Problem Set 14

Configuration Interaction

1. For the H_2 molecule, with one alpha and one beta electron in the σ and σ^* orbitals, you may construct the following four determinants:

$$|\Phi_1\rangle = |\phi_\sigma \alpha \phi_\sigma \beta\rangle$$

$$|\Phi_2\rangle = |\phi_{\sigma^*} \alpha \phi_{\sigma^*} \beta\rangle$$

$$|\Phi_3\rangle = |\phi_\sigma \alpha \phi_{\sigma^*} \beta\rangle$$

$$|\Phi_4\rangle = |\phi_{\sigma^*} \alpha \phi_\sigma \beta\rangle$$

   Write the Hamiltonian in matrix form in the basis of these determinants. Obtain expressions for each matrix element in terms of integrals over the spatial coordinates. Evaluate the matrix numerically for H_2 with bond lengths of 0.7 Å, 2.0 Å, and 10 Å. Use the numerical values for the integrals that are provided.

2. For H_2 with bond lengths of 0.7 Å, 2.0 Å, and 10 Å, diagonalize the Hamiltonian to obtain energies and wavefunctions for the ground and excited states of H_2 at each of these three geometries.

3. For each geometry of H_2, find the $\hat{S}^2$ eigenvalue corresponding to each of the states in order to determine if they are singlet or triplet states. Square the wavefunction coefficients to determine the electronic configuration(s) that best describe the character of the wavefunction.

Note that:

$$\langle \phi_i | \hat{h} | \phi_j \rangle = \langle \phi_j | \hat{h} | \phi_i \rangle$$

and

$$\langle \phi_i \phi_j | \frac{1}{r_{12}} | \phi_k \phi_l \rangle = \langle \phi_k \phi_j | \frac{1}{r_{12}} | \phi_i \phi_l \rangle = \langle \phi_i \phi_l | \frac{1}{r_{12}} | \phi_k \phi_j \rangle = \langle \phi_k \phi_l | \frac{1}{r_{12}} | \phi_i \phi_j \rangle =$$
$$\langle \phi_j \phi_i | \frac{1}{r_{12}} | \phi_l \phi_k \rangle = \langle \phi_l \phi_i | \frac{1}{r_{12}} | \phi_j \phi_k \rangle = \langle \phi_j \phi_k | \frac{1}{r_{12}} | \phi_l \phi_i \rangle = \langle \phi_l \phi_k | \frac{1}{r_{12}} | \phi_j \phi_i \rangle$$

Some Potentially Useful Equations

$$\hat{H} = -\sum_{i}^{\text{elec}} \frac{\hbar}{2m}\nabla_i^2 - \sum_{i}^{\text{elec}}\sum_{A}^{\text{nuc}} \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} + \sum_{i>j}^{\text{elec}} \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{A>B}^{\text{nuc}} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r_{AB}}$$

$$\hat{h}(i) = -\frac{\hbar}{2m}\nabla_i^2 - \sum_{A}^{\text{nuc}} \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}}$$

$$\hat{H} = \sum_{i}^{\text{elec}} \hat{h}(i) + \sum_{i>j}^{\text{elec}} \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{A>B}^{\text{nuc}} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r_{AB}}$$

$$|\phi_i\sigma\phi_j\sigma\ldots\phi_k\sigma\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_i(\mathbf{r}_1)\sigma(\omega_1) & \phi_j(\mathbf{r}_1)\sigma(\omega_1) & \cdots & \phi_k(\mathbf{r}_1)\sigma(\omega_1) \\ \phi_i(\mathbf{r}_2)\sigma(\omega_2) & \phi_j(\mathbf{r}_2)\sigma(\omega_2) & \cdots & \phi_k(\mathbf{r}_2)\sigma(\omega_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_i(\mathbf{r}_N)\sigma(\omega_N) & \phi_j(\mathbf{r}_N)\sigma(\omega_N) & \cdots & \phi_k(\mathbf{r}_N)\sigma(\omega_N) \end{vmatrix}$$

$$\sigma(\omega) = \begin{cases} \alpha(\omega) \\ \beta(\omega) \end{cases}$$

$$\langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1 \qquad \langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle = 0$$

$$\hat{S}_x|\alpha\rangle = \tfrac{\hbar}{2}|\beta\rangle \qquad \hat{S}_x|\beta\rangle = \tfrac{\hbar}{2}|\alpha\rangle$$

$$\hat{S}_y|\alpha\rangle = \tfrac{i\hbar}{2}|\beta\rangle \qquad \hat{S}_y|\beta\rangle = -\tfrac{i\hbar}{2}|\alpha\rangle$$

$$\hat{S}_z|\alpha\rangle = \tfrac{\hbar}{2}|\alpha\rangle \qquad \hat{S}_z|\beta\rangle = -\tfrac{\hbar}{2}|\beta\rangle$$

$$\hat{S}_+ = \hat{S}_x + i\hat{S}_y \qquad \hat{S}_- = \hat{S}_x - i\hat{S}_y$$

$$\hat{S}_+|\alpha\rangle = 0 \qquad \hat{S}_+|\beta\rangle = \hbar|\alpha\rangle$$

$$\hat{S}_-|\alpha\rangle = \hbar|\beta\rangle \qquad \hat{S}_-|\beta\rangle = 0$$

$$[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z \qquad [\hat{S}_y, \hat{S}_z] = i\hbar\hat{S}_x$$

$$[\hat{S}_z, \hat{S}_x] = i\hbar\hat{S}_y$$

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 = \hat{S}_+\hat{S}_- - \hbar\hat{S}_z + \hat{S}_z^2 = \hat{S}_-\hat{S}_+ + \hbar\hat{S}_z + \hat{S}_z^2$$

