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Quiz 3

Chemistry 3BB3; Winter 2003

In this problem set, you may assume that the Born-Oppenheimer assumption is made. You may use atomic units except where instructed otherwise.

1. Sketch the dependence of the effective nuclear charge of the Lithium atom versus the distance from the nucleus. Make sure you label the values of the effective nuclear charge at $r = 0$ and as $r \rightarrow \infty$.
2. Write a Slater determinantal wave function that approximates the ground state of the Boron atom. Assume the 2p electron is in the $2p_z$ orbital.
3. Why do the 2p orbitals fill after the 2s orbitals. That is, why is the electron configuration of Be $1s^2 2s^2$ instead of $1s^2 2p^2$ or $1s^2 2s^1 2p^1$? (The answer should be in words, but it can be very brief. WRITE NEATLY!!)

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4. If the orbitals in the Slater determinant, Φ_B , in problem 2 are orthonormal, what is normalization factor? That is, what constant, A_B , must one multiply the Slater determinant by in order to ensure that $\Psi_B = A\Phi_B$ is normalized?

5. Suppose you evaluated the energy of the Slater determinant in problem 2,

$$E_{\#2} = \frac{\langle \Phi_B | \hat{H}_{Boron} | \Phi_B \rangle}{\langle \Phi_B | \Phi_B \rangle} \quad (4.1)$$

The energy from Eq. (4.1), $E_{\#2}$, is

- (a) Less than the true ground state energy of the Boron atom
 - (b) Equal to the true ground state energy of the Boron atom
 - (c) Greater than the true ground state energy of the Boron atom
6. The orbitals in the Slater determinant from problem two can be generalized by expanding them in terms of Slater functions. Thus, we can write the P^{th} orbital with orbital angular momentum quantum number L and magnetic quantum number M , as

$$\psi^{(P,L,M)}(\mathbf{r}) \equiv \left(\sum_{i=1}^{\infty} \sum_{n=L+1}^{\infty} k_{i,n}^{(P,L,M)} r^n e^{-\zeta_{i,n}r} \right) Y_L^M(\theta, \phi) \quad (5.1)$$

Any orbital can be expressed *exactly* in the form (5.1), provided the series contain an infinite number of terms. Suppose you write each orbital in your Slater determinant in problem 2 in the form of Eq. (5.1). Then you choose the free parameters in Eq. (5.1) ($k_{i,n}^{(P,L,M)}$ and $\zeta_{i,n}$) so the energy of the Slater determinant in Eq. (4.1) is as small as possible. Define the energy from this procedure as,

$$E_{\#5} = \min_{\{k_{i,n}^{(P,L,M)}, \zeta_{i,n}\}_{i,n}} \frac{\langle \Phi_B | \hat{H}_{Boron} | \Phi_B \rangle}{\langle \Phi_B | \Phi_B \rangle}. \quad (5.2)$$

The energy from Eq. (5.2), $E_{\#5}$, is

- (a) Less than the true ground state energy of the Boron atom
 - (b) Equal to the true ground state energy of the Boron atom
 - (c) Greater than the true ground state energy of the Boron atom
7. Using separation of variables, write the Schrödinger equation for the radial wave function of the one-electron atom with atomic number Z . Do not use atomic units.
8. Below, there is a formula for the radial component of the wave function for the 4f orbital of the one-electron atom with atomic number Z . Fill in the missing constants (denoted by []). A_{4f} is the normalization factor.

$$R_{4f}(r) = A_{4f} \cdot r^{| \quad |} e^{[\quad]} |r$$

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9. Which of the following “Cartesian” orbitals can be written as the product of a radial factor and a spherical harmonic, $\phi(r) = R_{n,l}(r)Y_l^m(\theta, \phi)$? (There may be more than one answer, so you should circle EACH of the orbitals for which this is true!)

- | | | |
|-----------------------|---------------------------------|--------------------------------------|
| (a) $2p_x$ orbital | (f) $3d_{x^2-y^2}$ orbital | (j) $4f_{z(x^2-y^2)}$ orbital |
| (b) $2p_y$ orbital | (g) $3d_{2z^2-x^2-y^2}$ orbital | (k) $4f_{z(2z^2-3x^2-3y^2)}$ orbital |
| (c) $2p_z$ orbital | (h) $4f_{x(x^2-3y^2)}$ orbital | (l) $4f_{x(4z^2-x^2-y^2)}$ orbital |
| (d) $3d_{xy}$ orbital | (i) $4f_{xyz}$ orbital | |
| (e) $3d_{xz}$ orbital | | |

10. When measuring the NMR spectrum of a molecule, one is essentially measuring the difference in energy between two spin-states of a nucleus in the magnetic field. For a field of magnitude 14 Tesla, transitions between the spin-states of the proton are induced by photons with a frequency of about 600 million Hz $\left(= 6.0 \cdot 10^8 \frac{1}{s}\right)$. The energy of the photons is the same as the difference of energy between the two spin-states of the proton. We deduce that the difference in energy between the spin-states of the proton is thus
- (a) much smaller than the atomic unit of energy.
 - (b) much larger than the atomic unit of energy.
 - (c) about the same size as the atomic unit of energy.

