Chapter 8 Answers

1. (a) $\Psi(2,1,3,4) = -\Psi(1,2,3,4)$

   (b) $\Psi(2,4,3,1) = -\Psi(1,4,3,2) = \Psi(1,2,3,4)$

2. In the Hartree-Fock description for the 2n electron system, the Fock operator is written as

$$\hat{F} = \hat{h} + \sum_{i=1}^{n} (2\hat{J}_i - \hat{K}_i)$$

Therefore, for an occupied MO ϕ_k, its energy e_k is given by

$$e_k = \langle \phi_k | \hat{F} | \phi_k \rangle = \langle \phi_k | \hat{h} + \sum_{i=1}^{n} (2\hat{J}_i - \hat{K}_i) | \phi_k \rangle = h_k + \sum_{i=1}^{n} (2J_{ik} - K_{ik})$$

For any occupied MO ϕ_k, there occurs the cancellation $2J_{kk} - K_{kk} = J_{kk}$. However, for an unoccupied MO ϕ_k, there is no such cancellation. Thus, the occupied orbital energy e_k refers to the effective potential an electron in the MO ϕ_k feels. However, the unoccupied orbital energy e_m refers to the effective potential an electron in the MO ϕ_m would feel if we were to add an electron in ϕ_m. Therefore, the occupied orbital energies refer to the effective potentials generated by 2n – 1 electrons, but the unoccupied orbital energies to the effective potentials generated by 2n electrons.

3. As described in problem [2], the Hartree-Fock potential overestimates optical energy gaps, while the DFT functional underestimate them. By employing the hybrid functional in DFT calculations, one can obtain a reasonable description of optical energy gaps. This approach amounts to introducing an empirical parameter (e.g., how much HF potential one should mix?) into the first principles electronic structure calculation.

4. a) The MO's of the reactant (H_2 + D_2) and the product (2 HD) were given in Fig. 5.5. The symmetries (S: symmetric, A: antisymmetric) of the MO's can be classified with respect to the mirror planes of symmetry m first and m' second. Then the MO correlation diagram is given as shown in Fig. 1b.

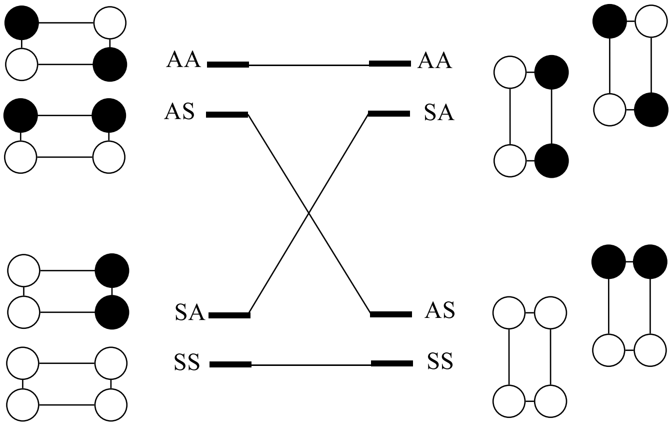

Fig. 1b

1) The MO correlation diagram for the thermal reaction is shown in Fig. 1c,

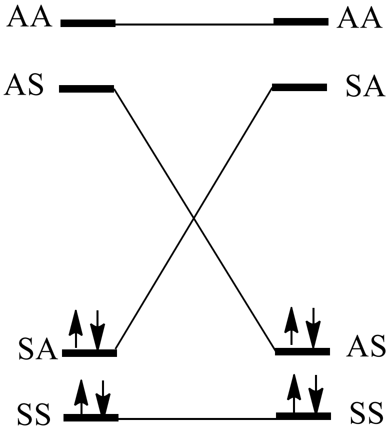

Fig. 1c

where an occupied MO of the reactant becomes an unoccupied MO of the product as the reaction proceeds. Therefore, this reaction is symmetry-forbidden.

2) The MO correlation diagram for the photochemical reaction is shown in Fig. 1d,

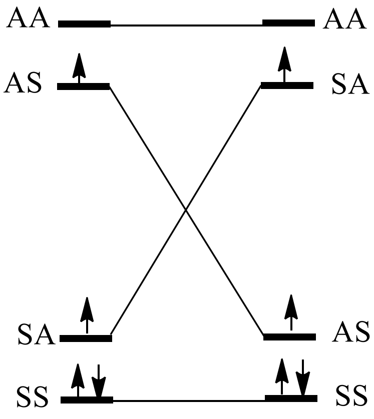

Fig. 1d

where all occupied MOs of the reactant become occupied MO of the product as the reaction proceeds. Therefore, this reaction is symmetry-allowed.

b) Let us now construct the state correlation diagram. On the reactant and product sides, the ground and firs-excited states are given by

Reactant: $\Psi_G = (SS)^2(SA)^2$, $\Psi_{E1} = (SS)^2(SA)^1(AS)^1$

Product: $\Phi_G = (SS)^2(AS)^2$, $\Phi_{E1} = (SS)^2(SA)^1(AS)^1$

According to the MO correlation diagram, the Ψ_G of the reactant becomes the higher excited state Φ_{E2} of the product, and the Φ_G of the product becomes the higher excited state Ψ_{E2} of the reactant. Consequently, the state correlation diagram is given as shown in Fig. 1e,

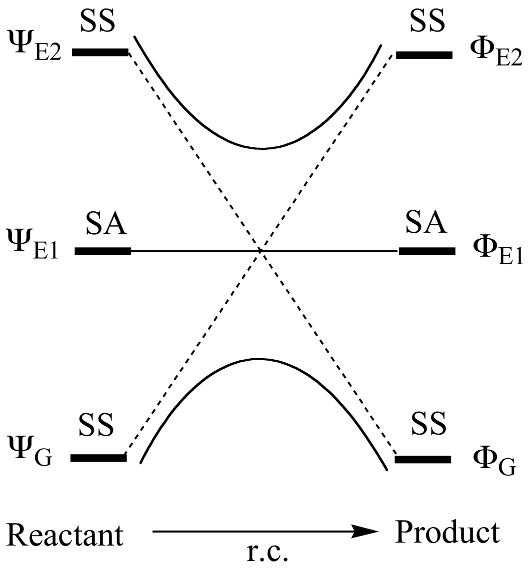

Fig. 1e

the dashed lines represent the intended correlation. However, the Ψ_G, Ψ_{E2}, Φ_G and Φ_{E2} states have the same symmetry, so that the intended crossing is forbidden. As a consequence, the thermal reaction is symmetry-forbidden because it shows an activation energy along the reaction coordinate, whereas the photochemical reaction is symmetry-allowed because it shows no activation energy along the reaction coordinate.

5. a) The MO's of the reactant (cis-butadiene) and the product (cyclobutene) are given in Fig. 2b, where the symmetries (S: symmetric, A: antisymmetric) of the MO's are classified with respect to the mirror planes of symmetry m.

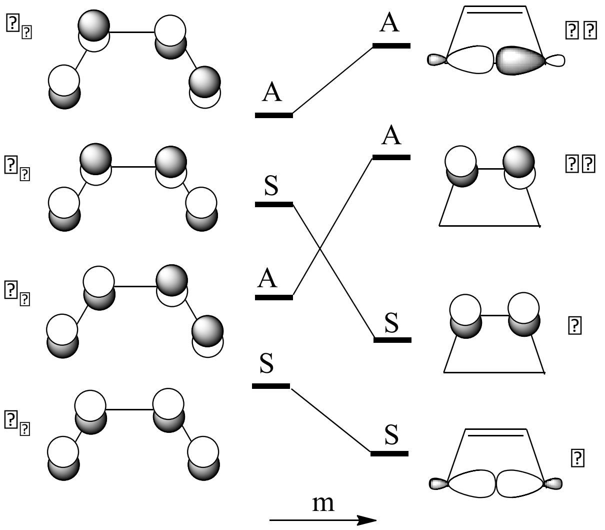

Fig. 2b

1) The MO correlation diagram for the thermal reaction is shown in Fig. 2c,

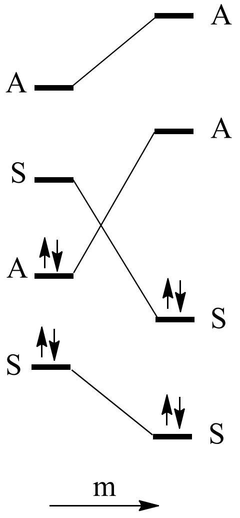

Fig. 2c

where an occupied MO of the reactant becomes an unoccupied MO of the product as the reaction proceeds. Therefore, this reaction is symmetry-forbidden.

2) The MO correlation diagram for the photochemical reaction is shown in Fig. 2d,

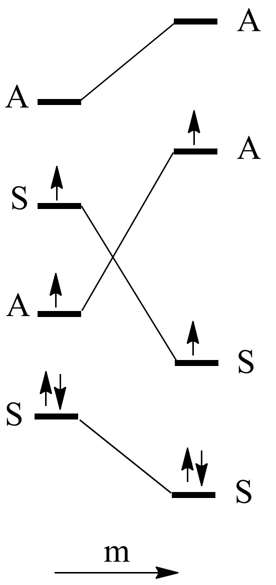

Fig. 2d

where all occupied MOs of the reactant become occupied MO of the product as the reaction proceeds. Therefore, this reaction is symmetry-allowed.

(b) Let us now construct the state correlation diagram. On the reactant and product sides, the ground and firs-excited states are given by

Reactant: $\Psi_G = (\phi_1)^2(\phi_2)^2$, $\Psi_{E1} = (\phi_1)^2(\phi_2)^1(\phi_3)^1$

Product: $\Phi_G = (\sigma)^2(\pi)^2$, $\Phi_{E1} = (\sigma)^2(\pi)^1(\pi*)^1$

According to the MO correlation diagram, the Ψ_G of the reactant becomes the higher excited state Φ_{E2} of the product, and the Φ_G of the product becomes the higher excited state Ψ_{E2} of the reactant. Consequently, the state correlation diagram is given as shown in Fig. 2e,

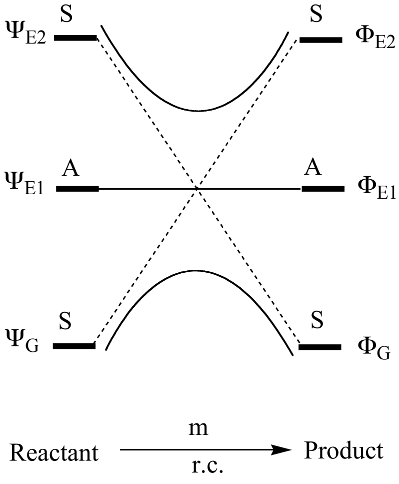

Fig. 2e

the dashed lines represent the intended correlation. However, the Ψ_G, Ψ_{E2}, Φ_G and Φ_{E2} states have the same symmetry, so that the intended crossing is forbidden. As a consequence, the thermal reaction is symmetry-forbidden because it shows an activation energy along the reaction coordinate, whereas the photochemical reaction is symmetry-allowed because it shows no activation energy along the reaction coordinate.

[6] (a) The MO's of the reactant (cis-butadiene) and the product (cyclobutene) are given in Fig. 3b, where the symmetries (S: symmetric, A: antisymmetric) of the MO's are classified with respect to the two-fold rotational symmetry C_2.

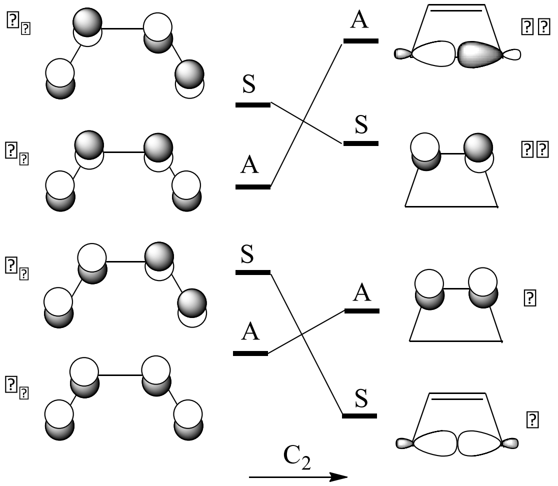

Fig. 3b

1) The MO correlation diagram for the thermal reaction is shown in Fig. 3c,

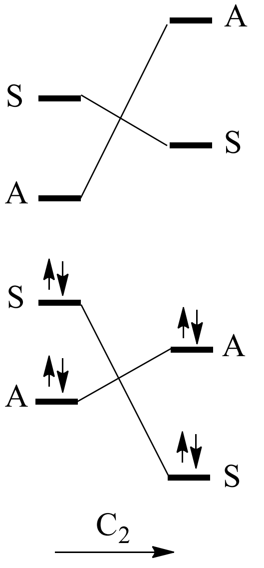

Fig. 3c

where all occupied MOs of the reactant become occupied MO of the product as the reaction proceeds. Therefore, this reaction is symmetry-allowed.

2) The MO correlation diagram for the photochemical reaction is shown in Fig. 3d,

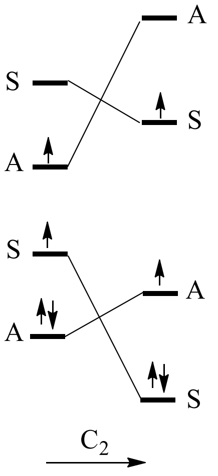

Fig. 3d

where an occupied MO of the reactant becomes an unoccupied MO of the product as the reaction proceeds. Therefore, this reaction is symmetry-forbidden. (b) Let us now construct the state correlation diagram. On the reactant and product sides, the ground and firs-excited states are given by

Reactant: $\Psi_G = (\phi_1)^2(\phi_2)^2$, $\Psi_{E1} = (\phi_1)^2(\phi_2)^1(\phi_3)^1$

Product: $\Phi_G = (\sigma)^2(\pi)^2$, $\Phi_{E1} = (\sigma)^2(\pi)^1(\pi*)^1$

According to the MO correlation diagram, the Ψ_G of the reactant becomes the Φ_G of the product, and the first excited state Φ_{E1} of the reactant becomes the higher excited state Ψ_{E2} of the product. Consequently, the state correlation diagram is given as shown in Fig. 3e,

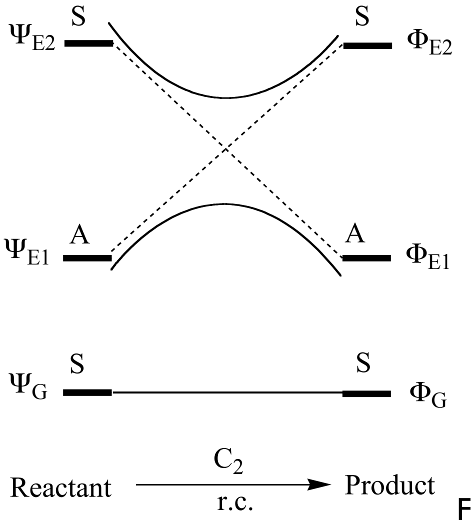

Fig. 3e

the dashed lines represent the intended correlation. However, the Ψ_{E1}, Ψ_{E2}, Φ_{E1} and Φ_{E2} states have the same symmetry, so that the intended crossing is forbidden. As a consequence, the thermal reaction is symmetry-allowed because it shows no activation energy along the reaction coordinate whereas the photochemical reaction is symmetry-forbidden because it shows an activation energy along the reaction coordinate.