmatrix} \psi_{1s}\alpha & \psi_{1s}\beta & \psi_{2s}\alpha & \psi_{3s}\beta \end{vmatrix} &= \begin{vmatrix} \psi_{1s}\alpha & \psi_{1s}\beta & \psi_{2s}\alpha & \psi_{3s}\beta \end{vmatrix} \\
 \hat{L}_z \begin{vmatrix} \psi_{1s}\alpha & \psi_{1s}\beta & \psi_{2s}\alpha & \psi_{3s}\beta \end{vmatrix} &= \begin{vmatrix} \psi_{1s}\alpha & \psi_{1s}\beta & \psi_{2s}\alpha & \psi_{3s}\beta \end{vmatrix} \\
 \hat{S}^2 \begin{vmatrix} \psi_{1s}\alpha & \psi_{1s}\beta & \psi_{2s}\alpha & \psi_{3s}\beta \end{vmatrix} &= \begin{vmatrix} \psi_{1s}\alpha & \psi_{1s}\beta & \psi_{2s}\alpha & \psi_{3s}\beta \end{vmatrix} \\
 \hat{S}_z \begin{vmatrix} \psi_{1s}\alpha & \psi_{1s}\beta & \psi_{2s}\alpha & \psi_{3s}\beta \end{vmatrix} &= \begin{vmatrix} \psi_{1s}\alpha & \psi_{1s}\beta & \psi_{2s}\alpha & \psi_{3s}\beta \end{vmatrix} \\
 \hat{J}^2 \begin{vmatrix} \psi_{1s}\alpha & \psi_{1s}\beta & \psi_{2s}\alpha & \psi_{3s}\beta \end{vmatrix} &= \begin{vmatrix} \psi_{1s}\alpha & \psi_{1s}\beta & \psi_{2s}\alpha & \psi_{3s}\beta \end{vmatrix} \\
 \hat{J}_z \begin{vmatrix} \psi_{1s}\alpha & \psi_{1s}\beta & \psi_{2s}\alpha & \psi_{3s}\beta \end{vmatrix} &= \begin{vmatrix} \psi_{1s}\alpha & \psi_{1s}\beta & \psi_{2s}\alpha & \psi_{3s}\beta \end{vmatrix} \\
 \hat{L}^2 \begin{vmatrix} \psi_{2p_1}\alpha & \psi_{2p_1}\beta \end{vmatrix} &= \begin{vmatrix} \psi_{2p_1}\alpha & \psi_{2p_1}\beta \end{vmatrix} \\
 \hat{L}_z \begin{vmatrix} \psi_{2p_1}\alpha & \psi_{2p_1}\beta \end{vmatrix} &= \begin{vmatrix} \psi_{2p_1}\alpha & \psi_{2p_1}\beta \end{vmatrix} \\
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 \hat{J}_z \begin{vmatrix} \psi_{2p_1}\alpha & \psi_{2p_1}\beta \end{vmatrix} &= \begin{vmatrix} \psi_{2p_1}\alpha & \psi_{2p_1}\beta \end{vmatrix}
 \end{aligned}$$

After graduation, you've decided to sell your services to the highest bidder. You have two job offers, each from groups that wish you to do quantum mechanics to help them in their quest for world domination. In order to satisfy your zeal for power and avoid the gulag, you'll need to decide which of the following groups is most likely to rule the world, given that they plan to model materials use the Born-Oppenheimer approximation.

Name: "We put the 'g' in God"

Leaders: Bill "Blue Screen" Gates
Andy "The Genius" Grove

Slogan: "After installing this software you ~~may~~ *will* have to ~~reboot your~~ *buy a new* computer"

Weapon of Mass Destruction: Computer Hardware/Software

Materials of Interest: Silicon and Silicon oxides

Name: Franco-American Alliance for Cardiac Medicine

Leaders: Jacques "Crème Fraîche" Chirac
Dick "Replace your cooking oil with crude" Cheney

Slogan: "Would you like gravy with your fries?"

Weapon of Mass Destruction: Cholesterol/Fat

Materials of Interest: Fats; hydrocarbons.

20. You don't want to wind up in the gulag. Based on what you know about the accuracy of the Born-Oppenheimer approximation, your best bet is to

- (a) Model SiO_2 for the Gates/Grove cartel.
- (b) Model oleanoic acid ($\text{C}_{30}\text{H}_{48}\text{O}_3$) for the Franco-American Alliance.

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 use 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 of the same type.

1a. Show that $[\hat{L}^2, \hat{J}_z] = 0$. (3 pts.)

- 1b. Show that $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ and \hat{J}_z commute. You may find it helpful to know that $[\hat{S}^2, \hat{J}_z] = 0$ for the same reason that $[\hat{L}^2, \hat{J}_z] = 0$. (7 pts.)

Though a lot of quantum chemists think that they are off their proverbial rockers, inorganic chemists are constantly talking about the role of *d*-orbitals in the binding of the sulfur atom. In order for d-orbitals to be involved in bonding, of course, one must first “promote” electrons from the p-orbitals to the d-orbitals of the sulfur atom. This is my excuse for asking the following question. If you don’t like it, blame the inorganic chemists, not me....

- 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. You should use the “shorthand” notation for Slater determinants. (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

$$\langle \psi_{n,l,m} | r^2 | \psi_{n,l,m} \rangle = \frac{n^2}{2Z^2} (5n^2 - 3l(l+1) + 1)$$

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

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

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.

1. Concavity of the Energy.

The total energy of a system clearly depends on the Hamiltonian, and so we can say that the energy is a functional of the Hamiltonian, $E[\hat{H}]$. Suppose the Hamiltonian for a system can be written as the sum of two Hamiltonians,

$$\hat{H}_{AB} = \hat{H}_A + \hat{H}_B$$

(a) Show that the ground state energy for the whole system “***AB***” is greater than the sum of the ground state energies of the two subsystems, “***A***” and “***B***”. That is, (8 pts.)

$$E[\hat{H}_{AB}] \geq E[\hat{H}_A] + E[\hat{H}_B]$$

(b) When is this relationship an equality, instead of an inequality? That is, when is

$$E[\hat{H}_{AB}] = E[\hat{H}_A] + E[\hat{H}_B]?$$

(2 pts.)