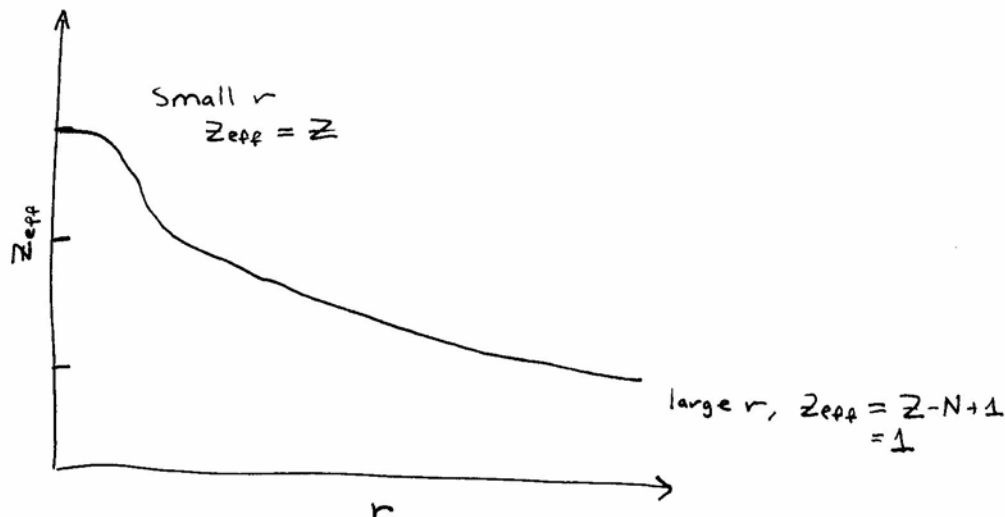
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2. Write a Slater determinantal wave function that approximates the ground state of the Boron atom. Assume the 2p electron is in the $2p_z$ orbital.

$$\Phi_B \equiv \begin{vmatrix} \psi_{1s}(\mathbf{r}_1)\alpha(1) & \psi_{1s}(\mathbf{r}_1)\beta(1) & \psi_{2s}(\mathbf{r}_1)\alpha(1) & \psi_{2s}(\mathbf{r}_1)\beta(1) & \psi_{2p_z}(\mathbf{r}_1)\alpha(1) \\ \psi_{1s}(\mathbf{r}_2)\alpha(2) & \psi_{1s}(\mathbf{r}_2)\beta(2) & \psi_{2s}(\mathbf{r}_2)\alpha(2) & \psi_{2s}(\mathbf{r}_2)\beta(2) & \psi_{2p_z}(\mathbf{r}_2)\alpha(2) \\ \psi_{1s}(\mathbf{r}_3)\alpha(3) & \psi_{1s}(\mathbf{r}_3)\beta(3) & \psi_{2s}(\mathbf{r}_3)\alpha(3) & \psi_{2s}(\mathbf{r}_3)\beta(3) & \psi_{2p_z}(\mathbf{r}_3)\alpha(3) \\ \psi_{1s}(\mathbf{r}_4)\alpha(4) & \psi_{1s}(\mathbf{r}_4)\beta(4) & \psi_{2s}(\mathbf{r}_4)\alpha(4) & \psi_{2s}(\mathbf{r}_4)\beta(4) & \psi_{2p_z}(\mathbf{r}_4)\alpha(4) \\ \psi_{1s}(\mathbf{r}_5)\alpha(5) & \psi_{1s}(\mathbf{r}_5)\beta(5) & \psi_{2s}(\mathbf{r}_5)\alpha(5) & \psi_{2s}(\mathbf{r}_5)\beta(5) & \psi_{2p_z}(\mathbf{r}_5)\alpha(5) \end{vmatrix}$$

3. Why do the 2p orbitals fill after the 2s orbitals. That is, why is the electron configuration of Be $1s^2 2s^2$ instead of $1s^2 2p^2$ or $1s^2 2s^1 2p^1$? (The answer should be in words, but it can be very brief. WRITE NEATLY!!)

The essential argument is clear from the answer in question 1. The 2s-orbital is “shielded” from the nucleus less than the 2p-orbital because the 2s-orbital has some density in the immediate vicinity of the nucleus, while the 2p orbital does not (the 2p-orbital density is zero at the nucleus and, owing to the fact the orbital density grows as $(Zr)^2$ near the nucleus, has very little density until $r \approx \frac{1}{Z}$). The “key words” are “orbital shielding” and/or the fact that the “effective nuclear charge” of the 2s orbital is less than that of the 2p orbital.

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4. If the orbitals in the Slater determinant, Φ_B , in problem 2 are orthonormal, what is normalization factor? That is, what constant, A_B , must one multiply the Slater determinant by in order to ensure that $\Psi_B = A\Phi_B$ is normalized?

The normalization factor is, in general, $\frac{1}{\sqrt{N!}}$, where N is the number of electrons. For Boron, this is $\frac{1}{\sqrt{5!}} = \frac{1}{\sqrt{120}}$.

5. Suppose you evaluated the energy of the Slater determinant in problem 2,

$$E_{\#2} = \frac{\langle \Phi_B | \hat{H}_{\text{Boron}} | \Phi_B \rangle}{\langle \Phi_B | \Phi_B \rangle} \quad (4.1)$$

The energy from Eq. (4.1), $E_{\#2}$, is

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7. Using separation of variables, write the Schrödinger equation for the radial wave function of the one-electron atom with atomic number Z . Do not use atomic units.
- $$\left(-\frac{\hbar^2}{2m_e} \left(\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{l(l+1)}{r^2} \right) - \frac{Ze^2}{4\pi\epsilon_0 r} \right) R_{n,l}(r) = E_n R_{n,l}(r)$$
8. Below, there is a formula for the radial component of the wave function for the 4f orbital of the one-electron atom with atomic number Z . Fill in the missing constants (denoted by []). A_{4f} is the normalization factor.

$$R_{4f}(r) = A_{4f} \cdot r^3 \left[e^{\left[\frac{-Z}{4} \right] r} \right]$$

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9. Which of the following “Cartesian” orbitals can be written as the product of a radial factor and a spherical harmonic, $\phi(r) = R_{n,l}(r)Y_l^m(\theta, \phi)$? (There may be more than one answer, so you should circle EACH of the orbitals for which this is true!)

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