

Chapter 2

Electronic Structures of Symmetric Diradical Systems

Abstract In general, the electronic structures of a molecular system is characterized by using the “diradical character”, which is well defined in quantum chemistry and implies a chemical index of a bond nature. In this chapter, we present analytical expressions for electronic energies and wavefunctions of the ground- and excited states as well as for the excitation energies and transition properties based on symmetric two-site diradical models with different diradical characters using the valence configuration interaction method.

Keywords Symmetric diradical system • Diradical character • Excitation energy • Transition moment • Valence configuration interaction

2.1 Symmetric Diradical Model Using the Valence Configuration Interaction Method

In this section, we consider a symmetric two-site diradical molecular model, $\dot{A} - \dot{B}$ with two electrons in two active orbitals, which can present the essential features of the electronic structures of general diradical molecules including open-shell polycyclic aromatic hydrocarbons (PAHs) [1, 2], transition-metal dinuclear systems [3–7] and so on. The symmetry-adapted bonding (g) and anti-bonding (u) molecular orbitals (MOs), which are the natural orbitals (NOs) obtained from the spin-unrestricted, i.e., broken-symmetry (BS), solutions like the spin-unrestricted Hartree-Fock (UHF) solution, are described using the atomic orbitals (AO), χ_A and χ_B (which are mutually nonorthogonal and have an overlap S_{AB}):

$$\begin{aligned} g(x) &= \frac{1}{\sqrt{2(1+S_{AB})}} [\chi_A(x) + \chi_B(x)], \quad \text{and} \\ u(x) &= \frac{1}{\sqrt{2(1-S_{AB})}} [\chi_A(x) - \chi_B(x)]. \end{aligned} \quad (2.1.1)$$

The localized natural orbital (LNO) is defined as [8, 9]

$$\begin{aligned} a(x) &\equiv \frac{1}{\sqrt{2}}[g(x) + u(x)] \approx \chi_A(x), \quad \text{and} \\ b(x) &\equiv \frac{1}{\sqrt{2}}[g(x) - u(x)] \approx \chi_B(x). \end{aligned} \quad (2.1.2)$$

which are well localized on one site (A or B), while have generally small tails on the other site, satisfying the orthogonal condition, $\langle a|b \rangle = 0$. In the dissociation limit ($S_{AB} = 0$), the LNOs are apparently identical with the AOs. Using these two types of basis sets, we describe the singlet BS MO solution. The BS MOs for the α and β spins (referred to as ψ_H^α and ψ_H^β , respectively) are described using symmetry-adapted MOs, g and u , by [10–12]

$$\psi_H^\alpha = (\cos \theta)g + (\sin \theta)u, \quad \text{and} \quad \psi_H^\beta = (\cos \theta)g - (\sin \theta)u. \quad (2.1.3)$$

where θ is a mixing parameter of g and u and takes a value between 0 and $\pi/4$. In another way using the LNOs, a and b , the BS MOs are given by [10–12]

$$\psi_H^\alpha = (\cos \omega)a + (\sin \omega)b, \quad \text{and} \quad \psi_H^\beta = (\cos \omega)b + (\sin \omega)a, \quad (2.1.4)$$

where $\omega (0 \leq \omega \leq \pi/4)$ is a mixing parameter of these LNOs ($\approx$ AOs). In the case of $\theta = 0 (\omega = \pi/4)$, the BS MOs are reduced to the symmetry-adapted MO, $\psi_H^\alpha = \psi_H^\beta = g$. In contrast, in the case of $\theta = \pi/4 (\omega = 0)$, the BS MOs correspond to the LNOs, $\psi_H^\alpha = a$ and $\psi_H^\beta = b$. Thus, we can consider the two limits: (i) weak correlation limit (MO limit) at $\theta = 0 (\omega = \pi/4)$, giving symmetry-adapted closed-shell MO (g), and (ii) strong correlation limit [valence bond (VB) limit] at $\theta = \pi/4 (\omega = 0)$, giving LNOs (a and b). Namely, the different orbitals for different spins (DODS) MOs represented by Eqs. (2.1.3) and (2.1.4) can describe both weak and strong correlation limits, i.e., MO and VB limits, as well as the intermediate correlation regime [10–12].

Let us consider a symmetric two-site diradical system with two electrons in two orbitals, g and u (a and b) and the z -component of spin angular momentum $M_s = 0$ (singlet and triplet). For $M_s = 0$, there are two neutral and ionic determinants:

$$|a\bar{b}\rangle \equiv |\text{core } a\bar{b}\rangle, \quad |\bar{b}a\rangle \equiv |\text{core } \bar{b}a\rangle \quad (\text{neutral}), \quad (2.1.5a)$$

and

$$|a\bar{a}\rangle \equiv |\text{core } a\bar{a}\rangle, \quad \text{and} \quad |b\bar{b}\rangle \equiv |\text{core } b\bar{b}\rangle \quad (\text{ionic}), \quad (2.1.5b)$$

where core denotes the closed-shell inner orbitals, and the upper- and non-bar indicate β and α spins, respectively. The electronic Hamiltonian H (in atomic units (a.u.), $\hbar = m = e = 1$) for this model system is represented by

$$H = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^2 \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} = \sum_{i=1}^N h(i) + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}}. \quad (2.1.6)$$

The valence configuration interaction (VCI) matrix of this Hamiltonian using the LNO basis takes the form [8, 9]:

$$\begin{pmatrix} \langle a\bar{b}|H|a\bar{b} \rangle & \langle a\bar{b}|H|b\bar{a} \rangle & \langle a\bar{b}|H|a\bar{a} \rangle & \langle a\bar{b}|H|b\bar{b} \rangle \\ \langle b\bar{a}|H|a\bar{b} \rangle & \langle b\bar{a}|H|b\bar{a} \rangle & \langle b\bar{a}|H|a\bar{a} \rangle & \langle b\bar{a}|H|b\bar{b} \rangle \\ \langle a\bar{a}|H|a\bar{b} \rangle & \langle a\bar{a}|H|b\bar{a} \rangle & \langle a\bar{a}|H|a\bar{a} \rangle & \langle a\bar{a}|H|b\bar{b} \rangle \\ \langle b\bar{b}|H|a\bar{b} \rangle & \langle b\bar{b}|H|b\bar{a} \rangle & \langle b\bar{b}|H|a\bar{a} \rangle & \langle b\bar{b}|H|b\bar{b} \rangle \end{pmatrix} \quad (2.1.7)$$

$$= \begin{pmatrix} 0 & K_{ab} & t_{ab} & t_{ab} \\ K_{ab} & 0 & t_{ab} & t_{ab} \\ t_{ab} & t_{ab} & U & K_{ab} \\ t_{ab} & t_{ab} & K_{ab} & U \end{pmatrix},$$

where the energy of the neutral determinant, $\langle a\bar{b}|H|a\bar{b} \rangle = \langle b\bar{a}|H|b\bar{a} \rangle$, is taken as the energy origin (0). U denotes the difference between on- and neighbor-site Coulomb repulsions [$U \equiv U_{aa} - U_{bb} = (aa|aa) - (bb|bb)$]. K_{ab} is a direct exchange integral [$K_{ab} = (ab|ba) \geq 0$], and t_{ab} is a transfer integral [$t_{ab} = \langle a\bar{b}|H|b\bar{b} \rangle = \langle a|f|b \rangle \leq 0$, where f is the Fock operator in the LNO representation] [9]. Each matrix element is derived as follows.