2. Show why each of the following results is true (5 pts total; 1 pt. each)

(a) The ground state energy of the Lithium cation is less than the three times the energy of the hydride anion.

$$E_{Li^+} < 3E_{H^-}$$

(b) Twice ground state energy of the Lithium cation is less than the three times the energy of the Helium atom.

$$2E_{Li^+} < 3E_{He}$$

(c) The ground state energy of the Lithium cation is less than the sum of the energies of the Helium atom and the hydride anion.

$$E_{Li^+} < E_{H^-} + E_{He}$$

(d) The ground state energy of the Lithium cation is less than the sum of the energies of the Helium atom and the hydrogen atom.

$$E_{Li^+} < E_H + E_{He}$$

(e) The ground state energy of the Lithium atom is less than the sum of the ground state energies of the Helium atom and the Hydrogen atom.

$$E_{Li} < E_H + E_{He}$$

As we began our discussion of diatomic molecules, we talked about the united-atom limit (where the two atoms were placed on top of each other) and the separated atom limit (where the two atoms were infinitely far apart). The ground-state electronic energy in the united atom limit is always less than the ground state electronic energy in the separated atom limit. (The nuclear-nuclear repulsion energy is not included in the united-atom limit, because it would be infinite.) We could now prove this in the general case, but let us instead try just a special case:

- (f) **The ground-state energy of the Boron atom is less than the sum of the ground-state energies of the Lithium and Helium atoms. That is,**

$$E_B < E_{Li} + E_{He}$$

(2 pts.)

It is a general principle that the energies of the atoms decrease faster than linearly. That is, the energy of the atoms is a concave function of the atomic number, Z . In practical terms, this means that the change in energy between an atom and the entry in the periodic table that precedes it is less than the change in energy that same atom and the entry in the periodic table that follows it. We will now show this for a special case.

(g) Show that

$$E_B - E_C > E_{Be} - E_B$$

(3 pts.)

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. *Show the dependence on the fundamental physical constants, $\hbar, m_e, e, \epsilon_0$, etc..*

Quantity	Quantum-Mechanical Operator in <u>SI units</u>
nuclear kinetic energy, \hat{T}_n	$\sum_{\alpha=1}^P \frac{-\hbar^2}{2M_{\alpha}} \nabla_{\alpha}^2$
electronic kinetic energy, \hat{T}_e	$\sum_{i=1}^N \frac{-\hbar^2}{2m_e} \nabla_i^2$
nuclear-electron attraction energy, \hat{V}_{ne}	$\sum_{i=1}^N \sum_{\alpha=1}^P \frac{-Z_{\alpha} e^2}{4\pi\epsilon_0 \mathbf{r}_i - \mathbf{R}_{\alpha} }$
nuclear-nuclear repulsion energy, \hat{V}_{nn}	$\sum_{\alpha=1}^{P-1} \sum_{\beta=\alpha+1}^P \frac{Z_{\alpha} Z_{\beta} e^2}{4\pi\epsilon_0 \mathbf{R}_{\alpha} - \mathbf{R}_{\beta} }$
electron-electron repulsion energy, \hat{V}_{ee}	$\sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{e^2}{4\pi\epsilon_0 \mathbf{r}_i - \mathbf{r}_j }$

3. When we wrote the molecular Schrodinger equation using terms like those in the table, we were making several approximations. List two of the approximations.

gravitational forces are neglected

nuclear forces/interactions are neglected. (E.g., the “weak force” between electrons and nucleons is neglected)

relativistic effects are neglected

atomic nuclei are assumed to be infinitely small. (That is, atomic nuclei are assumed to be point charges. In the Born-Oppenheimer approximation, atomic nuclei are actually assumed to be infinitely massive point charges.)

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

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

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

$$\hat{T}_n + U_{BO} \mathbf{R}_1, \dots, \mathbf{R}_P \chi_n \mathbf{R}_1, \dots, \mathbf{R}_P = E^{BO} \chi_n \mathbf{R}_1, \dots, \mathbf{R}_P$$

5. Let $\Psi \mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; \dots; \mathbf{r}_N, \sigma_N$ 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.

From antisymmetry

$$\Psi \dots \mathbf{r}_i, \sigma_i, \dots \mathbf{r}_j, \sigma_j, \dots = -\Psi \dots \mathbf{r}_j, \sigma_j, \dots \mathbf{r}_i, \sigma_i, \dots \\ \Psi \dots \mathbf{r}_i, \sigma_i, \dots \mathbf{r}_i, \sigma_i, \dots = -\Psi \dots \mathbf{r}_i, \sigma_i, \dots \mathbf{r}_i, \sigma_i, \dots$$

where, in the second line, we've used the fact that \mathbf{r}_i and \mathbf{r}_j and σ_i and σ_j are the same. Then,

$$\Psi \dots \mathbf{r}_i, \sigma_i, \dots \mathbf{r}_i, \sigma_i, \dots + \Psi \dots \mathbf{r}_i, \sigma_i, \dots \mathbf{r}_i, \sigma_i, \dots = 0 \\ \Psi \dots \mathbf{r}_i, \sigma_i, \dots \mathbf{r}_i, \sigma_i, \dots = 0 \\ |\Psi \dots \mathbf{r}_i, \sigma_i, \dots \mathbf{r}_i, \sigma_i, \dots|^2 = 0$$

and so the probability of seeing two electrons in the same place at the same time is zero.

6. High-resolution spectra are often resolved to about $.1 \text{ cm}^{-1}$. In order to accurately model such spectra, one needs to solve the Schrödinger equation with an accuracy of about

(a) 10^6 Hartree
(b) 10^3 Hartree

(c) 1 Hartree
(d) 10^{-3} Hartree

(e) 10^{-6} Hartree

7. Write the radial Schrödinger equation for the Hydrogen atom in atomic units, showing the dependence on the angular momentum quantum number, l .

$$-\frac{1}{2r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{l(l+1)}{2r^2} - \frac{Z}{r} R_{n,l} r = E_{n,l} R_{n,l} r$$

