

Quiz 2

Chemistry 3BB3; Winter 2004

1. Write the electronic Schrödinger Equation for the Lithium atom in SI units, showing the dependence on \hbar , e , ε_0 , and m_e . You may use the Born-Oppenheimer approximation.
2. Write a Slater determinant wave function for the $1s^2 2s^2$ state of the Beryllium atom. Do not use the “shorthand” notation. Denote the spatial part of the 1s orbital with $\psi_{1s}(\mathbf{r})$ and the spatial part of the 2s orbital with $\psi_{2s}(\mathbf{r})$.

Suppose we take the Slater determinant in part two (denoted Φ_{Be} in this problem) and minimize the energy of this determinant over all possible choices of the orbitals, $\psi_{1s}(\mathbf{r})$ and $\psi_{2s}(\mathbf{r})$:

$$E_{approx} \equiv \min_{\psi_{1s}, \psi_{2s}} \frac{\langle \Phi_{Be} | \hat{H} | \Phi_{Be} \rangle}{\langle \Phi_{Be} | \Phi_{Be} \rangle} \quad (1)$$

3. This is called the _____ approximation.

(a) Hylleraas	(d) Slater
(b) Hartree	(e) naked charge
(c) Hartree-Fock	(f) hydrogenic
4. The energy from Eq. (1), E_{approx} , is _____ than the exact energy of the Beryllium atom.

(a) greater than	(c) equal to
(b) less than	

Name:

Using separation of variables, the wave function for the hydrogen atom can be written as

$$\Psi_{n,l,m}(\mathbf{r}) = R_{n,l}(r) Y_l^m(\theta, \phi).$$

5. Write the Schrödinger equation for radial wave function, $R_{n,l}(r)$, in the hydrogen atom. You may use atomic units.
6. Suppose $l = 5$. What is the energy of the lowest-energy state. You may use atomic units.
7. For which of the following systems is the Born-Oppenheimer approximation most justified? In other words, neglecting all other effects, for which system do you expect corrections to the Born-Oppenheimer approximation will be least important.
- (a) F_2 (c) HI
(b) HF (d) I_2
8. Sketch the effective nuclear charge as a function of distance for the Boron atom. Carefully label the value of the effective nuclear charge at the nucleus and infinitely far from the nucleus.
9. Is $\Psi(\mathbf{r}_1, \sigma(1), \mathbf{r}_2, \sigma(2)) \propto e^{-\zeta r_1} e^{-\zeta r_2} (1 + b|\mathbf{r}_1 - \mathbf{r}_2| + c|\mathbf{r}_1 - \mathbf{r}_2|^2)(\alpha(1)\beta(2) + \alpha(2)\beta(1))$ an acceptable approximate wave function for the Helium atom?
- (a) yes (b) no
10. Number the following quantities in order of *increasing* energy. (That is, put “1” next to the smallest quantity of energy, “2” next to the next smallest, etc.)

_____ 1 Hartree

_____ 1 electron volt

_____ 1 kJ/mol

_____ 1 cm^{-1}

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1. Write the electronic Schrödinger Equation for the Lithium atom in SI units, showing the dependence on \hbar , e , ϵ_0 , and m_e . You may use the Born-Oppenheimer approximation.

$$\left(\sum_{i=1}^3 \left(-\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{3e^2}{4\pi\epsilon_0 r_i} \right) + \sum_{i=1}^3 \sum_{j=i+1}^3 \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \right) \Psi(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; \mathbf{r}_3, \sigma_3) = E \Psi(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; \mathbf{r}_3, \sigma_3)$$

Here the nucleus is chosen to be at the origin.

2. Write a Slater determinant wave function for the $1s^2 2s^2$ state of the Beryllium atom. Do not use the “shorthand” notation. Denote the spatial part of the 1s orbital with $\psi_{1s}(\mathbf{r})$ and the spatial part of the 2s orbital with $\psi_{2s}(\mathbf{r})$

$$\Psi(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; \mathbf{r}_3, \sigma_3; \mathbf{r}_4, \sigma_4) = \frac{1}{\sqrt{4!}} \begin{vmatrix} \psi_{1s}(\mathbf{r}_1)\alpha(1) & \psi_{1s}(\mathbf{r}_1)\beta(1) & \psi_{2s}(\mathbf{r}_1)\alpha(1) & \psi_{2s}(\mathbf{r}_1)\beta(1) \\ \psi_{1s}(\mathbf{r}_2)\alpha(2) & \psi_{1s}(\mathbf{r}_2)\beta(2) & \psi_{2s}(\mathbf{r}_2)\alpha(2) & \psi_{2s}(\mathbf{r}_2)\beta(2) \\ \psi_{1s}(\mathbf{r}_3)\alpha(3) & \psi_{1s}(\mathbf{r}_3)\beta(3) & \psi_{2s}(\mathbf{r}_3)\alpha(3) & \psi_{2s}(\mathbf{r}_3)\beta(3) \\ \psi_{1s}(\mathbf{r}_4)\alpha(4) & \psi_{1s}(\mathbf{r}_4)\beta(4) & \psi_{2s}(\mathbf{r}_4)\alpha(4) & \psi_{2s}(\mathbf{r}_4)\beta(4) \end{vmatrix}$$

