7   Molecular Orbital Theory

11/17:   1. The bonding and antibonding potential energy surfaces of H_2^+ were derived in class by applying the linear variational principle to the trial wave function

$$\psi_{\text{trial}} = c_1 1s_A + c_2 1s_B$$

(a) Estimate the ground-state potential energy surface by computing the first-order *perturbative* change in the energy where the reference Hamiltonian

$$\hat{H}_0 = -\frac{1}{2}\nabla^2 - \frac{1}{r_A}$$

is the Hamiltonian of the hydrogen atom at position A and the perturbation

$$\hat{V} = -\frac{1}{r_B} + \frac{1}{R}$$

is the interaction of a second proton at position B with the proton at position A where R is the internuclear distance. The reference wave function

$$\psi_0 = 1s_A$$

is the $1s$ orbital of hydrogen centered at position A.

Answer. If we let

$$\hat{H} = \hat{H}_0 + \lambda\hat{V}$$

then we want to find the first-order approximation

$$E(1) = E(0) + (1)\frac{\mathrm{d}E}{\mathrm{d}\lambda}\Big|_0$$

of $E(\lambda)$ with respect to $\hat{H}$ where $\lambda = 1$. Let's begin.

We know that the ground state energy of the unperturbed hydrogen atom is

$$E(0) = -\frac{1}{2}E_{\text{h}}$$

Additionally, we know that the first-order perturbation

$$\begin{aligned}
\frac{\mathrm{d}E}{\mathrm{d}\lambda}\Big|_0 &= \int \psi_0^* \hat{V} \psi_0 \, \mathrm{d}\vec{r} \\
&= \int \mathrm{d}\vec{r}\, 1s_A^* \left(-\frac{1}{r_B} + \frac{1}{R}\right) 1s_A \\
&= J
\end{aligned}$$

$$\boxed{\frac{\mathrm{d}E}{\mathrm{d}\lambda}\Big|_0 = e^{-2R}\left(1 + \frac{1}{R}\right)}$$
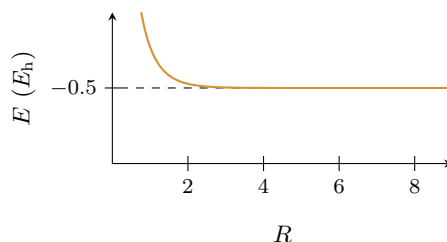
Thus, the ground state potential energy surface is

$$\boxed{E(1) = -\frac{1}{2} + e^{-2R}\left(1 + \frac{1}{R}\right)}$$

$\square$

(b) Make a sketch of the potential energy surface from part (a) as a function of R.
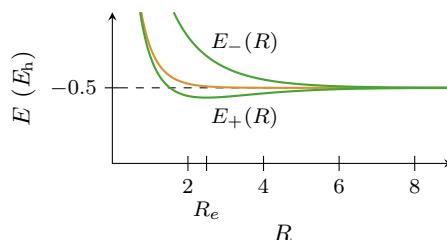
Answer.

(c) Does the approximation in part (a) produce a stable, bound ground state for H_2^+?

Answer. No . Since the function is decreasing on $(0, \infty)$, energy can only be lowered by increasing the internuclear distance, so the atoms will drift apart forever.

(d) In a second sketch, compare the potential energy surface in part (a) with the bonding and anti-bonding potential energy surfaces of H_2^+ that were derived in class from the trial wave function above.

Answer.

(e) Using the trial wave function for comparison, explain briefly in terms of bonding — the sharing of electrons — the limitation of the wave function in part (a).

Answer. The wave function in part (a) does not describe bonding particularly well since it is centered strictly at one atom and does not represent an equal, symmetric sharing of electrons.

(f) Furnish the trial wave function that within the variational approximation would give the same potential energy surface as the application of first-order perturbation theory in (a).