8. The “g factor” for an electron is approximately

(a) 1.0
(b) 0.5

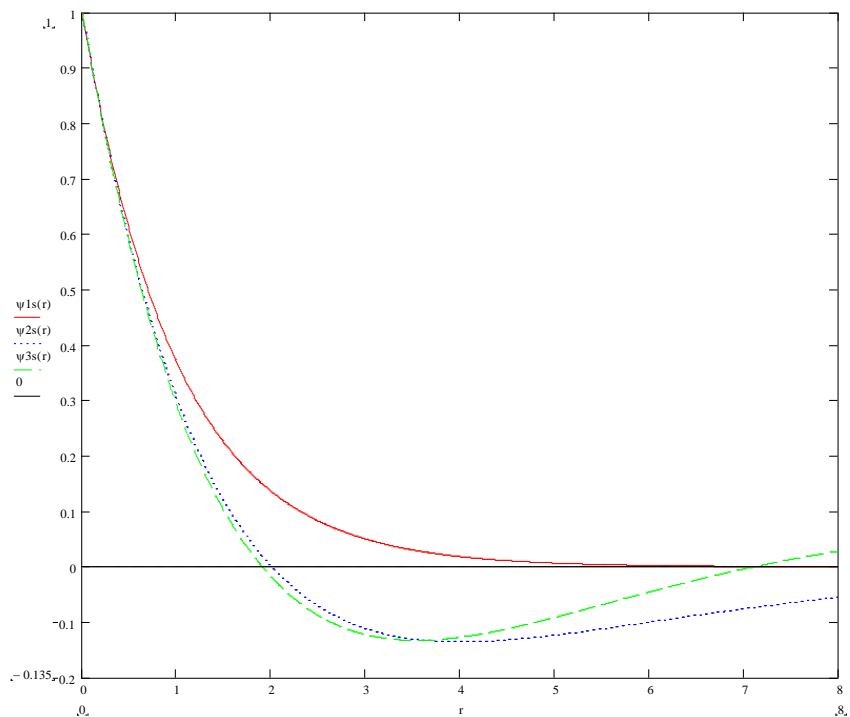
(c) 2.0
(d) π

(e) $\ln(2)$
(f) $\ln \hbar$

Name:

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

You just need to make sure that the 1s orbital has zero nodes, the 2s orbital has one node, and the 3s orbital has two nodes; plus, the nodes should be interleaved. The exact figure looks like:



10. Write an appropriate Slater determinant for the $1s^2 2s^2 2p^1$ electron configuration. You can write either the first two rows, or the first two columns of the Slater determinant. (You do not have to write *all* the rows and columns!) Remember to include the appropriate normalization constant for orthogonal and normalized orbitals.

$$\Phi = \frac{1}{\sqrt{5!}} \begin{vmatrix} \psi_{1s} \mathbf{r}_1 \alpha 1 & \psi_{1s} \mathbf{r}_1 \beta 1 & \psi_{2s} \mathbf{r}_1 \alpha 1 & \psi_{2s} \mathbf{r}_1 \beta 1 & \psi_{2p_0} \mathbf{r}_1 \alpha 1 \\ \psi_{1s} \mathbf{r}_2 \alpha 2 & \psi_{1s} \mathbf{r}_2 \beta 2 & \psi_{2s} \mathbf{r}_2 \alpha 2 & \psi_{2s} \mathbf{r}_2 \beta 2 & \psi_{2p_0} \mathbf{r}_2 \alpha 2 \\ \psi_{1s} \mathbf{r}_3 \alpha 3 & \psi_{1s} \mathbf{r}_3 \beta 3 & \psi_{2s} \mathbf{r}_3 \alpha 3 & \psi_{2s} \mathbf{r}_3 \beta 3 & \psi_{2p_0} \mathbf{r}_3 \alpha 3 \\ \psi_{1s} \mathbf{r}_4 \alpha 4 & \psi_{1s} \mathbf{r}_4 \beta 4 & \psi_{2s} \mathbf{r}_4 \alpha 4 & \psi_{2s} \mathbf{r}_4 \beta 4 & \psi_{2p_0} \mathbf{r}_4 \alpha 4 \\ \psi_{1s} \mathbf{r}_5 \alpha 5 & \psi_{1s} \mathbf{r}_5 \beta 5 & \psi_{2s} \mathbf{r}_5 \alpha 5 & \psi_{2s} \mathbf{r}_5 \beta 5 & \psi_{2p_0} \mathbf{r}_5 \alpha 5 \end{vmatrix}$$

11. Suppose the Slater determinant in problem 10 is the solution to the unrestricted Hartree-Fock method for this state. Which of the following statements are true:

(a) This Slater determinant has a lower energy than any other Slater determinant of orbitals for this system.

(b) This Slater determinant has a higher energy than any other Slater determinant of orbitals for this system.

(c) The 2s alpha-spin and the 2s beta-spin orbitals are the same.

(d) The 2s alpha-spin and the 2s beta-spin orbitals are different.

(e) This Slater determinant is an eigenfunction of \hat{S}^2 .

(f) This Slater determinant is not an eigenfunction of \hat{S}^2 .

The ionization potential is defined as “the amount of energy it takes to remove one electron from a system.” The second ionization potential is defined as “the amount of energy it takes to remove the second electron from the system.” (For a neutral molecule, the second ionization potential is the amount of energy it takes to remove an electron from the cation; for a cation, the second ionization potential is the amount of energy it takes to remove an electron from the dication; etc..) The energy of the Lithium cation, Li^+ , is -7.279903 Hartree.

12. What is the first ionization potential of the Lithium cation?

$$IP_1 = E_{\text{Li}^{+2}} - E_{\text{Li}^+} = -\frac{3^2}{2 \cdot 1^2} - -7.279903 = 7.279903 - \frac{9}{2} = 2.779903 \text{ Hartree}$$

13. What is the second ionization potential of the Lithium cation?

$$IP_2 = -E_{\text{Li}^{+2}} = -\frac{-3^2}{2 \cdot 1^2} = 4.5 \text{ Hartree}$$

Suppose you are given the following information about the probability of observing an electron in the Helium cation (with atomic number equal to two).

- very close to the nucleus, the probability of observing an electron is proportional to r^2 .
- very far from the nucleus, the probability of observing an electron decays as e^{-r} .