Suppose we take the Slater determinant in part two (denoted Φ_{Be} in this problem) and minimize the energy of this determinant over all possible choices of the orbitals, $\psi_{1s}(\mathbf{r})$ and $\psi_{2s}(\mathbf{r})$:

$$E_{approx} \equiv \min_{\psi_{1s}, \psi_{2s}} \frac{\langle \Phi_{Be} | \hat{H} | \Phi_{Be} \rangle}{\langle \Phi_{Be} | \Phi_{Be} \rangle} \quad (1)$$

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(e) naked charge
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(c) Hartree-Fock

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- (a) greater than**
(b) less than

- (c) equal to

Name:

Using separation of variables, the wave function for the hydrogen atom can be written as

$$\Psi_{n,l,m}(\mathbf{r}) = R_{n,l}(r) Y_l^m(\theta, \phi).$$

5. Write the Schrödinger equation for radial wave function, $R_{n,l}(r)$, in the hydrogen atom. You may use atomic units.

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

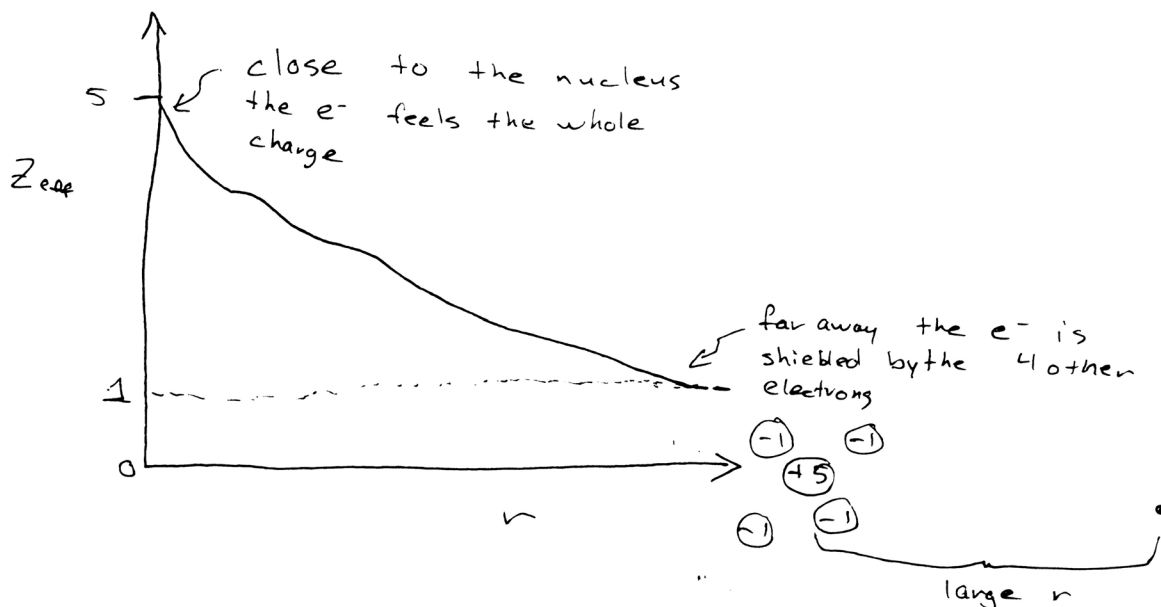
6. Suppose $l = 5$. What is the energy of the lowest-energy state. You may use atomic units.

$$E = \frac{-Z^2}{2n^2} \text{ where } n \geq l + 1. \text{ The lowest energy state is when } n = l + 1 = 6 \text{ which gives } E = \frac{-Z^2}{2 \cdot 6^2} = \frac{-Z^2}{72}$$

7. For which of the following systems is the Born-Oppenheimer approximation most justified? In other words, neglecting all other effects, for which system do you expect corrections to the Born-Oppenheimer approximation will be least important.

- (a) F_2 (c) HI
(b) HF (d) I_2

8. Sketch the effective nuclear charge as a function of distance for the Boron atom. Carefully label the value of the effective nuclear charge at the nucleus and infinitely far from the nucleus.



9. Is $\Psi(\mathbf{r}_1, \sigma(1), \mathbf{r}_2, \sigma(2)) \propto e^{-\zeta r_1} e^{-\zeta r_2} (1 + b|\mathbf{r}_1 - \mathbf{r}_2| + c|\mathbf{r}_1 - \mathbf{r}_2|^2)(\alpha(1)\beta(2) + \alpha(2)\beta(1))$ an acceptable approximate wave function for the Helium atom?

- (a) yes (b) no

This wave function for the Helium atom is not antisymmetric with respect to the exchange of the electrons. It violates the Pauli-exclusion principle.

10. Number the following quantities in order of *increasing* energy. (That is, put "1" next to the smallest quantity of energy, "2" next to the next smallest, etc.)

_____4_____ 1 Hartree

_____3_____ 1 electron volt

_____2_____ 1 kJ/mol

_____1_____ 1 cm⁻¹

Name: