

Please answer all questions, showing all calculations

1. Which of the following could be valid wavefunction in the region 0 to infinity? (5 points)

- A)  $A \sin^2 kx$       B)  $A e^{kx}$       C)  $A \sin^2 x e^{-kx}$       D)  $A e^{-kx} / \sin x$       E)  $A x e^{-x}$

The fundamental idea to remember is that a wavefunction should be continuous, continuous first and second derivatives, and not have multiple singularities. Answer A) is not strong because it is not normalizable (integration of the squared wavefunction leads to infinite value and thus a normalization constant of 0). Answer B) goes to infinity at large x values. Answer C) is integrable, and has continuous derivatives and thus is valid wavefunction. Answer D) has multiple infinity values at x values of 0,  $\pi/2$ ,  $3\pi/2$  etc. Answer E) is valid, with no discontinuities in any derivatives and going to a value of 0 as x approaches infinity.

2. Which of the following excited state wavefunctions are allowed under the Pauli principle for a He-H molecule where  $\alpha(n)$  and  $\beta(n)$  refer to spin wavefunctions for the nth electron and  $\psi_1(n)$  and  $\psi_2(n)$  refer to molecular orbit wavefunctions constructed from 1s and 2s orbitals on the H and He atoms? (15 points)

In this problem you need to look at effect of exchanging two electrons (1 and 2 for instance). If wavefunction changes sign, then it is valid. This must be true for all possible exchanges of electrons. If wavefunction does not change sign or is a different wavefunction, then it is invalid.

A)  $\alpha_1(2) \{ \alpha_2(2) - \beta_2(2) \} \{ \alpha_1(1) \alpha_2(3) \alpha_1(3) - \alpha_2(1) \alpha_1(3) \alpha_1(3) \}$

This wavefunction fails when you exchange either the electrons 1 and 2 giving

$$\alpha_1(1) \{ \alpha_1(1) - \beta_1(1) \} \{ \alpha_1(2) \alpha_2(3) \alpha_2(3) - \alpha_2(2) \alpha_1(3) \alpha_2(3) \}$$

or electrons 3 and 2. In both cases, you get a  $\alpha_2(2)$  term which is not present in original wavefunction.

B)  $\{ \alpha_1(1) \alpha_2(2) - \alpha_1(2) \alpha_2(1) \} \alpha_1(3) \alpha_1(2) \alpha_2(3) +$   
 $\alpha_1(1) \alpha_1(2) \alpha_2(3) \alpha_2(3) \{ \alpha_2(2) \alpha_1(1) - \alpha_1(2) \alpha_2(1) \} +$   
 $\alpha_1(2) \alpha_1(3) \alpha_2(1) \alpha_2(1) \alpha_1(3) - \alpha_1(1) \alpha_1(3) \alpha_2(2) \alpha_2(3) \alpha_1(2)$

This wavefunction changes sign when you exchange electrons 1 and 2 but fails when you exchange either the electrons 1 and 3 giving

$$\{ \alpha_1(3) \alpha_2(2) - \alpha_1(2) \alpha_2(3) \} \alpha_1(1) \alpha_1(1) \alpha_2(3) +$$

$$\alpha_1(3) \alpha_1(2) \alpha_2(1) \alpha_1(1) \{ \alpha_2(2) \alpha_3(3) - \alpha_3(2) \alpha_2(1) \} +$$

$$\alpha_1(2) \alpha_1(1) \alpha_2(3) \alpha_2(3) \alpha_1(1) - \alpha_1(1) \alpha_1(3) \alpha_2(2) \alpha_2(3) \alpha_1(2)$$

In this case, the  $\beta(1)\beta(2)\beta(3)$  term has a completely different spatial wavefunction.

C)  $\{ \alpha_1(1) \alpha_1(2) \alpha_2(3) - \alpha_1(3) \alpha_2(1) \alpha_1(2) \} \alpha_1(2) \alpha_2(3) +$   
 $\{ \alpha_1(2) \alpha_2(1) \alpha_1(3) - \alpha_1(1) \alpha_2(2) \alpha_1(3) \} \alpha_1(2) \alpha_2(3) +$   
 $\{ \alpha_1(3) \alpha_1(1) \alpha_2(2) - \alpha_1(2) \alpha_1(1) \alpha_2(3) \} \alpha_2(3) \alpha_1(2)$

This wavefunction is valid and any exchange produces the same wavefunction back with a negative coefficient in front, take the 2 and 3 exchange as an example (last two lines are reversed so spin states

correspond between the two expressions).

$$\begin{aligned} & \{ \psi_1(3) \psi_1(2) \psi_2(1) - \psi_1(1) \psi_2(3) \psi_1(2) \} \psi(1) \psi(2) \psi(3) + \\ & \{ \psi_1(1) \psi_1(3) \psi_2(2) - \psi_1(2) \psi_1(3) \psi_2(1) \} \psi(1) \psi(2) \psi(3) + \\ & \{ \psi_1(2) \psi_2(1) \psi_1(3) - \psi_1(1) \psi_2(2) \psi_1(3) \} \psi(3) \psi(1) \psi(2) \end{aligned}$$

Notice all three spatial coefficients (upon proper ordering of terms) are identical as the initial wavefunction with a sign change.

**D)**

$$\begin{aligned} & \{ \psi_1(1) \psi_1(2) \psi_2(3) + \psi_1(3) \psi_2(1) \psi_1(2) \} \psi(1) \psi(2) \psi(3) - \\ & \{ \psi_1(2) \psi_2(1) \psi_1(3) - \psi_1(1) \psi_2(2) \psi_1(3) \} \psi(1) \psi(2) \psi(3) + \\ & \{ \psi_1(3) \psi_1(1) \psi_2(2) + \psi_1(2) \psi_1(1) \psi_2(3) \} \psi(3) \psi(1) \psi(2) \end{aligned}$$

This wavefunction looks very similar to the one in C on the outset, but notice the differing signs in this case. The sign differences result in the exchange problems that render this wavefunction invalid.

Take the 1 and 3 exchange example below (again swapping last two lines).

$$\begin{aligned} & \{ \psi_1(3) \psi_1(2) \psi_2(1) + \psi_1(1) \psi_2(3) \psi_1(2) \} \psi(1) \psi(2) \psi(3) + \\ & \{ \psi_1(1) \psi_1(3) \psi_2(2) + \psi_1(2) \psi_1(3) \psi_2(1) \} \psi(1) \psi(2) \psi(3) - \\ & \{ \psi_1(2) \psi_2(3) \psi_1(1) - \psi_1(3) \psi_2(2) \psi_1(1) \} \psi(3) \psi(1) \psi(2) \end{aligned}$$

You will notice a variety of problems in this exchanged function. The first term is identical in both cases, the second and third change sign between the two spatial parts. Thus the wavefunction is an entirely new one and thus invalid.

**E)**

$$\psi_1(1) \psi_1(2) \psi_2(3) \psi(1) \psi(2) \psi(3)$$

This simple wavefunction is rendered invalid under ANY exchange since the sign will never change and in any exchange you will also get a NEW wavefunction! Look at the 1 and 3 exchange below.

$$\psi_1(3) \psi_1(2) \psi_2(1) \psi(1) \psi(2) \psi(3)$$

Here the spatial portion is completely different while the spin portion is unchanged. As well, no sign change has occurred.

3. What is the bond order for a  $\text{CF}^-$  molecule? (5 points)

- A) 0                      B) 1                      C) 1.5                      D) 2                      E) 2.5

The proper energy level diagram will have a  $4 + 7 + 1 = 12$  electrons filling the orbitals  $\sigma(1s)^2 \sigma^*(1s)^2 \sigma(2s)^2 \sigma^*(2s)^2 \sigma(2p_x)^2 \pi(2p)^4 \pi^*(2p)^2$  and we count 10 bonding and 6 nonbonding electrons for a bond order of  $(10-6)/2 = 2$  (D).

4. Describe in your own words the Born-Oppenheimer approximation. (12 points)

The B-O approximation is simply the idea of separating the nuclear coordinates from the electronic coordinates. In this approximation, the electronic energy is calculated for each nuclear coordinate possibility. To get the energy of a molecule, the nuclear coordinates are optimized to minimize the electronic energy. From this lowest energy configuration, nuclear motions may be studied (vibration/rotation), by assuming the electronic wavefunction changes to meet each nuclear configuration on a timescale rendering the nuclear motion adiabatic.

5. Write the Hückel matrix for the cycloheptatriene carboanion ( $C_7H_7^-$ , negative charge on one carbon). Calculate (using Maple) the 7 energy levels (in terms of  $\alpha$  and  $\beta$ , usual definitions) which constitute the bonding system and indicate lowest energy transition. (15 points)

The Hückel matrix for this molecule is given below:

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0$$

$$x = \frac{\alpha - E}{\beta}$$

$$\alpha = \int \psi_{p_q}^*(n) H \psi_{p_z}(n) \quad \text{where } \Psi_{p_z}(n) \text{ is the } P_z \text{ orbit on the } n\text{th atom}$$

$$\beta = \int \psi_{p_q}^*(n) H \psi_{p_z}(m)$$

This gives the polynomial  $0 = 2 - 7x + 14x^3 - 7x^5 + x^7$  which has solutions of  $x = \{-2.000, -1.247, -1.247, 0.445, 0.445, 1.802, 1.802\}$ . Notice the degeneracy of the 2nd/3rd, 4th/5th and 6th/7th pairs of energy levels. These seven levels will be filled with the 8 electrons, filling the 1st, 2nd/3rd levels completely and each of the 4th/5th with one electron. The transitions you might observe would be from the 1st to the 4th/5th or from the 2nd/3rd to the 4th/5th or from the 4th/5th to the 6th/7th. Energies for these transitions are  $2.445\beta$ ,  $1.692\beta$ ,  $1.357\beta$  respectively. Assuming that  $\beta$  takes the usual value, we would have transitions with wavelengths of 150.9 nm, 218.1 nm and 272.0 nm. Any other transition will have higher energy, thus the lowest energy is the 4/5 to 6/7 transition at 272.0 nm.

6. Calculate the absorbance at 550 nm from a solution prepared by mixing 10 ml of 3M  $CuSO_4$  with 10 ml of 2M  $FeSO_4$  and diluted to 100 ml in a 1.0 cm pathlength cell given the molar absorptivity at 550 nm is  $\epsilon_{Cu} = 2300 M^{-1} cm^{-1}$  and  $\epsilon_{Fe} = 7100 M^{-1} cm^{-1}$ . (10 points)

$$A = \epsilon_{Cu} c_{Cu} l + \epsilon_{Fe} c_{Fe} l = (2300 M^{-1} cm^{-1}) \times (10 ml \times 3 M / 100 ml) \times 1.0 cm + (7100 M^{-1} cm^{-1}) \times (10 ml \times 2 M / 100 ml) \times 1.0 cm = 2110$$

7. Assuming that the dipole moment operator is just  $\mu_x = e\mathbf{x}$ , calculate the x component of the transition dipole moment from the  $n = 1$  to the  $n = K$  level in the one-dimensional particle in a box. What transitions will be allowed? (10 points, use Maple to perform required integral.)

$$\Psi_n = (2/a)^{1/2} \sin(n\pi x/a)$$

$$\mu_{K1} = \int_0^a \Psi_K^* \mu_x \Psi_1 dx = \int_0^a \frac{2}{a} e x \sin \frac{K\pi x}{a} \sin \frac{\pi x}{a} dx = -\frac{2ae}{\pi^2} \frac{2K \cos(\pi K) + K \sin(\pi K)}{(K-1)^2 (K+1)^2} + \frac{2K}{(K-1)^2 (K+1)^2}$$

This expression may be simplified remembering that  $K$  is an integer starting at 2, 3, 4 .... and that  $\sin(K\pi)$  will thus always be 0 and  $\cos(K\pi)$  will be  $(-1)^K$ .

$$\mu_{K1} = -\frac{2ae}{\pi^2} \frac{2K(-1)^K}{(K-1)^2(K+1)^2} + \frac{2K}{(K-1)^2(K+1)^2} = -\frac{4Kae}{(K-1)^2(K+1)^2\pi^2} \left( (-1)^K + 1 \right)$$

which will have a value of 0 whenever  $K$  is odd and a steadily decreasing value (remember that  $e$  is the charge on an electron or  $-1.6 \times 10^{-19}$  C) for even  $K$ . This indicates that only transitions from  $n = 1$  to an even  $K$  will be allowed with the most favorable being the 1 to 2 transition.