14. The electron in He^+ is in what type of orbital.

$r^2 \rightarrow p$ orbital

$$e^{-\frac{Zr}{n}} = e^{-r} \quad Z = 2 \text{ for He}$$

$$e^{-\frac{2 \cdot 2 \cdot r}{n}} = e^{-r}$$

$$e^{-\frac{4r}{n}} = e^{-r}$$

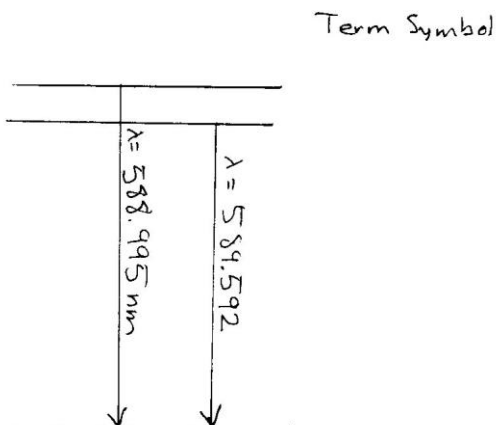
$$n = 4$$

The electron is in a 4p orbital.

15. What is the energy of this state of He^+ ?

$$E = \frac{-Z^2}{2n^2} = -\frac{2^2}{2 \cdot 4^2} = -\frac{4}{2 \cdot 16} = -\frac{1}{8} \text{ Hartree}$$

16. Back when I pretended to be a physicist, I would often calibrate a spectrometer using the emission from the sodium “D” line (where “D” stands for “doublet” in typically confused physics parlance). The sodium “D” line corresponds to the $1s^2 2s^2 2p^6 3p^1 \rightarrow 1s^2 2s^2 2p^6 3s^1$ transition. Use term symbols to label the each state on the energy level diagram.



The highest-energy state is $^2P_{3/2}$. The next state is $^2P_{1/2}$. The ground state is $^2S_{1/2}$. This is just an application of Hund's third rule.

17. Some physicists think that the speed of light, c , might not be exactly constant, but instead might be decreasing slightly. If these physicists are correct, then a few billion years from now the speed of light will be significantly smaller than it is now and the separation between the two lines in the Sodium doublet will be

(a) smaller than it is today.

(b) larger than it is today.

(Remember that Hund's third rule is related to the spin-orbit interaction, which is a relativistic effect. The splitting is small because the speed of light is big (and relativistic effects are small). If the speed of light were much smaller, then relativistic effects like the spin-orbit interaction would be much more important!

18,19. 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.)

$$\begin{aligned}\hat{L}^2 \left| \psi_{1s}\alpha \quad \psi_{1s}\beta \quad \psi_{2s}\alpha \quad \psi_{3s}\beta \right| &= 0 \left| \psi_{1s}\alpha \quad \psi_{1s}\beta \quad \psi_{2s}\alpha \quad \psi_{3s}\beta \right| \\ \hat{L}_z \left| \psi_{1s}\alpha \quad \psi_{1s}\beta \quad \psi_{2s}\alpha \quad \psi_{3s}\beta \right| &= 0 \left| \psi_{1s}\alpha \quad \psi_{1s}\beta \quad \psi_{2s}\alpha \quad \psi_{3s}\beta \right| \\ \hat{S}^2 \left| \psi_{1s}\alpha \quad \psi_{1s}\beta \quad \psi_{2s}\alpha \quad \psi_{3s}\beta \right| &= \text{no eigenvalue} \left| \psi_{1s}\alpha \quad \psi_{1s}\beta \quad \psi_{2s}\alpha \quad \psi_{3s}\beta \right| \\ \hat{S}_z \left| \psi_{1s}\alpha \quad \psi_{1s}\beta \quad \psi_{2s}\alpha \quad \psi_{3s}\beta \right| &= 0 \left| \psi_{1s}\alpha \quad \psi_{1s}\beta \quad \psi_{2s}\alpha \quad \psi_{3s}\beta \right| \\ \hat{J}^2 \left| \psi_{1s}\alpha \quad \psi_{1s}\beta \quad \psi_{2s}\alpha \quad \psi_{3s}\beta \right| &= \text{no eigenvalue} \left| \psi_{1s}\alpha \quad \psi_{1s}\beta \quad \psi_{2s}\alpha \quad \psi_{3s}\beta \right| \\ \hat{J}_z \left| \psi_{1s}\alpha \quad \psi_{1s}\beta \quad \psi_{2s}\alpha \quad \psi_{3s}\beta \right| &= 0 \left| \psi_{1s}\alpha \quad \psi_{1s}\beta \quad \psi_{2s}\alpha \quad \psi_{3s}\beta \right| \\ \hat{L}^2 \left| \psi_{2p_1}\alpha \quad \psi_{2p_1}\beta \right| &= 6\hbar^2 \left| \psi_{2p_1}\alpha \quad \psi_{2p_1}\beta \right| \quad (L = 2) \\ \hat{L}_z \left| \psi_{2p_1}\alpha \quad \psi_{2p_1}\beta \right| &= 2\hbar \left| \psi_{2p_1}\alpha \quad \psi_{2p_1}\beta \right| \quad (M_L = 2) \\ \hat{J}^2 \left| \psi_{2p_1}\alpha \quad \psi_{2p_1}\beta \right| &= 6\hbar^2 \left| \psi_{2p_1}\alpha \quad \psi_{2p_1}\beta \right| \quad (\text{Since } S=0, J = L = 2!) \\ \hat{J}_z \left| \psi_{2p_1}\alpha \quad \psi_{2p_1}\beta \right| &= 2\hbar \left| \psi_{2p_1}\alpha \quad \psi_{2p_1}\beta \right| \quad (M_J = M_L + M_S = 2)\end{aligned}$$

After graduation, you’ve decided to sell your services to the highest bidder. You have two job offers, each from groups that wish you to do quantum mechanics to help them in their quest for world domination. In order to satisfy your zeal for power and avoid the gulag, you’ll need to decide which of the following groups is most likely to rule the world, given that they plan to model materials use the Born-Oppenheimer approximation.

Name: “We put the ‘g’ in God”

Leaders: Bill “Blue Screen” Gates

Andy “The Genius” Grove

Slogan: “After installing this software you ~~may~~ *will* have to ~~reboot your~~ *buy a new* computer”

Weapon of Mass Destruction: Computer Hardware/Software

Materials of Interest: Silicon and Silicon oxides

Name: Franco-American Alliance for Cardiac Medicine

Leaders: Jacques “Crème Fraîche” Chirac

Dick “Replace your cooking oil with crude” Cheney

Slogan: “Would you like gravy with your fries?”