Answer. Based on the above, we can guess that

$$\psi_{\text{trial}} = 1s_A$$

Indeed, with this trial wave function, we find

$$E = \frac{\int 1s_A^* \hat{H} 1s_A \, d\tau}{\int 1s_A^* 1s_A \, d\tau}$$
$$= \frac{E_{1s} + J}{1}$$
$$= E(1)$$

as desired. Therefore, the desired trial wave function is indeed
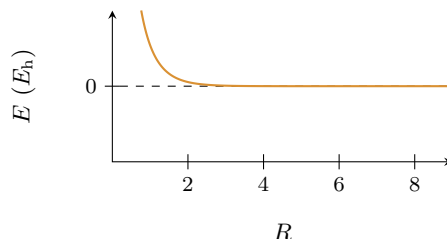
$$\boxed{\psi_{\text{trial}} = 1s_A}$$

2. The Coulomb integral for H_2^+ is given by

$$J(R) = e^{-2R}\left(1 + \frac{1}{R}\right)$$

(a) By making a sketch of $J(R)$ as a function of the internuclear distance R, show that $J(R)$ is nonnegative for all R.

Answer.

(b) The $J(R)$ results from two competing forces: (i) the attraction of an electron on A to the proton at B and (ii) the repulsion of the proton at A from the proton at B. What does the nonnegativity of $J(R)$ in part (a) say about the relative strengths of these competing forces?

Answer. Since we have that

$$0 < \int d\vec{r}\, 1s_A^* \left(-\frac{1}{r_B} + \frac{1}{R}\right) 1s_A$$

$$0 < \int d\vec{r}\, 1s_A^* \left(\frac{1}{R}\right) 1s_A - \int d\vec{r}\, 1s_A^* \left(\frac{1}{r_B}\right) 1s_A$$

$$\int d\vec{r}\, 1s_A^* \left(\frac{1}{r_B}\right) 1s_A < \int d\vec{r}\, 1s_A^* \left(\frac{1}{R}\right) 1s_A$$

where the right term above describes the internuclear repulsion and the left term above describes the electronic attraction, the $\boxed{\text{internuclear repulsion is stronger than the electronic attraction}}$.
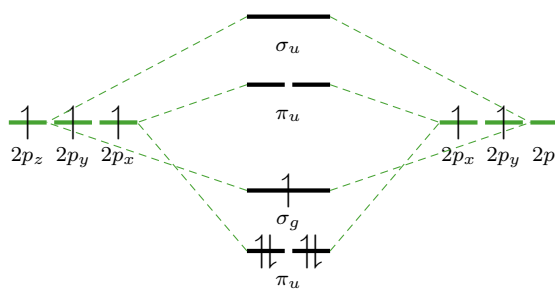
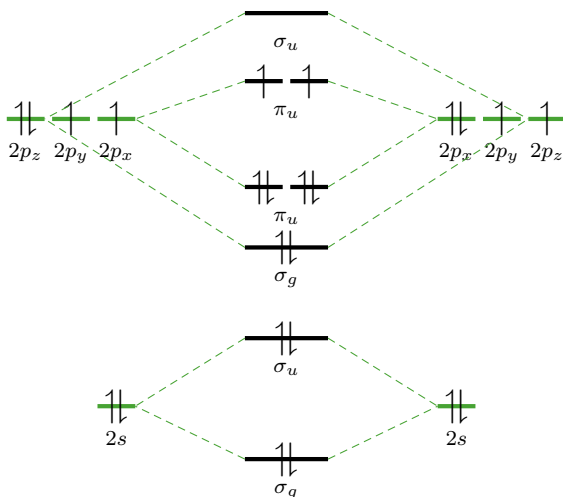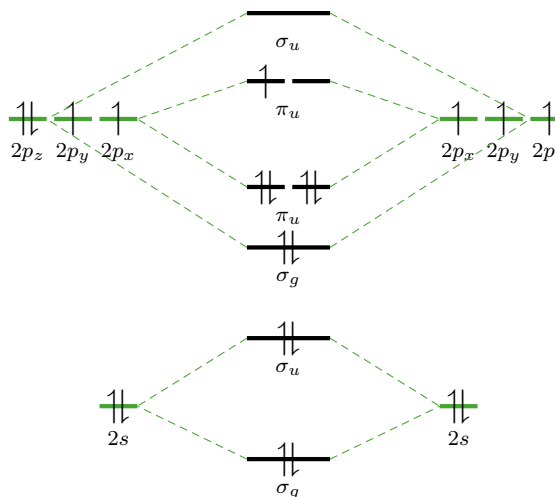3. (a) Give the molecular orbital diagrams for the molecules N_2, N_2^+, O_2, and O_2^+.

