Chem 332: Problem Set #8

Due in class, Friday, April 5

(1) Write out the full hamiltonian for the Be atom. Use SI units and explicitly expand all summations. You do not need to expand the Laplacian operators.

(2) Which of the following are valid wavefunctions for He? Justify your results and ignore normalization.

(a) 1s(1)2s(2)[α(1)β(2) – β(1)α(2)]

(b) [1s(1)2s(1) – 2s(1)1s(1)]α(1)α(2)

(c) [1s(1)2s(2) – 2s(1)1s(2)][α(1)β(2) – β(1)α(2)]

(d) 1s(1)2s(2)α(1)β(2) – 2s(1)1s(2)β(1)α(2) + 1s(1)2s(2)β(1)α(2) – 2s(1)1s(2)α(1)β(2)

(3) The operator for the square of the total spin angular momentum of <u>two</u> electrons is given by

$$\hat{S}^2 = \left(\hat{s}_1 + \hat{s}_2\right)^2 = \hat{s}_1^2 + \hat{s}_2^2 + 2\left(\hat{s}_{1x}\hat{s}_{2x} + \hat{s}_{1y}\hat{s}_{2y} + \hat{s}_{1z}\hat{s}_{2z}\right)$$

Given that

$$\hat{s}_{ix}\alpha(i) = \frac{\hbar}{2}\beta(i) \qquad \hat{s}_{iy}\alpha(i) = \frac{i\hbar}{2}\beta(i) \qquad \hat{s}_{iz}\alpha(i) = \frac{\hbar}{2}\alpha(i)$$

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Show that α(1)α(2) and β(1)β(2) are each eigenfunctions of the operator S^2. What is the eigenvalue in each case?

(4) (a) Write a Slater determinant wavefunction for the $1s^2 2s^2 2p^1$ ground state of the boron atom. Be very specific in your labels. Note there are several possible correct results.

(b) Is your Slater determinant an eigenfunction for the exact hamiltonian?

(c) If interelectronic repulsion terms are neglected in *H*, what energy is associated with your Slater determinantal wavefunction?