Weapon of Mass Destruction: Cholesterol/Fat

Materials of Interest: Fats; hydrocarbons.

20. You don’t want to wind up in the gulag. Based on what you know about the accuracy of the Born-Oppenheimer approximation, your best bet is to

(a) Model SiO₂ for the Gates/Grove cartel.

(b) Model oleanoic acid (C₃₀H₄₈O₃) for the Franco-American Alliance.

Part 2. Closed-Book Derivation

The following results may be helpful for this problem.

$$\begin{aligned} [\hat{S}_x, \hat{S}_y] &= i\hbar \hat{S}_z & [\hat{L}_x, \hat{L}_y] &= i\hbar \hat{L}_z \\ [\hat{S}_y, \hat{S}_z] &= i\hbar \hat{S}_x & [\hat{L}_y, \hat{L}_z] &= i\hbar \hat{L}_x \\ [\hat{S}_z, \hat{S}_x] &= i\hbar \hat{S}_y & [\hat{L}_z, \hat{L}_x] &= i\hbar \hat{L}_y \end{aligned}$$

You may also use 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 of the same type.

1a. Show that $[\hat{L}^2, \hat{J}_z] = 0$. (3 pts.)

$$\begin{aligned} [\hat{L}^2, \hat{J}_z] &= [\hat{L}^2, \hat{L}_z + \hat{S}_z] && \text{sub. in definition of } \hat{J}_z \\ [\hat{L}^2, \hat{J}_z] &= [\hat{L}^2, \hat{L}_z] + [\hat{L}^2, \hat{S}_z] && \left(\begin{array}{l} \text{the commutator of a sum is} \\ \text{the sum of the commutators} \end{array} \right) \\ [\hat{L}^2, \hat{J}_z] &= 0 + 0 && \left(\begin{array}{l} [\hat{L}^2, \hat{L}_z] = 0 \\ [\hat{L}^2, \hat{S}_z] = 0 \quad \left(\begin{array}{l} \text{spin and orb. ang.} \\ \text{mom. commute} \end{array} \right) \end{array} \right) \end{aligned}$$

1b. Show that $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ and \hat{J}_z commute. You may find it helpful to know that $[\hat{S}^2, \hat{J}_z] = 0$ for the same reason that $[\hat{L}^2, \hat{J}_z] = 0$. (7 pts.)

Remember that $\hat{J}^2 = \hat{\mathbf{L}} + \hat{\mathbf{S}} \cdot \hat{\mathbf{L}} + \hat{\mathbf{S}} = \hat{L}^2 + \hat{S}^2 + 2 \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$. So

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{1}{2} \hat{J}^2 - \hat{L}^2 - \hat{S}^2.$$

$$\begin{aligned} [\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}, \hat{J}_z] &= \left[\frac{1}{2} \hat{J}^2 - \hat{L}^2 - \hat{S}^2, \hat{J}_z \right] \\ &= \frac{1}{2} [\hat{J}^2, \hat{J}_z] - [\hat{L}^2, \hat{J}_z] - [\hat{S}^2, \hat{J}_z] \\ &= \frac{1}{2} 0 - 0 - 0 \end{aligned}$$

where the second two commutators are given in the statement of this problem.

Though a lot of quantum chemists think that they are off their proverbial rockers, inorganic chemists are constantly talking about the role of *d*-orbitals in the binding of the sulfur atom. In order for *d*-orbitals to be involved in bonding, of course, one must first “promote” electrons from the *p*-orbitals to the *d*-orbitals of the sulfur atom. This is my excuse for asking the following question. If you don’t like it, blame the inorganic chemists, not me....

- 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.)

We start with the p^3 part of the term symbol:

	M_L		
M_S	2	1	0
$\frac{3}{2}$			$ \psi_1\alpha \ \psi_0\alpha \ \psi_{-1}\alpha $
$\frac{1}{2}$	$ \psi_1\alpha \ \psi_1\beta \ \psi_0\alpha $	$ \psi_1\alpha \ \psi_0\alpha \ \psi_0\beta $ $ \psi_1\alpha \ \psi_0\alpha \ \psi_0\beta $	$ \psi_1\beta \ \psi_0\alpha \ \psi_{-1}\alpha $ $ \psi_1\alpha \ \psi_0\beta \ \psi_{-1}\alpha $ $ \psi_1\alpha \ \psi_0\alpha \ \psi_{-1}\beta $

Here the notation is that $\psi_{3p_{m_l}} \mathbf{r} = \psi_{m_l} \mathbf{r}$. Using the “color-coding” trick, we cross out terms to obtain, 4S , 2D , and 2P .

We now couple these states together with the *d* orbital:

$$\begin{aligned}
 ^4S &\xrightarrow{^2D} ^3D, ^5D \\
 ^2P &\xrightarrow{^2D} ^3F, ^3D, ^3P; ^1F, ^1D, ^1P \\
 ^2D &\xrightarrow{^2D} ^3G, ^3F, ^3D, ^3P, ^3S; ^1G, ^1F, ^1D, ^1P, ^1S
 \end{aligned}$$

Based on Hund’s rules, we’d predict energies in the order:

$$^5D, ^3G, ^2^3F, ^3^3D, ^2^3P, ^3S, ^1G, ^2^1F, ^2^2D, ^2^1P, ^1S$$

We would not expect the actual ordering to resemble this very much, except possibly at the low-energy end of this sequence.

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

$$\begin{aligned} J &= |L + S|, \dots |L - S| \\ &= |2 + 2|, \dots |2 - 2| \\ &= 4, 3, 2, 1, 0 \end{aligned}$$

2c. Write a Slater determinant that is associated with the lowest-energy term. You should use the “shorthand” notation for Slater determinants. (2 pts.)

$$\left| \psi_{1s}\alpha \quad \psi_{1s}\beta \quad \psi_{2s}\alpha \quad \psi_{2s}\beta \quad \psi_{2p_{-1}}\alpha \quad \psi_{2p_{-1}}\beta \quad \psi_{2p_0}\alpha \quad \psi_{2p_0}\beta \quad \psi_{2p_{+1}}\alpha \quad \psi_{2p_{+1}}\beta \quad \psi_{3s}\alpha \quad \psi_{3s}\beta \quad \psi_{3p_{-1}}\alpha \quad \psi_{3p_0}\alpha \quad \psi_{3p_{+1}}\alpha \quad \psi_{4d_{+2}}\alpha \right|$$

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.)