Integrals for H_2 (in au)

Bond length: 0.7 Å

$\langle \phi_\sigma | \hat{h} | \phi_\sigma \rangle = -1.2778530$
$\langle \phi_\sigma | \hat{h} | \phi_{\sigma^*} \rangle = 0.0000000$
$\langle \phi_{\sigma^*} | \hat{h} | \phi_{\sigma^*} \rangle = -0.4482997$

$\langle \phi_\sigma \phi_\sigma | \frac{1}{r_{12}} | \phi_\sigma \phi_\sigma \rangle = 0.682390$
$\langle \phi_{\sigma^*} \phi_\sigma | \frac{1}{r_{12}} | \phi_\sigma \phi_\sigma \rangle = 0.000000$
$\langle \phi_{\sigma^*} \phi_{\sigma^*} | \frac{1}{r_{12}} | \phi_\sigma \phi_\sigma \rangle = 0.179001$
$\langle \phi_{\sigma^*} \phi_{\sigma^*} | \frac{1}{r_{12}} | \phi_\sigma \phi_{\sigma^*} \rangle = 0.000000$
$\langle \phi_{\sigma^*} \phi_\sigma | \frac{1}{r_{12}} | \phi_{\sigma^*} \phi_\sigma \rangle = 0.670733$
$\langle \phi_{\sigma^*} \phi_{\sigma^*} | \frac{1}{r_{12}} | \phi_{\sigma^*} \phi_\sigma \rangle = 0.000000$
$\langle \phi_{\sigma^*} \phi_{\sigma^*} | \frac{1}{r_{12}} | \phi_{\sigma^*} \phi_{\sigma^*} \rangle = 0.705106$

Bond length: 2.0 Å

$\langle \phi_\sigma | \hat{h} | \phi_\sigma \rangle = -0.7789220$
$\langle \phi_\sigma | \hat{h} | \phi_{\sigma^*} \rangle = 0.0000000$
$\langle \phi_{\sigma^*} | \hat{h} | \phi_{\sigma^*} \rangle = -0.6702667$

$\langle \phi_\sigma \phi_\sigma | \frac{1}{r_{12}} | \phi_\sigma \phi_\sigma \rangle = 0.509463$
$\langle \phi_{\sigma^*} \phi_\sigma | \frac{1}{r_{12}} | \phi_\sigma \phi_\sigma \rangle = 0.000000$
$\langle \phi_{\sigma^*} \phi_{\sigma^*} | \frac{1}{r_{12}} | \phi_\sigma \phi_\sigma \rangle = 0.259138$
$\langle \phi_{\sigma^*} \phi_{\sigma^*} | \frac{1}{r_{12}} | \phi_\sigma \phi_{\sigma^*} \rangle = 0.000000$
$\langle \phi_{\sigma^*} \phi_\sigma | \frac{1}{r_{12}} | \phi_{\sigma^*} \phi_\sigma \rangle = 0.519201$
$\langle \phi_{\sigma^*} \phi_{\sigma^*} | \frac{1}{r_{12}} | \phi_{\sigma^*} \phi_\sigma \rangle = 0.000000$
$\langle \phi_{\sigma^*} \phi_{\sigma^*} | \frac{1}{r_{12}} | \phi_{\sigma^*} \phi_{\sigma^*} \rangle = 0.534664$

Bond length: 10.0 Å

$\langle \phi_\sigma | \hat{h} | \phi_\sigma \rangle = -0.5194996$
$\langle \phi_\sigma | \hat{h} | \phi_{\sigma^*} \rangle = 0.0000000$
$\langle \phi_{\sigma^*} | \hat{h} | \phi_{\sigma^*} \rangle = -0.5194996$

$\langle \phi_\sigma \phi_\sigma | \frac{1}{r_{12}} | \phi_\sigma \phi_\sigma \rangle = 0.413762$
$\langle \phi_{\sigma^*} \phi_\sigma | \frac{1}{r_{12}} | \phi_\sigma \phi_\sigma \rangle = 0.000000$
$\langle \phi_{\sigma^*} \phi_{\sigma^*} | \frac{1}{r_{12}} | \phi_\sigma \phi_\sigma \rangle = 0.360844$
$\langle \phi_{\sigma^*} \phi_{\sigma^*} | \frac{1}{r_{12}} | \phi_\sigma \phi_{\sigma^*} \rangle = 0.000000$
$\langle \phi_{\sigma^*} \phi_\sigma | \frac{1}{r_{12}} | \phi_{\sigma^*} \phi_\sigma \rangle = 0.413762$
$\langle \phi_{\sigma^*} \phi_{\sigma^*} | \frac{1}{r_{12}} | \phi_{\sigma^*} \phi_\sigma \rangle = 0.000000$
$\langle \phi_{\sigma^*} \phi_{\sigma^*} | \frac{1}{r_{12}} | \phi_{\sigma^*} \phi_{\sigma^*} \rangle = 0.413762$