

Quantum Mechanics and Spectroscopy

CHEM 3PA3

Assignment 19

Name: _____

1. Label the following approximate (unnormalized) molecular orbitals using σ , π , δ , u , g , and $+$, $-$ designations, and make a rough sketch of the shape of the orbitals. Here, we denote the $1s$ orbital on the "left-hand" atom as $\psi_{1s}^{(l)}(\mathbf{r})$, with the obvious generalization of notation to the other orbitals and the "right-hand" atom.

(a) $\psi_{2s}^{(l)}(\mathbf{r}) + \psi_{2s}^{(r)}(\mathbf{r})$

(e) $\psi_{3d_{z^2}}^{(l)}(\mathbf{r}) + \psi_{3d_{z^2}}^{(r)}(\mathbf{r})$

(b) $\psi_{2s}^{(l)}(\mathbf{r}) - \psi_{2s}^{(r)}(\mathbf{r})$

(f) $\psi_{3d_{z^2}}^{(l)}(\mathbf{r}) - \psi_{3d_{z^2}}^{(r)}(\mathbf{r})$

(c) $\psi_{2p_x}^{(l)}(\mathbf{r}) + \psi_{2p_x}^{(r)}(\mathbf{r})$

(g) $\psi_{2p_z}^{(l)}(\mathbf{r}) + \psi_{2p_z}^{(r)}(\mathbf{r})$

(d) $\psi_{2p_x}^{(l)}(\mathbf{r}) - \psi_{2p_x}^{(r)}(\mathbf{r})$

(h) $\psi_{2p_z}^{(l)}(\mathbf{r}) - \psi_{2p_z}^{(r)}(\mathbf{r})$

2. Write a Slater determinant of molecular orbitals that is appropriate for the ground state of Li_2^{2+} cation. Label the molecular orbitals with symmetry labels. Use the long form of the Slater determinant, writing out all the rows and columns.
3. The state of the electron in a (Li^{2+}) ion is described by the normalized wavefunction,

$$\Psi_{\text{Li}^{2+}}(\mathbf{r}) = -\left(\frac{1}{3}\right)^{1/2} R_{4,2}(r)Y_{2,-1}(\theta, \phi) + \left(\frac{2i}{3}\right) R_{3,2}(r)Y_{2,1}(\theta, \phi) - \left(\frac{2}{9}\right)^{1/2} R_{1,0}(r)Y_{0,0}(\theta, \phi)$$

Here, ψ_{label} are the normalized eigenfunctions of the He^+ Hamiltonian and the subscripts indicate the n , l and m_l quantum numbers.

- (a) If the total energy of different Li^{2+} ions in this state is measured, what values will be found?
- (b) If more than one value is found, what is the probability of obtaining each result and what is the average value?
- (c) If the magnitude of the total angular momentum is measured, what values will be found?
- (d) If more than one values is possible, what is the probability of obtaining each result and what is the average value?