This is straight from the notes; it is 1P .

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

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

What follows is what I think is the easiest way to do this; there are many ways to do it, though.

Start by rewriting the Schrödinger equation as

$$\begin{aligned} -\frac{\nabla^2}{2} - \frac{Z}{r} \psi_{n,l,m}(\mathbf{r}) &= -\frac{Z^2}{2n^2} \psi_{n,l,m}(\mathbf{r}) \\ -\frac{\nabla^2}{2Z} - \frac{1}{r} \psi_{n,l,m}(\mathbf{r}) &= -\frac{Z}{2n^2} \psi_{n,l,m}(\mathbf{r}) \end{aligned}$$

and introduce the new coordinate, $\lambda = \frac{1}{Z}$, so that

$$-\lambda \frac{\nabla^2}{2} - \frac{1}{r} \psi_{n,l,m}(\mathbf{r}) = -\frac{1}{2\lambda n^2} \psi_{n,l,m}(\mathbf{r})$$

The “energy” in this equation is $-\frac{1}{2\lambda n^2}$ and so, from the Hellmann-Feynman theorem,

$$\begin{aligned} \frac{\partial E}{\partial \lambda} &= \left\langle \psi_{n,l,m} \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \psi_{n,l,m} \right\rangle \\ \frac{\partial}{\partial \lambda} \left(-\frac{1}{2\lambda n^2} \right) &= \left\langle \psi_{n,l,m} \left| \frac{\partial}{\partial \lambda} \left(-\lambda \frac{\nabla^2}{2} - \frac{1}{r} \right) \right| \psi_{n,l,m} \right\rangle \\ \frac{1}{2\lambda^2 n^2} &= \left\langle \psi_{n,l,m} \left| -\frac{\nabla^2}{2} \right| \psi_{n,l,m} \right\rangle \end{aligned}$$

Now we substitute in $Z = \frac{1}{\lambda}$ to obtain

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

3b. Using the fact that

$$\langle \psi_{n,l,m} | r^2 | \psi_{n,l,m} \rangle = \frac{n^2}{2Z^2} (5n^2 - 3l(l+1) + 1)$$

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

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

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

Because the average position of an electron in the hydrogen atom is at the nucleus (that is, there is no greater likelihood for the electron to be on the “right side” of the nucleus than on the “left side” of the nucleus, $\langle \mathbf{r} \rangle = 0$). Similarly, $\langle \hat{\mathbf{p}} \rangle = 0$ because there is no net momentum of the hydrogen atom; the hydrogen atom is assumed to be still (with the nucleus fixed at the origin). We have, then, that

$$\left[\sqrt{\langle \psi_{n,l,m} | \hat{\mathbf{p}} \cdot \hat{\mathbf{p}} | \psi_{n,l,m} \rangle - 0} \sqrt{\langle \psi_{n,l,m} | \mathbf{r} \cdot \mathbf{r} | \psi_{n,l,m} \rangle - 0} \right] \geq \frac{\hbar}{2}$$

Next, consider that $T = \langle \psi_{n,l,m} | -\frac{\nabla^2}{2} | \psi_{n,l,m} \rangle = \langle \frac{p^2}{2} \rangle$ and use the result of 3a to obtain

$$\frac{Z^2}{n^2} = \langle \psi_{n,l,m} | \hat{\mathbf{p}} \cdot \hat{\mathbf{p}} | \psi_{n,l,m} \rangle$$

Substitute this and the equation in the question into the Heisenberg uncertainty relation, and so

$$\begin{aligned} \left[\sqrt{\langle \psi_{n,l,m} | \hat{\mathbf{p}} \cdot \hat{\mathbf{p}} | \psi_{n,l,m} \rangle - 0} \sqrt{\langle \psi_{n,l,m} | \mathbf{r} \cdot \mathbf{r} | \psi_{n,l,m} \rangle - 0} \right] &\geq \frac{\hbar}{2} \\ \sqrt{\frac{Z^2}{n^2} \frac{n^2}{2Z^2} (5n^2 - 3l(l+1) + 1)} &\geq \frac{\hbar}{2} \\ \sqrt{\frac{1}{2} (5n^2 - 3l(l+1) + 1)} &\geq \frac{\hbar}{2} \end{aligned}$$

We want to show that this inequality always holds; recall that $\hbar = 1$ in atomic units. We have

$$\begin{aligned} \sqrt{\frac{1}{2} (5n^2 - 3l(l+1) + 1)} &\geq \frac{\hbar}{2} \\ \sqrt{\frac{1}{2} (5n^2 - 3l(l+1) + 1)} &\geq \frac{1}{2} \\ \frac{1}{2} (5n^2 - 3l(l+1) + 1) &\geq \frac{1}{4} \\ 5n^2 - 3l(l+1) + 1 &\geq \frac{1}{2} \\ 5n^2 - 3l(l+1) &\geq -\frac{1}{2} \end{aligned}$$

This inequality is obviously satisfied when $l = 0$, for example. The left-hand-side of this equation is smallest when the second term is as large as possible, which means that if the inequality is ever violated, it will be when $l = n - 1$, since that is the largest possible value of n . We have, then, that

$$\begin{aligned} 5n^2 - 3n - 1 &\geq -\frac{1}{2} \\ 5n^2 - 3n^2 + 3n &\geq -\frac{1}{2} \\ 2n^2 + 3n &\geq -\frac{1}{2} \end{aligned}$$

This is obviously true, since $n \geq 1 > 0$.

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.