$$\begin{aligned} \langle a\bar{b}|H|a\bar{b} \rangle &= \langle a\bar{b} | \sum_{i=1}^N h(i) | a\bar{b} \rangle + \langle a\bar{b} | \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} | a\bar{b} \rangle \\ &= \langle a|h|a \rangle + \langle b|h|b \rangle + \sum_c^{\text{core}} \langle c|h|c \rangle + \frac{1}{2} \langle a\bar{b} || a\bar{b} \rangle \\ &\quad + \frac{1}{2} \langle \bar{b}a || \bar{b}a \rangle + \frac{1}{2} \sum_c^{\text{core}} \langle ac || ac \rangle + \frac{1}{2} \sum_c^{\text{core}} \langle ca || ca \rangle \\ &\quad + \frac{1}{2} \sum_c^{\text{core}} \langle \bar{b}c || \bar{b}c \rangle + \frac{1}{2} \sum_c^{\text{core}} \langle c\bar{b} || c\bar{b} \rangle + \frac{1}{2} \sum_c^{\text{core}} \sum_{c'}^{\text{core}} \langle cc' || cc' \rangle \\ &= \langle a|h|a \rangle + \langle b|h|b \rangle + \frac{1}{2} \langle a\bar{b} || a\bar{b} \rangle + \frac{1}{2} \langle \bar{b}a || \bar{b}a \rangle + (\text{core}) \\ &= (a|h|a) + (b|h|b) + \frac{1}{2} \{ (aa|bb) + (bb|aa) \} + (\text{core}) \\ &= 2h_{aa} + U_{ab} + (\text{core}), \end{aligned} \quad (2.1.8a)$$

where all the terms concerning the core are denoted by “(core)”, and $h_{aa}[\equiv \langle a|h|a \rangle] = h_{bb}$ due to the symmetry of the model system. Similarly, we obtain

$$\langle b\bar{a}|H|b\bar{a} \rangle = 2h_{aa} + U_{ab} + (\text{core}). \quad (2.1.8b)$$

Since these energies are defined as the energy origin [$2h_{aa} + U_{ab} + (\text{core}) = 0$], the energies of ionic determinants are represented by

$$\begin{aligned} \langle a\bar{a}|H|a\bar{a} \rangle &= \langle b\bar{b}|H|b\bar{b} \rangle = 2h_{aa} + U_{aa} + (\text{core}) \\ &= U_{aa} - U_{ab} = U, \end{aligned} \quad (2.1.8c)$$

where we use the relations: $\sum_c^{\text{core}} \langle ac||ac \rangle = \sum_c^{\text{core}} \langle bc||bc \rangle$, $h_{aa} = h_{bb}$ and $U_{aa} = U_{bb}$, which come from the symmetry of the present system.

For off-diagonal elements, we obtain

$$\langle a\bar{b}|H|b\bar{a} \rangle = \langle b\bar{a}|H|a\bar{b} \rangle = \langle a\bar{b}||b\bar{a} \rangle = (ab|ba) = K_{ab}, \quad (2.1.8d)$$

$$\begin{aligned} \langle a\bar{b}|H|a\bar{a} \rangle &= \langle a\bar{a}|H|a\bar{b} \rangle = \langle \bar{b}|h|\bar{a} \rangle + \langle \bar{b}a||\bar{a}a \rangle \\ &+ \sum_c^{\text{core}} \langle \bar{b}c||\bar{a}c \rangle = \langle \bar{b}|\hat{f}|\bar{a} \rangle = t_{ab}, \end{aligned} \quad (2.1.8e)$$

$$\begin{aligned} \langle a\bar{b}|H|b\bar{b} \rangle &= \langle b\bar{b}|H|a\bar{b} \rangle = \langle b\bar{a}|H|a\bar{a} \rangle = \langle a\bar{a}|H|b\bar{a} \rangle \\ &= \langle b\bar{a}|H|b\bar{b} \rangle = \langle b\bar{b}|H|b\bar{a} \rangle = t_{ab}, \end{aligned} \quad (2.1.8f)$$

and

$$\langle a\bar{a}|H|b\bar{b} \rangle = \langle b\bar{b}|H|a\bar{a} \rangle = \langle a\bar{a}||b\bar{b} \rangle = (ab|ab) = K_{ab}, \quad (2.1.8g)$$

where $t_{ab} = t_{ba}$ is used. By diagonalizing the CI matrix of Eq. (2.1.7), the four solutions are obtained as follows [8].

(i) Neutral triplet state (u symmetry)

$$|T_{1u}\rangle = \frac{1}{\sqrt{2}}(|a\bar{b}\rangle - |b\bar{a}\rangle) \text{ with energy } {}^3E_{1u} = -K_{ab}. \quad (2.1.9)$$

This triple state consists of only neutral determinants and is pure diradical.

(ii) Ionic singlet state (u symmetry)

$$|S_{1u}\rangle = \frac{1}{\sqrt{2}}(|a\bar{a}\rangle - |b\bar{b}\rangle) \text{ with energy } {}^1E_{1u} = U - K_{ab}. \quad (2.1.10)$$

(iii) Lower singlet state (g symmetry)

$$|S_{1g}\rangle = \kappa(|a\bar{b}\rangle + |b\bar{a}\rangle) + \eta(|a\bar{a}\rangle + |b\bar{b}\rangle), \quad (2.1.11a)$$

where $2(\kappa^2 + \eta^2) = 1$ and $\kappa > \eta > 0$. The energy is

$${}^1E_{1g} = K_{ab} + \frac{U - \sqrt{U^2 + 16t_{ab}^2}}{2}. \quad (2.1.11b)$$

In this state, $2\kappa^2$ and $2\eta^2$ represent the weight of neutral and ionic contributions, respectively, and the weight of neutral determinant is larger than that of ionic one.