Answer.
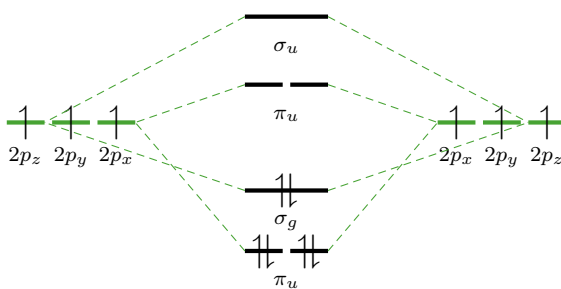
(a) N_2.

(b) N_2^+.

(c) O_2.

(d) $O_2{}^+$.

☐

(b) What is the bond order for each molecule?

Answer. We have that

$$BO_{N_2} = \frac{1}{2}(8-2) \qquad BO_{N_2{}^+} = \frac{1}{2}(7-2) \qquad BO_{O_2} = \frac{1}{2}(8-4) \qquad BO_{O_2{}^+} = \frac{1}{2}(8-3)$$

$$\boxed{BO_{N_2} = 3} \qquad \boxed{BO_{N_2{}^+} = 2.5} \qquad \boxed{BO_{O_2} = 2} \qquad \boxed{BO_{O_2{}^+} = 2.5}$$

☐

(c) Explain why N_2 has a larger dissociation energy than $N_2{}^+$, but $O_2{}^+$ has a larger dissociation energy than O_2.

Answer. Bond order, as a measure of stability, positively correlates with dissociation energy. Thus, since $BO_{N_2} > BO_{N_2{}^+}$ and $BO_{O_2{}^+} > BO_{O_2}$, N_2 has a larger dissociation energy than $N_2{}^+$ and $O_2{}^+$ has a larger dissociation energy than O_2. ☐

(d) Using Grassmann notation, give the ground-state wave function for N_2 in molecular orbital theory.

Answer. We have

$$\psi = \sigma_g 1s\alpha(1) \wedge \sigma_g 1s\beta(2) \wedge \sigma_u 1s\alpha(3) \wedge \sigma_u 1s\beta(4) \wedge \sigma_g 2s\alpha(5) \wedge \sigma_g 2s\beta(6) \wedge \sigma_u 2s\alpha(7) \wedge \sigma_u 2s\beta(8)$$
$$\wedge \pi_u 2p_x\alpha(9) \wedge \pi_u 2p_x\beta(10) \wedge \pi_u 2p_y\alpha(11) \wedge \pi_u 2p_y\beta(12) \wedge \sigma_g 2p_z\alpha(13) \wedge \sigma_g 2p_z\beta(14)$$

where $\psi = \psi(1,2,3,4,5,6,7,8,9,10,11,12,13,14)$ is a function of the fourteen sets of four (three spatial and one spin) coordinates describing each electron. ☐

4. Using the worksheet "Huckel Theory" with the Quantum Chemistry Toolbox for Maple, answer the lettered questions.

   (a) Order the energies from lowest to highest.

   Answer. We have

   $$\boxed{\alpha + 2\beta \leq \alpha = \alpha \leq \alpha - 2\beta}$$

   ☐

   (b) How many molecular orbitals are degenerate?

Answer. If there is one eigenvalue/energy with nontrivial multiplicity, then there exist ⟨two⟩ molecular orbitals that are degenerate.

□

(c) Normalize each of the four eigenvectors generated by Maple.

Answer. The normalized eigenvectors are

□

$$
\begin{bmatrix} 0 \\ -1/\sqrt{2} \\ 0 \\ 1/\sqrt{2} \end{bmatrix}
\qquad
\begin{bmatrix} -1/\sqrt{2} \\ 0 \\ 1/\sqrt{2} \\ 0 \end{bmatrix}
\qquad
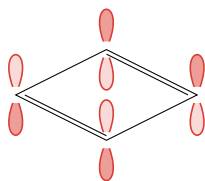\begin{bmatrix} -1/2 \\ 1/2 \\ -1/2 \\ 1/2 \end{bmatrix}
\qquad
\begin{bmatrix} 1/2 \\ 1/2 \\ 1/2 \\ 1/2 \end{bmatrix}
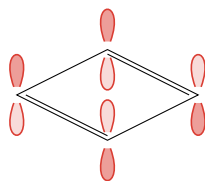$$

(a) (b) (c) (d)

(d) Draw a sketch of each of the molecular orbitals including the relative phases between the p_z orbitals as indicated by the computed eigenvectors.
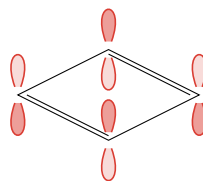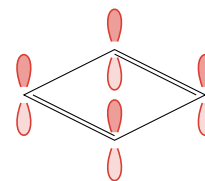
Answer.