1. Concavity of the Energy.

The total energy of a system clearly depends on the Hamiltonian, and so we can say that the energy is a functional of the Hamiltonian, $E[\hat{H}]$. Suppose the Hamiltonian for a system can be written as the sum of two Hamiltonians,

$$\hat{H}_{AB} = \hat{H}_A + \hat{H}_B$$

(a) Show that the ground state energy for the whole system “**AB**” is greater than the sum of the ground state energies of the two subsystems, “**A**” and “**B**”. That is, (8 pts.)

$$E[\hat{H}_{AB}] \geq E[\hat{H}_A] + E[\hat{H}_B]$$

This is a straightforward application of the variational principle. Let Ψ_{AB} denote the ground state eigenfunction for \hat{H}_{AB} , Ψ_A denote the ground state eigenfunction for \hat{H}_A , and Ψ_B denote the ground-state eigenfunction for Ψ_B . From the variational principle, we have that

$$\begin{aligned}\langle \Psi_A | \hat{H}_A | \Psi_A \rangle &\leq \langle \Psi_{AB} | \hat{H}_A | \Psi_{AB} \rangle \\ \langle \Psi_B | \hat{H}_B | \Psi_B \rangle &\leq \langle \Psi_{AB} | \hat{H}_B | \Psi_{AB} \rangle\end{aligned}$$

Adding the two inequalities together we have

$$\begin{aligned}\langle \Psi_A | \hat{H}_A | \Psi_A \rangle + \langle \Psi_B | \hat{H}_B | \Psi_B \rangle &\leq \langle \Psi_{AB} | \hat{H}_A + \hat{H}_B | \Psi_{AB} \rangle \\ \langle \Psi_A | \hat{H}_A | \Psi_A \rangle + \langle \Psi_B | \hat{H}_B | \Psi_B \rangle &\leq \langle \Psi_{AB} | \hat{H}_{AB} | \Psi_{AB} \rangle \\ E[\hat{H}_A] + E[\hat{H}_B] &\leq E[\hat{H}_{AB}]\end{aligned}$$

(b) When is this relationship an equality, instead of an inequality? That is, when is

$$E[\hat{H}_{AB}] = E[\hat{H}_A] + E[\hat{H}_B]?$$

(2 pts.)

This relationship is an equality if and only if Ψ_{AB} is a ground-state eigenfunction for both \hat{H}_A and \hat{H}_B . (This essentially never happens in practice, since it can only happen in certain “limiting” cases)

2. Show why each of the following results is true (5 pts total; 1 pt. each)

(a) The ground state energy of the Lithium cation is less than the three times the energy of the hydride anion.

$$E_{Li^+} < 3E_{H^-}$$

$$\begin{aligned} 3E_{H^-} &= \left\langle \Psi_{H^-} \left| 3 \left(\frac{-\nabla_1^2}{2} + \frac{-\nabla_2^2}{2} - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{|r_1 - r_2|} \right) \right| \Psi_{H^-} \right\rangle \\ &= \left\langle \Psi_{H^-} \left| \frac{-\nabla_1^2}{2} + \frac{-\nabla_2^2}{2} - \frac{3}{r_1} - \frac{3}{r_2} + \frac{1}{|r_1 - r_2|} \right| \Psi_{H^-} \right\rangle + 2 \left\langle \Psi_{H^-} \left| \frac{-\nabla_1^2}{2} + \frac{-\nabla_2^2}{2} + \frac{1}{|r_1 - r_2|} \right| \Psi_{H^-} \right\rangle \end{aligned}$$

The second term is positive because the kinetic energy $T = \left\langle \frac{p^2}{2m} \right\rangle$ and the electron-electron repulsion energy is positive. If we omit this positive term, we have

$$3E_{H^-} > \left\langle \Psi_{H^-} \left| \frac{-\nabla_1^2}{2} + \frac{-\nabla_2^2}{2} - \frac{3}{r_1} - \frac{3}{r_2} + \frac{1}{|r_1 - r_2|} \right| \Psi_{H^-} \right\rangle$$

The variational principle then implies that

$$\left\langle \Psi_{H^-} \left| \frac{-\nabla_1^2}{2} + \frac{-\nabla_2^2}{2} - \frac{3}{r_1} - \frac{3}{r_2} + \frac{1}{|r_1 - r_2|} \right| \Psi_{H^-} \right\rangle > \left\langle \Psi_{Li^+} \left| \frac{-\nabla_1^2}{2} + \frac{-\nabla_2^2}{2} - \frac{3}{r_1} - \frac{3}{r_2} + \frac{1}{|r_1 - r_2|} \right| \Psi_{Li^+} \right\rangle$$

where Ψ_{Li^+} is the ground-state wavefunction for the Lithium cation.

Consequently, we have that

$$3E_{H^-} > E_{Li^+}$$

(b) Twice ground state energy of the Lithium cation is less than the three times the energy of the Helium atom.

$$2E_{Li^+} < 3E_{He}$$

$$\begin{aligned} \frac{3}{2} E_{He} &= \left\langle \Psi_{He} \left| \frac{3}{2} \left(\frac{-\nabla_1^2}{2} + \frac{-\nabla_2^2}{2} - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{|r_1 - r_2|} \right) \right| \Psi_{He} \right\rangle \\ &= \left\langle \Psi_{He} \left| \frac{-\nabla_1^2}{2} + \frac{-\nabla_2^2}{2} - \frac{3}{r_1} - \frac{3}{r_2} + \frac{1}{|r_1 - r_2|} \right| \Psi_{He} \right\rangle + \frac{1}{2} \left\langle \Psi_{He} \left| \frac{-\nabla_1^2}{2} + \frac{-\nabla_2^2}{2} + \frac{1}{|r_1 - r_2|} \right| \Psi_{He} \right\rangle \end{aligned}$$

The second term is positive because the kinetic energy $T = \left\langle \frac{p^2}{2m} \right\rangle$ and the electron-electron repulsion energy is positive. If we omit this positive term, we have

$$\frac{3}{2} E_{He} > \left\langle \Psi_{He} \left| \frac{-\nabla_1^2}{2} + \frac{-\nabla_2^2}{2} - \frac{3}{r_1} - \frac{3}{r_2} + \frac{1}{|r_1 - r_2|} \right| \Psi_{He} \right\rangle$$

Just as in part (a), we then use the variational principle to infer that

The variational principle then implies that

$$\begin{aligned} \frac{3}{2} E_{He} &> \left\langle \Psi_{He} \left| \frac{-\nabla_1^2}{2} + \frac{-\nabla_2^2}{2} - \frac{3}{r_1} - \frac{3}{r_2} + \frac{1}{|r_1 - r_2|} \right| \Psi_{He} \right\rangle \\ &> \left\langle \Psi_{Li^+} \left| \frac{-\nabla_1^2}{2} + \frac{-\nabla_2^2}{2} - \frac{3}{r_1} - \frac{3}{r_2} + \frac{1}{|r_1 - r_2|} \right| \Psi_{Li^+} \right\rangle = E_{Li^+} \end{aligned}$$