(iv) Higher singlet state (g symmetry)

$$|S_{2g}\rangle = -\eta(|a\bar{b}\rangle + |b\bar{a}\rangle) + \kappa(|a\bar{a}\rangle + |b\bar{b}\rangle), \quad (2.1.12a)$$

where $2(\kappa^2 + \eta^2) = 1$ and $\kappa > \eta > 0$. The energy is

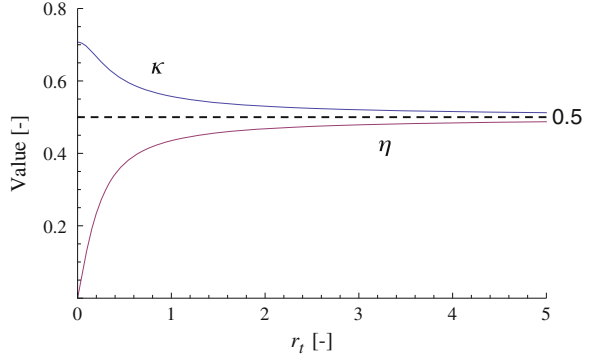
$${}^1E_{2g} = K_{ab} + \frac{U + \sqrt{U^2 + 16t_{ab}^2}}{2}. \quad (2.1.12b)$$

In this state, $2\kappa^2$ and $2\eta^2$ represent the weight of ionic and neutral contributions, respectively, and the weight of ionic determinant is larger than that of neutral one.

Here, we obtain [13]

$$\begin{aligned} \kappa &= \frac{1}{2} \sqrt{1 + \frac{U}{\sqrt{U^2 + 16t_{ab}^2}}} \quad \text{and} \\ \eta &= \frac{2|t_{ab}|}{\sqrt{(U + \sqrt{U^2 + 16t_{ab}^2})\sqrt{U^2 + 16t_{ab}^2}}}. \end{aligned} \quad (2.1.13)$$

Fig. 2.1 Variations of κ and η with respect to r_t



If we define r_t as $r_t \equiv |t_{ab}/U|$, κ and η are rewritten as [13],

$$\kappa = \frac{1}{2} \sqrt{1 + \frac{1}{\sqrt{1 + 16r_t^2}}} \quad \text{and} \quad \eta = \frac{2r_t}{\sqrt{(1 + \sqrt{1 + 16r_t^2})\sqrt{1 + 16r_t^2}}}. \quad (2.1.14)$$

A large t_{ab} and a small U , which lead to a large r_t , correspond to the ease of the electron transfer between sites A and B. Figure 2.1 shows the variations of κ and η with respect to r_t . As decreasing r_t , the coefficient (κ) of the neutral determinant increases toward $1/\sqrt{2}$ at $r_t = 0$, while that (η) of the ionic determinant decreases toward 0 at $r_t = 0$. This indicates that the mobility of electrons between sites A and B governs the relative neutral (covalent) and ionic natures of the state, resulting in determining the diradical nature.

2.2 Diradical Character of Symmetric Systems

2.2.1 Diradical Character in the VCI Model

The ground and excited states are also described using the symmetry-adapted MOs, g and u , [Eq. (2.1.1)] as

$$g(x) = \frac{1}{\sqrt{2}}[a(x) + b(x)] \quad \text{and} \quad u(x) = \frac{1}{\sqrt{2}}[a(x) - b(x)]. \quad (2.2.1)$$

We here employ the following determinants for $M_s = 0$ as an alternative basis to the LNO basis:

$ g\bar{g}\rangle$	ground-state configuration with two electrons in HOMO
$ g\bar{u}\rangle$ and $ u\bar{g}\rangle$	HOMO to LUMO singly excited configuration
$ u\bar{u}\rangle$	HOMO to LUMO doubly excited configuration

By employing these bases, we can obtain four wavefunctions for the z -component of spin angular momentum, $M_s = 0$, which are equivalent to those obtained by the VCI method using the LNOs [Eqs. (2.1.9), (2.1.10), (2.1.11a) and (2.1.12a)] [13]:

(i) Neutral triplet state (u symmetry)

$$|T_{1u}\rangle = \frac{1}{\sqrt{2}}(|g\bar{u}\rangle - |u\bar{g}\rangle) \quad (2.2.2)$$

(ii) Ionic singlet state (u symmetry)

$$|S_{1u}\rangle = \frac{1}{\sqrt{2}}(|g\bar{u}\rangle + |u\bar{g}\rangle) \quad (2.2.3)$$

(iii) Lower singlet state (g symmetry)

$$|S_{1g}\rangle = \xi|g\bar{g}\rangle - \zeta|u\bar{u}\rangle \quad (2.2.4)$$

(iv) Higher singlet state (g symmetry)

$$|S_{2g}\rangle = \zeta|g\bar{g}\rangle + \xi|u\bar{u}\rangle \quad (2.2.5)$$

By substituting Eq. (2.2.1) into Eq. (2.2.4), we obtain

$$\begin{aligned} |S_{1g}\rangle &= \xi|g\bar{g}\rangle - \zeta|u\bar{u}\rangle = \frac{1}{2}(\xi + \zeta)(|a\bar{b}\rangle + |b\bar{a}\rangle) \\ &\quad + \frac{1}{2}(\xi - \zeta)(|a\bar{a}\rangle + |b\bar{b}\rangle). \end{aligned} \quad (2.2.6)$$

By comparing the coefficients between Eqs. (2.1.11a) and (2.2.6), we obtain

$$\kappa = \frac{1}{2}(\xi + \zeta) \quad \text{and} \quad \eta = \frac{1}{2}(\xi - \zeta) \quad (2.2.7)$$

Therefore,

$$\zeta = \kappa - \eta. \quad (2.2.8)$$

The diradical character (y) is defined as twice the weight of the doubly excited configuration in the singlet ground state [14]:

$$y \equiv 2\zeta^2 = 1 - 4\kappa\eta. \quad (2.2.9)$$

Here, we use the orthonormal condition $2(\kappa^2 + \eta^2) = 1$ in Eq. (2.1.11a). By substituting Eq. (2.1.13) into Eq. (2.2.9), we obtain [13]