□

(a) (b) (c) (d)

(e) Label each sketch in part (d) by its molecular orbital energy.

Answer. We have

$$(a) = \alpha \qquad (b) = \alpha \qquad (c) = \alpha - 2\beta \qquad (d) = \alpha + 2\beta$$

□

(f) Do the molecular orbitals computed by the variational 2-RDM method agree with the qualitative features of those predicted by Huckel's theory?

Answer. The orbitals (c) and (d) from part (d) have variational 2-RDM analogues. However, the other two orbitals have definite qualitative distinctions (namely, we have to take linear combinations of the Huckel ones, which is allowed since they're degenerate, but still).

□

(g) In what ways do these orbital occupations agree with those predicted from Huckel theory, and in what ways do they not agree?

Answer. They agree in the sense that we have a bonding state that is nearly fully occupied and an antibonding state that is nearly empty, but they disagree on the degeneracy of the two middle states (Huckel theory predicts degeneracy in the middle states, but the states computed here differ in occupation by almost exactly an entire electron, suggesting that they have significantly different energies).

□

(h) Based on the computed bond distances, is the geometry of cyclobutadiene square or rectangular?

Answer. Since the bond lengths of C1-C3 and C2-C4 are equal but different than the bond lengths of C1-C2 and C3-C4, cyclobutadiene is ⟨rectangular⟩.

□

(i) Can you use the result from part (h) to explain the difference in the occupation numbers from the Variational 2-RDM calculations and those from Huckel's method?

Answer. Yes. Since the lowest and highest energy orbitals have a C_4 axis in both approximations but the molecule overall only has a C_2 axis in the variational 2-RDM approximation, the middle orbitals cannot be symmetric as they are in the Huckel approximation from part (d). This lack of symmetry implies nondegenerate energies, as one orbital must be more occupied than the other to stretch the molecule from square to rectangular. □

5. In photoelectron spectroscopy, radiation interacts with gaseous molecules to eject electrons whose kinetic energies are measured (recall the photoelectric effect).

   (a) Explain why measuring the kinetic energy of the ejected electrons tells us something about the molecular orbital energies.

   Answer. Using Einstein's Nobel prize equation

   $$KE = h\nu - W$$

   we know that the kinetic energy KE of the ejected electron is equal to the energy $h\nu$ of the impinging photon minus the ionization energy of the ejected electron (the molecular orbital energy). Thus, if we plot measured KE's versus known $h\nu$'s and perform a linear regression, the y-intercept gives an approximation for W. □

   (b) If the incident radiation has a wavelength of 57.8 nm, what is the largest electron binding energy that can be measured?
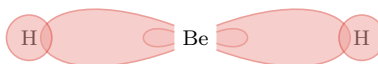
   Proof. Using the above equation again, if $\lambda = 5.78 \times 10^{-8}$ m, the largest electron binding energy that can be measured is that which gives a KE detectably greater than zero. Numerically,

   $$0 < KE$$
   $$0 < h\nu - W$$
   $$W < \frac{hc}{\lambda}$$
   $$= 3.44 \times 10^{-18}\,\text{J}$$

   i.e., the largest energy that can be measured is bounded by $\boxed{3.44 \times 10^{-18}\,\text{J}}$.   □

6. (a) Sketch the hybrid orbitals of Be in the molecule BeH_2 and illustrate their role in bonding.

   Answer.

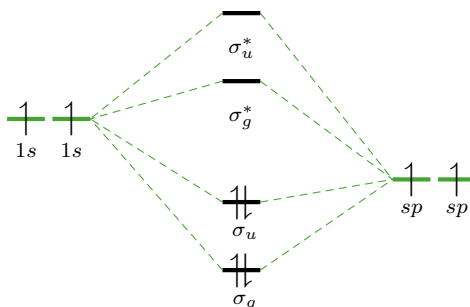   □

   (b) Using the hybrid orbitals, assemble a molecular orbital diagram for BeH_2.

   Answer.

(c) With Grassmann notation, express the MO ground-state wave function for BeH$_2$.

Answer. We have that

$$\psi(1,2,3,4,5,6) = 1s\alpha(1) \wedge 1s\beta(2) \wedge 1\sigma_g\alpha(3) \wedge 1\sigma_g\beta(4) \wedge 2\sigma_g\alpha(5) \wedge 2\sigma_g\beta(6)$$

☐

7. Using the *hybridized sp^3* wave functions of CH$_4$ on McQuarrie and Simon (1997, p. 376), give the probability that an electron in one of the *sp^3* wave functions is...

(a) In carbon's $2p_x$ orbital;

Answer. We have that the normalized *sp^3* wave functions are of the form

$$\psi = \frac{1}{2}(2s \pm 2p_x \pm 2p_y \pm 2p_z)$$

Thus, since the probability that an electron is in one of the component orbitals is equal to the square of the norm of its coefficient, we have that

$$\boxed{\text{Prob}_{2p_x} = \frac{1}{4}}$$

☐

(b) In carbon's $2p_z$ orbital.

Answer. By a completely symmetric argument to part (a),

$$\boxed{\text{Prob}_{2p_z} = \frac{1}{4}}$$

☐

(c) By symmetry, should the results in parts (a) and (b) be the same or different?

Answer. $\boxed{\text{Yes}}$.   ☐

8. The π-electrons may be approximated in conjugated and aromatic hydrocarbons through Huckel theory. Use Huckel theory to approximate the energies and the wave functions for...

(a) The allyl radical;

Answer. Consider the system $\mathbb{H}\vec{c} = E\mathbb{S}\vec{c}$ describing only the three adjacent $2p_z$ orbitals of the allyl radical, each of which contains one electron. Invoking the Huckel approximation, we get

$$\mathbb{H}\vec{c} = E\mathbb{I}\vec{c}$$
$$(\mathbb{H} - E\mathbb{I})\vec{c} = 0$$
$$\begin{pmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

as an approximation of the original system, where α, β are experimentally determined quantities. We want to find all energies E that give $\mathbb{H} - E\mathbb{I}$ a nontrivial null space, i.e., a nontrivial corresponding wave function. But these values of E will be the ones for which $\mathbb{H} - E\mathbb{I}$ is singular with determinant zero. Thus, set

$$\begin{aligned} 0 &= \begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} \\ &= \beta^3 \begin{vmatrix} (\alpha - E)/\beta & 1 & 0 \\ 1 & (\alpha - E)/\beta & 1 \\ 0 & 1 & (\alpha - E)/\beta \end{vmatrix} \\ &= \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} \\ &= x^3 - 2x \\ &= x(x + \sqrt{2})(x - \sqrt{2}) \end{aligned}$$
$$\frac{\alpha - E}{\beta} = 0, \pm\sqrt{2}$$
$$E = \alpha - (0, \pm\sqrt{2})\beta$$

to determine the desired approximate energies, which we may label

$$\boxed{E_1 = \alpha + \sqrt{2}\beta} \qquad\qquad \boxed{E_2 = \alpha} \qquad\qquad \boxed{E_3 = \alpha - \sqrt{2}\beta}$$

As for the corresponding wave functions, to determine the coefficients of ψ_i, we solve the original system with each E_i plugged in using Gauss-Jordan elimination. For example,

$$\begin{pmatrix} \frac{\alpha - E_1}{\beta} & 1 & 0 & \bigg| & 0 \\ 1 & \frac{\alpha - E_1}{\beta} & 1 & \bigg| & 0 \\ 0 & 1 & \frac{\alpha - E_1}{\beta} & \bigg| & 0 \end{pmatrix}$$
$$\begin{pmatrix} -\sqrt{2} & 1 & 0 & \bigg| & 0 \\ 1 & -\sqrt{2} & 1 & \bigg| & 0 \\ 0 & 1 & -\sqrt{2} & \bigg| & 0 \end{pmatrix}$$
$$\begin{pmatrix} 1 & 0 & -1 & \bigg| & 0 \\ 0 & 1 & -\sqrt{2} & \bigg| & 0 \\ 0 & 0 & 0 & \bigg| & 0 \end{pmatrix}$$

yields $\psi_1 = (1c_3)2p_{z_A} + (\sqrt{2}c_3)2p_{z_B} + (c_3)2p_{z_C}$. We can pick a particular solution by normalizing to get $c_3 = 1/2$, yielding

$$\boxed{\psi_1 = \frac{1}{2}2p_{z_A} + \frac{1}{\sqrt{2}}2p_{z_B} + \frac{1}{2}2p_{z_C}}$$

Repeating the process for E_2 and E_3 gives

$$\psi_2 = -\frac{1}{\sqrt{2}}2p_{z_A} + \frac{1}{\sqrt{2}}2p_{z_C}$$

$$\psi_3 = \frac{1}{2}2p_{z_A} - \frac{1}{\sqrt{2}}2p_{z_B} + \frac{1}{2}2p_{z_C}$$

□

(b) Cyclobutadiene;

Answer. The Huckel approximation system for cyclobutadiene is identical to the four-dimensional generalization of the system used in part (a), except that the bottom-left and upper-right matrix elements are β instead of zero, reflecting the fact that cyclobutadiene is ring-shaped and thus the $2p_{z_A}$ and $2p_{z_D}$ orbitals are actually adjacent. Symbolically, the system is

$$\begin{pmatrix} \alpha - E & \beta & 0 & \beta \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ \beta & 0 & \beta & \alpha - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

We may proceed from here in an identical fashion to part (a) to learn that

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

$$= x^2(x+2)(x-2)$$

$$E = \alpha - (0, \pm 2)\beta$$

i.e.,

$$\boxed{E_1 = \alpha + 2\beta} \qquad\qquad \boxed{E_2 = E_3 = \alpha} \qquad\qquad \boxed{E_4 = \alpha - 2\beta}$$

As before, these values then yield

$$\psi_1 = \frac{1}{2}(2p_{z_A} + 2p_{z_B} + 2p_{z_C} + 2p_{z_D})$$

Solving for ψ_2 and ψ_3 is somewhat more complicated however due to the degeneracy of their corresponding energies. Indeed, applying Gauss-Jordan elimination with either E_2 or E_3 plugged in gives a two-dimensional null space (i.e., two linearly independent families of solutions) described by

$$\psi_{2,3} = (-c_3)2p_{z_A} + (-c_4)2p_{z_B} + (c_3)2p_{z_C} + (c_4)2p_{z_D}$$

However, since wave functions should be orthogonal, choose $c_4 = 0$ for ψ_2 and $c_3 = 0$ for ψ_3, i.e., choose

$$\psi_2 = (-c_3)2p_{z_A} + (c_3)2p_{z_C} \qquad\qquad \psi_3 = (-c_4)2p_{z_B} + (c_4)2p_{z_D}$$

Normalizing then yields

$$\psi_2 = -\frac{1}{\sqrt{2}}2p_{z_A} + \frac{1}{\sqrt{2}}2p_{z_C}$$

$$\psi_3 = -\frac{1}{\sqrt{2}}2p_{z_B} + \frac{1}{\sqrt{2}}2p_{z_D}$$

Lastly, we can still solve for ψ_4 as we did in part (a):

$$\psi_4 = \frac{1}{2}(-2p_{z_A} + 2p_{z_B} - 2p_{z_C} + 2p_{z_D})$$

□

(c) The cyclopentadienyl radical.

Answer. Here, we proceed in an entirely analogous method to the previous two parts. No new modifications are needed. Indeed, we find the energies via

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

$$= (x+2)(x^2 - 2 - 1)^2$$

$$E = \alpha - \left(-2, \frac{1 \pm \sqrt{5}}{2}\right)\beta$$

to be

$$\boxed{E_1 = \alpha + 2\beta} \qquad \boxed{E_2 = E_3 = \alpha - \frac{1 - \sqrt{5}}{2}\beta} \qquad \boxed{E_4 = E_5 = \alpha - \frac{1 + \sqrt{5}}{2}\beta}$$

