Quantum Mechanics and Spectroscopy
CHEM 3PA3
Tutorial 7

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 $\psi^{(l)}(\mathbf{r})$, and $\psi^{(r)}(\mathbf{r})$ as the "right-hand" atom.

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

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

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

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

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

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

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

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

2. Write a Slater determinant of molecular orbitals that is appropiate 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. In Lithium Hydride, LiH, in the molecular orbital approximation, the ground state is predicted to be a singlet state, and the occupied molecular orbitals are both sigma orbitals. The electron configuration can then be written as $1\sigma^2 2\sigma^2$. Let $\phi_{1\sigma}(\mathbf{r})$ and $\phi_{2\sigma}(\mathbf{r})$ denote these molecular orbitals.

   (a) Write the Slater determinant for the $1\sigma^2 2\sigma^2$ electron configuration of LiH. Write the determinant out in its entirety, showing all the occupied orbitals and the coordinates of all the electrons explicitly. Remember the normalization factor.

   (b) Write a reasonable expression for the highest (the 2σ) occupied molecular orbtial in LiH.

4. Draw the molecular orbital diagram for BH_3.

5. Draw the molecular orbital diagram for CH_4.

① a) $\Psi_{2s}^{(l)}\{\vec{r}\} + \Psi_{2s}^{(r)}\{\vec{r}\}$

σ_g^+

b) $\Psi_{2s}^{(l)}\{\vec{r}\} - \Psi_{2s}^{(l)}\{\vec{r}\}$

σ_u^+

c) $\Psi_{2p_x}^{(l)}\{\vec{r}\} + \Psi_{2p_x}^{(r)}\{\vec{r}\}$.

π_u^+

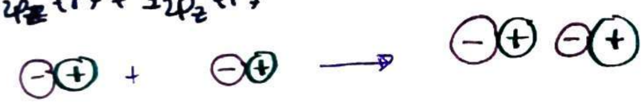
d) $\Psi_{2p_x}^{(l)}\{\vec{r}\} - \Psi_{2p_x}^{(r)}\{\vec{r}\}$

π_g^+

e) $\Psi_{2p_y}^{(l)}\{\vec{r}\} + \Psi_{2p_y}^{(r)}\{\vec{r}\}$

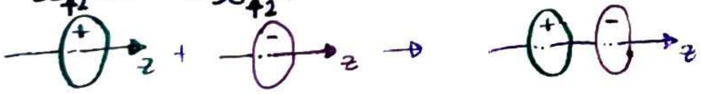
π_u^-

f) $\Psi_{2p_z}^{(l)}\{\vec{r}\} + \Psi_{2p_z}^{(r)}\{\vec{r}\}$



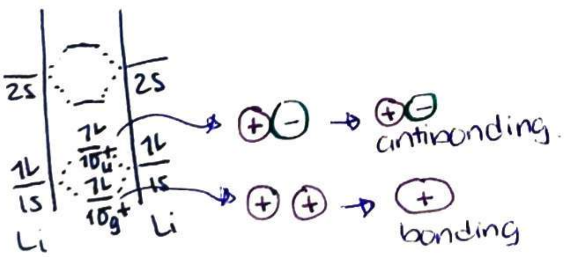
σ_u^+

g) $\Psi_{3d_{z^2}}^{(l)}\{\vec{r}\} - \Psi_{3d_{z^2}}^{(r)}\{\vec{r}\}$



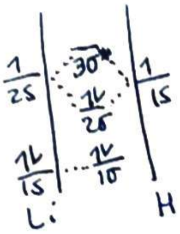
δ_u^+

② Li_2^{2+}: $(1\sigma_g^+)^2(1\sigma_u^+)^2$



$$\Psi_{Li_2^{2+}} = \frac{1}{\sqrt{4!}}\begin{bmatrix} \phi_{1\sigma_g^+}\{\vec{r}_1\}\alpha\{1\} & \phi_{1\sigma_g^+}\{\vec{r}_1\}\beta\{1\} & \phi_{1\sigma_u^+}\{\vec{r}_1\}\alpha\{1\} & \phi_{1\sigma_u^+}\{\vec{r}_1\}\beta\{1\} \\ \phi_{1\sigma_g^+}\{\vec{r}_2\}\alpha\{2\} & \cdots & \vdots & \vdots \\ \phi_{1\sigma_g^+}\{\vec{r}_3\}\alpha\{3\} & \cdots & \phi_{1\sigma} & \vdots \\ \phi_{1\sigma_g^+}\{\vec{r}_4\}\alpha\{4\} & & & \phi_{1\sigma_u^+}\{\vec{r}_4\}\beta\{4\} \end{bmatrix}$$

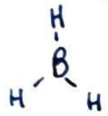
③ LiH: $(1\sigma^2)(2\sigma)^2$

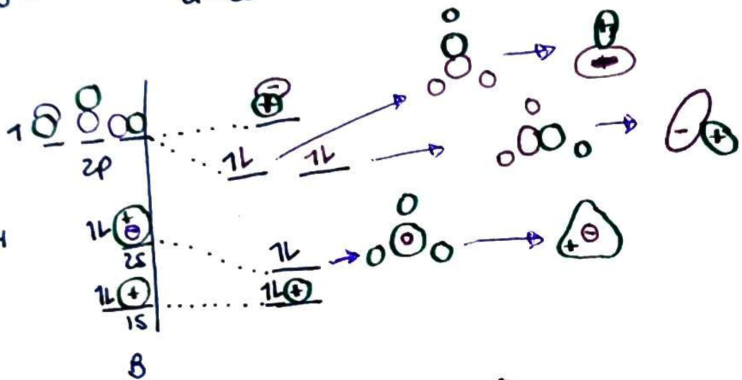


$$\Psi_{LiH} = \frac{1}{\sqrt{4!}} \begin{bmatrix} \phi_{1\sigma}(\vec{r}_1)\alpha(1) & \phi_{1\sigma}(\vec{r}_1)\beta(1) & \phi_{2\sigma}(\vec{r}_1)\alpha(1) & \phi_{2\sigma}(\vec{r}_1)\beta(1) \\ \vdots & & & \vdots \\ \phi_{1\sigma}(\vec{r}_4)\alpha(4) & \cdots & \cdots & \phi_{2\sigma}(\vec{r}_4)\beta(4) \end{bmatrix}$$

$$\phi_{2\sigma}(\vec{r}) = C\,\Psi_{Li-2s}(\vec{r}) + \sqrt{1-|C|^2}\;\Psi_{H-1s}(\vec{r}) .$$

④ BH_3.





⑤ CH_4.