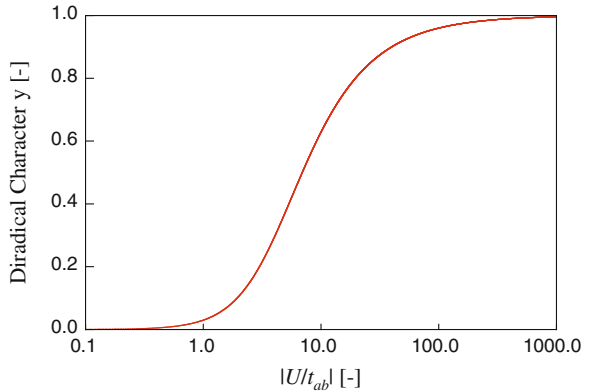
$$y = 1 - \frac{1}{\sqrt{1 + \left(\frac{U}{4t_{ab}}\right)^2}}, \quad (2.2.10)$$

which indicates that the diradical character is a function of U and t_{ab} . By using $r_t (= |t_{ab}/U|)$, y is rewritten as [13]

$$y = 1 - \frac{1}{\sqrt{1 + \left(\frac{1}{4r_t}\right)^2}}. \quad (2.2.11)$$

Figure 2.2 shows the variation of y as a function of $|t_{ab}/U| (\equiv 1/r_t)$. In the case of $|U/t_{ab}| \rightarrow \infty (r_t \rightarrow 0)$, y value approaches 1, while in the case of $|U/t_{ab}| \leq \sim 1 (r_t \geq \sim 1)$, it is close to 0. Because the transfer integral t_{ab} and the effective Coulomb repulsion U represent the ease and difficulty of electron transfer between sites A and B, respectively, $|U/t_{ab}| \rightarrow \infty (r_t \rightarrow 0)$ implies the localization of electrons on each site, leading to a pure diradical. On the contrary, the delocalization of electrons over two sites is realized for $|U/t_{ab}| \leq \sim 1 (r_t \geq \sim 1)$, corresponding to a stable bond. Variation in the mobility of electrons between sites A and B corresponds to that in the diradical character. For example, the elongation of the inter-site distance leads to the decrease in t_{ab} and the increase in U , which causes the decrease in r_t , i.e., the increase in y .

Fig. 2.2 Diradical character y versus $|U/t_{ab}| (= 1/r_t)$



2.2.2 Diradical Character in the Spin-Unrestricted Single Determinant Formalism with Spin-Projection Scheme

As mentioned in the previous section, although the diradical character (y) is originally defined in the multi-configuration (MC)-SCF theory by twice the weight of the doubly excited configuration in the singlet ground state [14], the MC-SCF methods are generally difficult to apply to many electron systems due to its huge computational demand. On the other hand, the single determinant scheme is computationally favorable, while the spin-restricted (symmetry-adapted) single determinant approaches like the spin-restricted Hartree-Fock (RHF) cannot be used for obtaining the y value because of its lack of multiply excited configurations. In contrast, the spin-unrestricted [broken-symmetry (BS)] single determinant approaches like the spin-unrestricted HF (UHF) can take account of the multiply excited configurations with low computational cost, which allows us to define the diradical character within this formalism. Nevertheless, the spin-unrestricted methods suffer from the spin contamination [15], which causes the unphysical inclusion of higher spin states like a triplet state in the singlet ground state. This could overshoot y value as compared to that at the MC-SCF level of theory, which gives correct spin states, since the triplet component originating from the spin contamination is a pure diradical state as shown by Eq. (2.1.9). Yamaguchi proposed an approximate spin-projection scheme, which effectively eliminates the spin contamination from the UHF solution, and presented an efficient calculation scheme of diradical character in the approximate spin-projected spin-unrestricted single determinant approaches [10, 11]. We here briefly explain this scheme.

The ground-state UHF wavefunction is written by

$$\Phi = |\psi_1^\alpha \psi_1^\beta \dots \psi_H^\alpha \psi_H^\beta\rangle, \quad (2.2.12)$$

where the MOs for the α and β spins (ψ_i^α and ψ_i^β , respectively) satisfy the orthonormal condition for each spin $\langle \psi_i^X | \psi_j^X \rangle = \delta_{ij}$ ($X = \alpha, \beta$), and “H” indicates the HOMO. The UHF MOs can be transformed to the corresponding orbitals (χ_i and η_i) with the unitary transformation [15] as

$$\chi_i = \sum_s \psi_s^\alpha U_{si} \quad \text{and} \quad \eta_j = \sum_s \psi_s^\beta V_{sj}, \quad (2.2.13)$$

the orbital overlap of which is diagonal, $T_{ij} = \langle \chi_i | \eta_j \rangle = T_i \delta_{ij}$. Because the wavefunction is invariant under the unitary transformation, the UHF wavefunction given by Eq. (2.2.13) is rewritten as

$$\Phi = |\chi_1 \bar{\eta}_1 \dots \chi_H \bar{\eta}_H\rangle. \quad (2.2.14)$$

The corresponding orbitals are connected with the natural orbitals (NOs) λ_i and μ_i of the UHF wavefunction by

$$\lambda_i = \frac{1}{\sqrt{2(1+T_i)}}(\chi_i + \eta_i) \quad \text{and} \quad \mu_i = \frac{1}{\sqrt{2(1-T_i)}}(\chi_i - \eta_i), \quad (2.2.15)$$

which satisfy the orthonormal condition:

$$\langle \lambda_i | \mu_j \rangle = 0 \quad \text{and} \quad \langle \lambda_i | \lambda_j \rangle = \langle \mu_i | \mu_j \rangle = \delta_{ij}. \quad (2.2.16)$$

From Eqs. (2.2.15) and (2.2.16), the corresponding orbitals χ_i and η_i are given with the NOs λ_i and μ_i as

$$\chi_i = \frac{\sqrt{2(1+T_i)}}{2} \lambda_i + \frac{\sqrt{2(1-T_i)}}{2} \mu_i. \quad (2.2.17)$$

and

$$\eta_i = \frac{\sqrt{2(1+T_i)}}{2} \lambda_i - \frac{\sqrt{2(1-T_i)}}{2} \mu_i. \quad (2.2.18)$$

Because the coefficients satisfy the following relation,

$$\left\{ \frac{\sqrt{2(1+T_i)}}{2} \right\}^2 + \left\{ \frac{\sqrt{2(1-T_i)}}{2} \right\}^2 = 1, \quad (2.2.19)$$

Equations (2.2.17) and (2.2.18) can be rewritten with a mixing parameter θ_i as,

$$\chi_i = \cos \theta_i \lambda_i + \sin \theta_i \mu_i \quad (2.2.20)$$

and

$$\eta_i = \cos \theta_i \lambda_i - \sin \theta_i \mu_i. \quad (2.2.21)$$

Here θ_i ranges from 0 to $\pi/4$ due to $\cos \theta_i \geq \sin \theta_i \geq 0$ [see Eq. (2.1.3)]. Using these equations, the overlap integral T_i is expressed by

$$T_i = \cos^2 \theta_i - \sin^2 \theta_i = \cos 2\theta_i, \quad (2.2.22)$$

where the orthonormal condition of NOs [Eq. (2.2.16)] is used.

We here confirm that λ_i and μ_i are the natural orbitals of the UHF wavefunction. Spin-less one-electron reduced density matrix of a N -electron system is defined as

$$\rho(\mathbf{r}_1, \mathbf{r}'_1) = N \int d\mathbf{r}_2 \dots d\mathbf{r}_N \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi^*(\mathbf{r}'_1, \mathbf{r}_2, \dots, \mathbf{r}_N). \quad (2.2.23)$$

For the Hartree–Fock wavefunction $\Psi^{\text{HF}} = |\phi_1 \dots \phi_N\rangle$, it is simplified as

$$\rho(\mathbf{r}_1, \mathbf{r}'_1) = \sum_a \phi_a(\mathbf{r}_1) \phi_a^*(\mathbf{r}'_1). \quad (2.2.24)$$

Since the wavefunction is invariant under the unitary transformation, $\rho(\mathbf{r}_1, \mathbf{r}'_1)$ of the UHF wavefunction can be given with the UHF MOs (ψ^α and ψ^β) and the corresponding orbitals (χ_i and η_i) as

$$\begin{aligned} \rho(\mathbf{r}_1, \mathbf{r}'_1) &= \sum_i \psi_i^\alpha(\mathbf{r}_1) \psi_i^{\alpha*}(\mathbf{r}'_1) + \sum_i \psi_i^\beta(\mathbf{r}_1) \psi_i^{\beta*}(\mathbf{r}'_1) \\ &= \sum_i \chi_i(\mathbf{r}_1) \chi_i^*(\mathbf{r}'_1) + \sum_i \eta_i(\mathbf{r}_1) \eta_i^*(\mathbf{r}'_1) \\ &= \sum_i 2\cos^2\theta_i \lambda_i(\mathbf{r}_1) \lambda_i^*(\mathbf{r}'_1) + \sum_i 2\sin^2\theta_i \mu_i(\mathbf{r}_1) \mu_i^*(\mathbf{r}'_1) \\ &= \sum_i (1 + T_i) \lambda_i(\mathbf{r}_1) \lambda_i^*(\mathbf{r}'_1) + \sum_i (1 - T_i) \mu_i(\mathbf{r}_1) \mu_i^*(\mathbf{r}'_1), \end{aligned} \quad (2.2.25)$$

where Eqs. (2.2.20)–(2.2.22) are used. From the last equality, λ_i and μ_i are shown to be natural orbitals of the UHF solution with the occupation numbers of $1 + T_i$ and $1 - T_i$, respectively. A corresponding orbital pair (χ_i and η_i) constructs a pair of NOs (λ_i and μ_i), where one of the NO pair (λ_i) possesses an occupation number more than 1 ($1 + T_i$), while the occupation of the other NO (μ_i) is less than 1 ($1 - T_i$). Namely, the total occupation of a NO pair is shown to be always 2 in the single determinant formalism. Also, the bonding and anti-bonding orbitals for the triplet state of this model obtained by the UHF method coincide with the NOs λ_i and μ_i , respectively, due to $T_i = 0$.

For singlet diradical systems with two electrons in the two highest occupied corresponding orbitals (χ_H and η_H), the wavefunction of the UHF ground state is described by using the corresponding orbitals as

$$\Phi^{\text{UHF}} = |\chi_H \bar{\eta}_H\rangle. \quad (2.2.26)$$

By substituting Eqs. (2.2.20) and (2.2.21) into this equation, Φ^{UHF} is represented with NOs as

$$\begin{aligned} \Phi^{\text{UHF}} &= \cos^2\theta |\lambda_H \bar{\lambda}_H\rangle - \sin^2\theta |\mu_L \bar{\mu}_L\rangle - \cos\theta \sin\theta (|\lambda_H \bar{\mu}_L\rangle - |\mu_L \bar{\lambda}_H\rangle) \\ &= \frac{1+T}{2} |\lambda_H \bar{\lambda}_H\rangle - \frac{1-T}{2} |\mu_L \bar{\mu}_L\rangle - \sqrt{\frac{1-T^2}{2}} \left\{ \frac{1}{\sqrt{2}} (|\lambda_H \bar{\mu}_L\rangle - |\mu_L \bar{\lambda}_H\rangle) \right\}, \end{aligned} \quad (2.2.27)$$

where Eq. (2.2.22) ($T \equiv T_H$) is used. The first term in the right-hand side of Eq. (2.2.27) represents the RHF ground configuration, while the second one indicates the doubly excited configuration from the highest occupied NO to the lowest unoccupied NO. Both of these terms represent singlet states. The UHF singlet ground state includes the RHF ground and doubly excited configurations, which enable the UHF method to describe the diradical nature of systems. On the other hand, the third term, composed of singly excited configurations, represents the triplet component, which is the origin of spin contamination in UHF wavefunctions.

As mentioned in Sect. 2.2.1, the diradical character is defined by twice the weight of the doubly excited configuration. We can define the diradical character of the UHF ground state from Eq. (2.2.27) based on this definition. Since the UHF wavefunction suffers from the spin contamination, we need to remove the triplet component to obtain a pure singlet wavefunction, the procedure of which is referred to as the spin-projection [10–12]. For simplicity, Φ^{UHF} is rewritten by

$$\Phi^{\text{UHF}} = C_I \Phi_G + C_{II} \Phi_S + C_{III} \Phi_D, \quad (2.2.28)$$

where $C_I = (1 + T)/2$, $C_{II} = -\sqrt{(1 - T^2)/2}$, and $C_{III} = -(1 - T)/2$. The first, second and third terms in the right-hand side of Eq. (2.2.28) denote the ground, singly excited and doubly excited configurations, respectively. The removal of the second term (triplet) from the UHF wavefunction with keeping the ratio of the coefficients of the first and third terms (C_I/C_{III}) provides the spin-projected UHF (PUHF) wavefunction,

$$\Phi^{\text{PUHF}} = C'_I \Phi_G + C'_{III} \Phi_D. \quad (2.2.29)$$

Here, the coefficients satisfy the relation: $C'_I/C'_{III} = C_I/C_{III}$. From the orthogonal condition of Φ^{UHF} , we obtain the relation,

$$\frac{C_I^2}{1 - C_{II}^2} + \frac{C_{III}^2}{1 - C_{II}^2} = 1. \quad (2.2.30)$$

From Eqs. (2.2.29) and (2.2.30), C'_I and C'_{III} can be determined by

$$C'_I = \frac{C_I}{\sqrt{1 - C_{II}^2}} \quad \text{and} \quad C'_{III} = \frac{C_{III}}{\sqrt{1 - C_{II}^2}}. \quad (2.2.31)$$

By inserting them into Eq. (2.2.29), we obtain

$$\Phi^{\text{PUHF}} = \frac{C_I}{\sqrt{1 - C_{II}^2}} \Phi_G + \frac{C_{III}}{\sqrt{1 - C_{II}^2}} \Phi_D = \frac{1 + T}{\sqrt{2(1 + T^2)}} \Phi_G - \frac{1 - T}{\sqrt{2(1 + T^2)}} \Phi_D. \quad (2.2.32)$$

Therefore, the diradical character in the PUHF formalism is defined by [10–12]

$$y^{\text{PUHF}} = 2C_{\text{III}}'^2 = 1 - \frac{2T}{1 + T^2}, \quad (2.2.33)$$

where the overlap integral T between the corresponding orbitals can be obtained from the occupation number of the LUNO: $n_{\text{LUNO}} = 1 - T$. From the one-electron reduced density matrix of the PUHF wavefunction, the spin-projected occupation numbers of the HONO and LUNO are represented by

$$n_{\text{HONO}}^{\text{PUHF}} = \frac{(1 + T)^2}{1 + T^2} = \frac{n_{\text{HONO}}^2}{1 + T^2} = 2 - y^{\text{PUHF}} \quad (2.2.34a)$$

and

$$n_{\text{LUNO}}^{\text{PUHF}} = \frac{(1 - T)^2}{1 + T^2} = \frac{n_{\text{LUNO}}^2}{1 + T^2} = y^{\text{PUHF}}, \quad (2.2.35b)$$

where $n_{\text{HONO}} = 1 + T$ and $n_{\text{LUNO}} = 1 - T$ are employed [see Eq. (2.2.25)]. Although these equations are defined in singlet diradical systems in relation to their HONO and LUNO, they can be extended to singlet multiradical systems. For a $2n$ -radical system, the perfect-pairing type (only considering a doubly excitation from HONO $- i$ to LUNO $+ i$) spin-projected diradical characters and occupation numbers are defined as follows [10–12].

$$y_i^{\text{PUHF}} = 1 - \frac{2T_i}{1 + T_i^2}, \quad (2.2.36)$$

and

$$n_{\text{HONO}-i}^{\text{PUHF}} = 2 - y_i^{\text{PUHF}}, \quad \text{and} \quad n_{\text{LUNO}+i}^{\text{PUHF}} = y_i^{\text{PUHF}}, \quad (2.2.37)$$

where T_i is obtained from the occupation number of LUNO $+ i$: $n_{\text{LUNO}+i} = 1 - T_i$.

2.3 Diradical Character Dependences of Excitation Energies and Transition Properties

We here consider only the singlet states for Chap. 4, where (hyper) polarizabilities of singlet molecular systems are discussed. The excitation energy of the triplet state $|T_{1u}\rangle$ is discussed in Chap. 5, which focuses on singlet fission. In a symmetric two-site diradical model ($A^\bullet - B^\bullet$) introduced in Sect. 2.1, there are three singlet

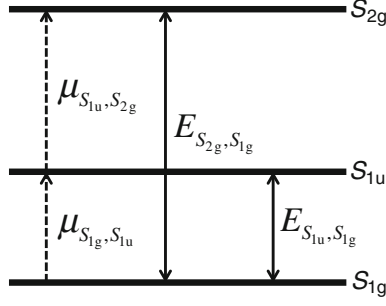


Fig. 2.3 Singlet states (S_{1g} , S_{1u} , S_{2g}) in a two-site diradical model. The excitation energies ($E_{S_{1u},S_{1g}}$, $E_{S_{2g},S_{1g}}$) and transition moments ($\mu_{S_{1g},S_{1u}}$, $\mu_{S_{1u},S_{2g}}$) are shown. The *dashed arrows* indicate optically-allowed transitions

states, $|S_{1g}\rangle$, $|S_{1u}\rangle$ and $|S_{2g}\rangle$. Because $|S_{1g}\rangle$ and $|S_{2g}\rangle$ have the same symmetry (g symmetry), the transition moment between these states disappears. Figure 2.3 shows the three-state model constructed from these singlet states together with the excitation energies and transition moments.

Firstly, we provide the analytical expressions of the excitation energies using several dimensionless physical quantities and diradical characters. Using Eqs. (2.1.10), (2.1.11b), (2.1.12b) and (2.2.11), we obtain [13]

$$\begin{aligned}
 E_{S_{1u},S_{1g}} &\equiv {}^1E_{1u} - {}^1E_{1g} = -2K_{ab} + U \left(1 - \frac{1 - \sqrt{1 + 16r_t^2}}{2} \right) \\
 &= \frac{U}{2} \left\{ 1 - 2r_K + \frac{1}{\sqrt{1 - (1 - y)^2}} \right\}, \tag{2.3.1}
 \end{aligned}$$

and

$$E_{S_{2g},S_{1g}} \equiv {}^1E_{2g} - {}^1E_{1g} = U \sqrt{1 + 16r_t^2} = \frac{U}{\sqrt{1 - (1 - y)^2}}, \tag{2.3.2}$$

where r_K is defined as $r_K \equiv 2K_{ab}/U$. Second, the analytical expressions of the transition moments along the A–B bond axis are considered. The transition moments between $|S_{1g}\rangle$ and $|S_{1u}\rangle$ are obtained from Eqs. (2.1.10) and (2.1.11a) as [13]

$$\begin{aligned}
\mu_{S_{1g}, S_{1u}} &= -\langle S_{1g} | r_1 + r_2 | S_{1u} \rangle \\
&= -\{ \kappa (\langle a\bar{b} | + \langle b\bar{a} |) + \eta (\langle a\bar{a} | + \langle b\bar{b} |) \} (r_1 + r_2) \left\{ \frac{1}{\sqrt{2}} (|a\bar{a}\rangle - |b\bar{b}\rangle) \right\} \\
&= -\frac{1}{\sqrt{2}} \kappa \langle \bar{b} | r | \bar{a} \rangle + \frac{1}{\sqrt{2}} \kappa \langle a | r | b \rangle - \frac{1}{\sqrt{2}} \kappa \langle b | r | a \rangle + \frac{1}{\sqrt{2}} \kappa \langle \bar{a} | r | \bar{b} \rangle \\
&\quad - \frac{1}{\sqrt{2}} \eta \{ \langle a | r | a \rangle + \langle \bar{a} | r | \bar{a} \rangle \} + \frac{1}{\sqrt{2}} \eta \{ \langle b | r | b \rangle + \langle \bar{b} | r | \bar{b} \rangle \} \\
&= \sqrt{2} \eta \{ (b|r|b) - (a|r|a) \},
\end{aligned} \tag{2.3.3}$$

where the following relations are employed:

$$\begin{cases} \langle a|r|b \rangle = \langle b|r|a \rangle = \langle \bar{a}|r|\bar{b} \rangle = \langle \bar{b}|r|\bar{a} \rangle = (a|r|b) \\ \langle a|r|a \rangle = \langle \bar{a}|r|\bar{a} \rangle = (a|r|a) \\ \langle b|r|b \rangle = \langle \bar{b}|r|\bar{b} \rangle = (b|r|b) \end{cases}. \tag{2.3.4}$$

Since $(a|r|a)$ and $(b|r|b)$ represent the expectation values of the bond-axis component of the position (r) of electrons using the LNOs a and b , respectively, $(b|r|b) - (a|r|a)$ indicates the dipole $\mu = eR_{BA}$ [with $R_{BA} \equiv R_{bb} - R_{aa} = (b|r|b) - (a|r|a)$, an effective distance between the two radicals], with the e , the electron charge magnitude, equal to 1 in a.u. Thus, we obtain [13]

$$\mu_{S_{1g}, S_{1u}} = \sqrt{2} \eta R_{BA}. \tag{2.3.5}$$

In the same manner, we obtain the transition moment between $|S_{1u}\rangle$ and $|S_{2g}\rangle$ [13],

$$\mu_{S_{1u}, S_{2g}} = -\langle S_{1u} | r_1 + r_2 | S_{2u} \rangle = \sqrt{2} \kappa \{ (b|r|b) - (a|r|a) \} = \sqrt{2} \kappa R_{BA}. \tag{2.3.6}$$

The transition moment ($\mu_{S_{1g}, S_{1u}}$) between $|S_{1g}\rangle$ and $|S_{1u}\rangle$ is proportional to the coefficient (η) of the ionic term in the singlet ground state $|S_{1g}\rangle$, while that ($\mu_{S_{1u}, S_{2g}}$) between $|S_{1u}\rangle$ and $|S_{2g}\rangle$ is to the coefficient (κ) of the neutral term in $|S_{1g}\rangle$, which is also that of the ionic term in the excited singlet state $|S_{2g}\rangle$. Therefore, the increase in the diradical character (corresponding to the increase in the weight of the neutral term) of the singlet ground state $|S_{1g}\rangle$ leads to the decrease in $\mu_{S_{1g}, S_{1u}}$ and the increase in $\mu_{S_{1u}, S_{2g}}$. This is because the ionic component of $|S_{1g}\rangle$ ($|S_{2g}\rangle$) decreases (increases) with respect to the increase in the diradical character of $|S_{1g}\rangle$ [see Eqs. (2.1.11a) and (2.1.12a)], while $|S_{1u}\rangle$ keeps the pure ionic nature [see Eq. (2.1.10)]. The transition moment between the ionic ($|a\bar{a}\rangle - |b\bar{b}\rangle$) and neutral ($|a\bar{b}\rangle + |b\bar{a}\rangle$) terms becomes 0, while that between the ionic terms ($|a\bar{a}\rangle - |b\bar{b}\rangle$)

and $|a\bar{a}\rangle + |b\bar{b}\rangle$ has a finite value ($= 2\{(a|r|a) - (b|r|b)\}$). Therefore, larger ionic components in $|S_{1g}\rangle$ and $|S_{2g}\rangle$ leads to larger amplitudes of the transition moments $\mu_{S_{1g},S_{1u}}$ and $\mu_{S_{1u},S_{2g}}$. We here present the expressions of the transition moments as a function of the diradical character y by using Eq. (2.1.14) [13],

$$\begin{aligned} (\mu_{S_{1g},S_{1u}})^2 &= \left(\sqrt{2}\eta R_{BA}\right)^2 = \frac{8r_t^2 R_{BA}^2}{(1 + \sqrt{1 + 16r_t^2})\sqrt{1 + 16r_t^2}} \\ &= \frac{R_{BA}^2}{2} \left\{ 1 - \sqrt{1 - (1 - y)^2} \right\}, \end{aligned} \quad (2.3.7)$$

and

$$\begin{aligned} (\mu_{S_{1u},S_{2g}})^2 &= \left(\sqrt{2}\kappa R_{BA}\right)^2 = \frac{R_{BA}^2}{2} \left(1 + \frac{1}{\sqrt{1 + 16r_t^2}} \right) \\ &= \frac{R_{BA}^2}{2} \left\{ 1 + \sqrt{1 - (1 - y)^2} \right\}. \end{aligned} \quad (2.3.8)$$

Next, we investigate the diradical character dependences of the transition moments and excitation energies for the singlet three states of the symmetric two-site model, which give us valuable information and help us understand the features of (non)linear optical responses in symmetric diradical systems. Since in usual cases, r_K takes a very small value, we here consider a symmetric two-site system with a fixed R_{BA} and $r_K = 0$. The nondimensional (ND) transition moments and excitation energies are defined by [13]

$$\begin{aligned} \mu_{ND\ S_{1g},S_{1u}} &\equiv \frac{\mu_{S_{1g},S_{1u}}}{R_{BA}}, & \mu_{ND\ S_{1u},S_{2g}} &\equiv \frac{\mu_{S_{1u},S_{2g}}}{R_{BA}}, \\ E_{ND\ S_{1u},S_{1g}} &\equiv \frac{E_{S_{1u},S_{1g}}}{U} & \text{and} & \quad E_{ND\ S_{2g},S_{1g}} \equiv \frac{E_{S_{2g},S_{1g}}}{U} \end{aligned} \quad (2.3.9)$$

Figure 2.4 shows the variations of the squared ND transition moments $(\mu_{ND\ S_{1g},S_{1u}})^2$ and $(\mu_{ND\ S_{1u},S_{2g}})^2$ with respect to the diradical character y . For $y = 0$, both $(\mu_{ND\ S_{1g},S_{1u}})^2$ and $(\mu_{ND\ S_{1u},S_{2g}})^2$ are equal to 0.5. As increasing y from 0 to 1, $(\mu_{ND\ S_{1g},S_{1u}})^2$ monotonically decreases toward 0, while $(\mu_{ND\ S_{1u},S_{2g}})^2$ increases toward 1. The diradical character dependences of the ND excitation energies $E_{ND\ S_{1u},S_{1g}}$ and $E_{ND\ S_{2g},S_{1g}}$ are shown in Fig. 2.5. With increasing the diradical character, both of the ND excitation energies decrease toward 1, where the decreases are rapid in the small diradical character region, while they are gradual in the intermediate and large diradical character regions. The reduction in the small diradical character region is significant in $E_{ND\ S_{1u},S_{1g}}$ as compared with $E_{ND\ S_{2g},S_{1g}}$. Finally, we consider the effect of r_K on the diradical character dependence of $E_{ND\ S_{1u},S_{1g}}$. From Eqs. (2.3.1), (2.3.2), (2.3.5) and (2.3.6), other

Fig. 2.4 Diradical character (y) dependences of squared nondimensional transition moments $(\mu_{\text{ND } S_{1g}, S_{1u}})^2$ and $(\mu_{\text{ND } S_{1u}, S_{2g}})^2$

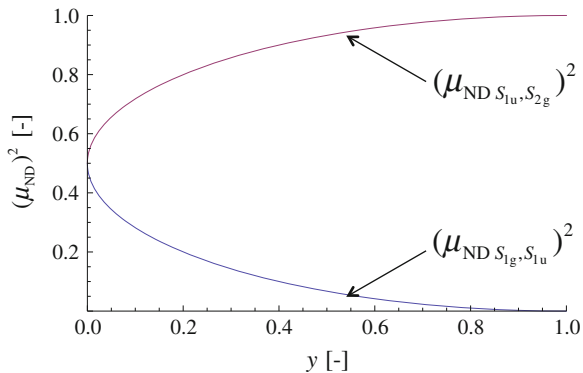


Fig. 2.5 Diradical character (y) dependences of nondimensional excitation energies $E_{\text{ND } S_{1u}, S_{1g}}$ and $E_{\text{ND } S_{2g}, S_{1g}}$ in the case of $r_K = 0$

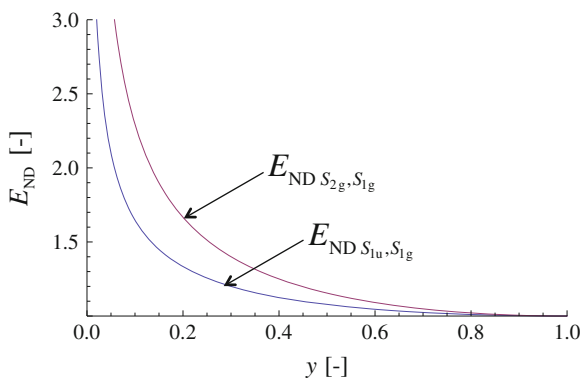
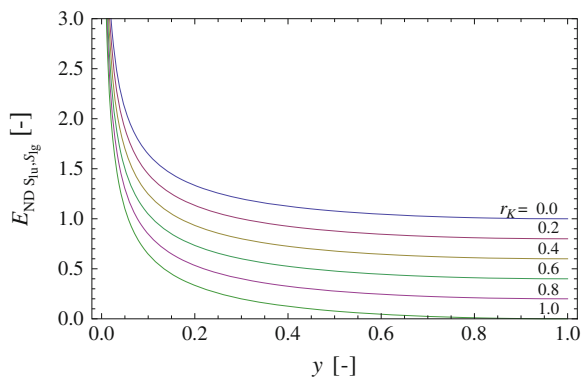


Fig. 2.6 Diradical character (y) dependences of nondimensional excitation energies $E_{\text{ND } S_{1u}, S_{1g}}$ with $r_K = 0.0 - 1.0$



nondimensional singlet excitation energies and transition moments are found to only depend on the diradical character. As seen from Eq. (2.3.1), $E_{\text{ND } S_{1u}, S_{1g}}$ decreases as increasing the diradical character and thus converges to a value, $1 - r_K$, which shows the decrease of $E_{\text{ND } S_{1u}, S_{1g}}$ with the increase of r_K as shown in

Fig. 2.6. As seen from Eq. (2.2.10), the diradical character y tends to increase when U becomes large. It is therefore predicted that the excitation energy $E_{S_{1u},S_{1g}}$ decreases, reaches a stationary value, and in some cases (with very large U) it increases with increasing y values [13, 16]. Such behavior is found to be contrasted with the well-known feature that a closed-shell π -conjugated system exhibits an increase of the oscillator strength of the first optically-allowed excitation and a decrease of the excitation energy with increasing the π -conjugation.

Finally, it is noteworthy that the diradical character y Eq. (2.2.10) can be expressed by the excitation energies [Eqs. (2.1.9), (2.1.10), (2.1.11b), and (2.1.12b)] as

$$y = 1 - \sqrt{1 - \left(\frac{{}^1E_{1u} - {}^3E_{1u}}{{}^1E_{2g} - {}^1E_{1g}} \right)^2} = 1 - \sqrt{1 - \left(\frac{\Delta E_{S(u)} - \Delta E_T}{\Delta E_{S(g)}} \right)^2}, \quad (2.3.10)$$

where the first right-hand side includes the energies of the four electronic states (see Sect. 2.1). The second rhs, $\Delta E_{S(g)} (\equiv {}^1E_{2g} - {}^1E_{1g})$, $\Delta E_{S(u)} (\equiv {}^1E_{2u} - {}^1E_{1g})$ and $\Delta E_T (\equiv {}^3E_{1u} - {}^1E_{1g})$ correspond to the excitation energies of the higher singlet state of g symmetry (two-photon allowed excited state), of the lower singlet state with u symmetry (one-photon allowed excited state), and of the triplet state with u symmetry, respectively, where $\Delta E_{S(u)}$ and $\Delta E_{S(g)}$ correspond to the lowest-energy peaks of the one- and two-photon absorption spectra, respectively, while ΔE_T can be obtained from phosphorescence and ESR measurement. Since the diradical character is not an observable but a purely theoretical quantity, this expression is very useful for estimating the diradical character for real molecular systems by experiments [12].

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