Gauss-Jordan elimination, picking orthogonal bases where necessary, and normalization then yields

$$\boxed{\psi_1 = \frac{1}{\sqrt{5}}(2p_{z_A} + 2p_{z_B} + 2p_{z_C} + 2p_{z_D} + 2p_{z_E})}$$

$$\boxed{\psi_2 = -\frac{1}{\sqrt{5 - \sqrt{5}}}2p_{z_A} - \frac{\sqrt{5}\sqrt{5 - \sqrt{5}}}{10}2p_{z_B} + \frac{\sqrt{5}\sqrt{5 - \sqrt{5}}}{10}2p_{z_C} + \frac{1}{\sqrt{5 - \sqrt{5}}}2p_{z_D}}$$

$$\boxed{\psi_3 = \frac{\sqrt{5}\sqrt{5 - \sqrt{5}}}{10}2p_{z_A} - \frac{\sqrt{5}\sqrt{5 - \sqrt{5}}}{10}2p_{z_B} + \frac{1}{\sqrt{5 - \sqrt{5}}}2p_{z_C} + \frac{1}{\sqrt{5 - \sqrt{5}}}2p_{z_E}}$$
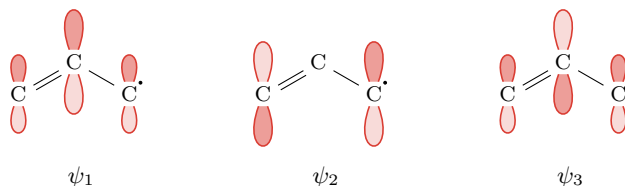
$$\boxed{\psi_4 = -\frac{1}{\sqrt{5 + \sqrt{5}}}2p_{z_A} - \frac{\sqrt{5}\sqrt{5 + \sqrt{5}}}{10}2p_{z_B} + \frac{\sqrt{5}\sqrt{5 + \sqrt{5}}}{10}2p_{z_C} + \frac{1}{\sqrt{5 + \sqrt{5}}}2p_{z_D}}$$

$$\boxed{\psi_5 = \frac{\sqrt{5}\sqrt{5 + \sqrt{5}}}{10}2p_{z_A} - \frac{\sqrt{5}\sqrt{5 + \sqrt{5}}}{10}2p_{z_B} + \frac{1}{\sqrt{5 + \sqrt{5}}}2p_{z_C} + \frac{1}{\sqrt{5 + \sqrt{5}}}2p_{z_E}}$$
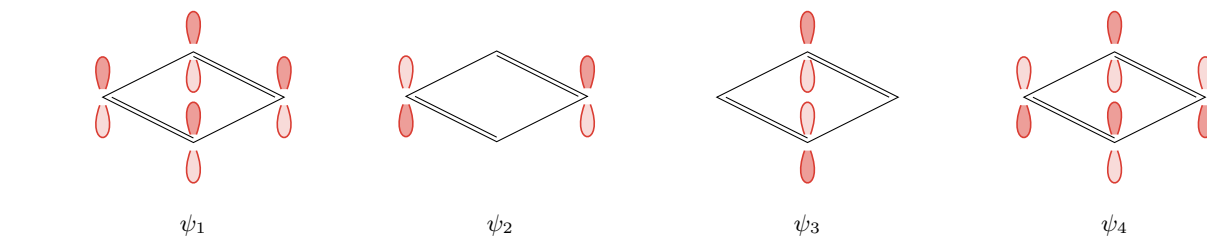
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(d) For each wave function computed in parts (a), (b), and (c), give a schematic sketch of the molecular orbital contributions. Refer to Figure 10.23 on McQuarrie and Simon (1997, p. 396) for an example of such a sketch.
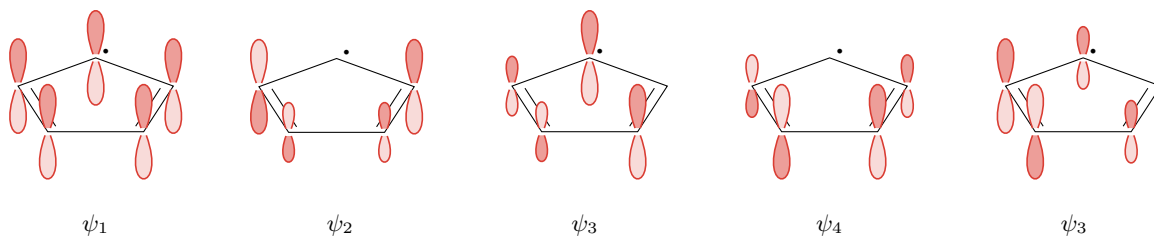
Answer.

ψ_1 ψ_2 ψ_3

Part (a).

ψ_1 ψ_2 ψ_3 ψ_4

Part (b).

ψ_1 ψ_2 ψ_3 ψ_4 ψ_3

Part (c).