(c) The ground state energy of the Lithium cation is less than the sum of the energies of the Helium atom and the hydride anion.

$$E_{Li^+} < E_{H^-} + E_{He}$$

Adding together results from (a) and (c) we have

$$\begin{aligned} E_{Li^+} &< 3E_{H^-} \\ 2E_{Li^+} &< 3E_{He} \\ 3E_{Li^+} &< 3E_{H^-} + 3E_{He} \\ E_{Li^+} &< E_{H^-} + E_{He} \end{aligned}$$

(d) The ground state energy of the Lithium cation is less than the sum of the energies of the Helium atom and the hydrogen atom.

$$E_{Li^+} < E_H + E_{He}$$

Because the hydride ion exists, it must have lower energy than hydrogen. (Otherwise the hydride anion would spontaneously dissociate to a hydrogen atom and a free electron.) Using $E_{H^-} < E_H$ in the result from part (c), we have

$$E_{Li^+} < E_{H^-} + E_{He} < E_H + E_{He}$$

(e) The ground state energy of the Lithium atom is less than the sum of the ground state energies of the Helium atom and the Hydrogen atom.

$$E_{Li} < E_H + E_{He}$$

Because the Lithium atom exists, it must have lower energy than Li^+ . (Otherwise Li would spontaneously dissociate to Li^+ and a free electron.) Using $E_{Li} < E_{Li^+}$ in the result from part (d), we have

$$E_{Li} < E_{Li^+} < E_H + E_{He}$$

which gives us the desired result.

As we began our discussion of diatomic molecules, we talked about the united-atom limit (where the two atoms were placed on top of each other) and the separated atom limit (where the two atoms were infinitely far apart). The ground-state electronic energy in the united atom limit is always less than the ground state electronic energy in the separated atom limit. (The nuclear-nuclear repulsion energy is not included in the united-atom limit, because it would be infinite.) We could now prove this in the general case, but let us instead try just a special case:

- (f) **The ground-state energy of the Boron atom is less than the sum of the ground-state energies of the Lithium and Helium atoms. That is,**

$$E_B < E_{Li} + E_{He}$$

(2 pts.)

The analogue of **(a)** and **(b)** lets us assert that

$$3E_B < 5E_{Li^{-2}}$$

$$2E_B < 5E_{He^{-3}}$$

The Lithium dianion and Helium trianion are fictitious atoms but, corresponding to the inequalities in part **(d)** we have

$$E_{Li^{-2}} = E_{Li^-} < E_{Li}$$

$$E_{He^{-3}} = E_{He^{-2}} = E_{He^{-1}} = E_{He}$$

and so

$$3E_B < 5E_{Li^{-2}} < 5E_{Li}$$

$$2E_B < 5E_{He^{-3}} = 5E_{He}$$

Adding together these inequalities gives

$$5E_B < 5E_{Li} + 5E_{He}$$

$$E_B < E_{Li} + E_{He}$$

which is what we were trying to show.

It is a general principle that the energies of the atoms decrease faster than linearly. That is, the energy of the atoms is a concave function of the atomic number, Z . In practical terms, this means that the change in energy between an atom and the entry in the periodic table that precedes it is less than the change in energy that same atom and the entry in the periodic table that follows it. We will now show this for a special case.

(g) Show that

$$E_B - E_C > E_{Be} - E_B$$

(3 pts.)

Start by writing the Hamiltonian of the Boron atom, and then separate it into two parts so that we can use the result in part 1 of this problem.

$$\begin{aligned}\hat{H}_B &= \sum_{i=1}^5 \frac{-\nabla_i^2}{2} + \sum_{i=1}^4 \sum_{j=i+1}^5 \frac{1}{|r_i - r_j|} + \sum_{i=1}^5 \frac{-5}{r_i} \\ &= \sum_{i=1}^5 \frac{-\nabla_i^2}{2} + \sum_{i=1}^4 \sum_{j=i+1}^5 \frac{1}{|r_i - r_j|} + \sum_{i=1}^5 \frac{-2}{r_i} + \sum_{i=1}^5 \frac{-3}{r_i} \\ &= \frac{1}{2} \left(\sum_{i=1}^5 \frac{-\nabla_i^2}{2} + \sum_{i=1}^4 \sum_{j=i+1}^5 \frac{1}{|r_i - r_j|} \right) + \sum_{i=1}^5 \frac{-2}{r_i} \\ &\quad + \frac{1}{2} \left(\sum_{i=1}^5 \frac{-\nabla_i^2}{2} + \sum_{i=1}^4 \sum_{j=i+1}^5 \frac{1}{|r_i - r_j|} \right) + \sum_{i=1}^5 \frac{-3}{r_i} \\ &= \frac{1}{2} \left(\sum_{i=1}^5 \frac{-\nabla_i^2}{2} + \sum_{i=1}^4 \sum_{j=i+1}^5 \frac{1}{|r_i - r_j|} + \sum_{i=1}^5 \frac{-4}{r_i} \right) \\ &\quad + \frac{1}{2} \left(\sum_{i=1}^5 \frac{-\nabla_i^2}{2} + \sum_{i=1}^4 \sum_{j=i+1}^5 \frac{1}{|r_i - r_j|} + \sum_{i=1}^5 \frac{-6}{r_i} \right) \\ &= \frac{1}{2} (\hat{H}_{Be^-} + \hat{H}_{C^+})\end{aligned}$$

Using the result from part 1, we have that

$$E[\hat{H}_B] > E\left[\frac{1}{2} \hat{H}_{Be^-}\right] + E\left[\frac{1}{2} \hat{H}_{C^+}\right]$$

where \hat{H}_{Be^-} is the Hamiltonian of the Beryllium anion and \hat{H}_{C^+} is the Hamiltonian of the carbon cation. The energies one obtains are then

$$E_B > \frac{1}{2} E_{Be^-} + E_{C^+}$$

The Beryllium anion does not exist since the Beryllium atom has zero electron affinity; $E_{Be^-} = E_{Be}$. The energy of the carbon atom is less than the energy of the carbon cation, so $E_C < E_{C^+}$. Substituting in these results yields

$$\begin{aligned}E_B &> \frac{1}{2} E_{Be} + E_C \\ 2E_B &> E_{Be} + E_C \\ E_B - E_C &> E_{Be} - E_B\end{aligned}$$