Z. ACCEPTOR–DONOR STRUCTURE CONTRIBUTIONS IN THE MO CONFIGURATION

In Chapter 14 the Slater determinants were constructed in three different ways using:

- molecular orbitals (MO picture),
- acceptor and donor orbitals (AD picture),
- atomic orbitals (VB picture).

Then, the problem appeared of how to express one picture by another, in particular this was of importance for expressing the MO picture as an AD. More specifically, we are interested in calculating the contribution of an acceptor–donor structure[1] in the Slater determinant written in the MO formalism, where the molecular orbitals are expressed by the donor (n) and acceptor (χ and χ^*) orbitals in the following way

$$\begin{aligned} \varphi_1 &= a_1 n + b_1 \chi - c_1 \chi^*, \\ \varphi_2 &= a_2 n - b_2 \chi - c_2 \chi^*, \\ \varphi_3 &= -a_3 n + b_3 \chi - c_3 \chi^*. \end{aligned} \tag{Z.1}$$

We assume that $\{\varphi_i\}$ form an orthonormal set. For simplicity, it is also assumed that in the first approximation the orbitals $\{n, \chi, \chi^*\}$ are also orthonormal. Then we may write that a Slater determinant in the MO picture (denoted by X_i) represents a linear combination of the Slater determinants (Y_j) containing exclusively donor and acceptor orbitals:

$$X_i = \sum_j c_i(Y_j) Y_j,$$

where the coefficient $c_i(Y_k) = \langle Y_k | X_i \rangle$ at the Slater determinant Y_k is the contribution of the acceptor–donor structure Y_k in X_i.

In Chapter 14 three particular cases are highlighted, and they will be derived below. We will use the antisymmetrizer

$$\hat{A} = \frac{1}{N!} \sum_P (-1)^p \hat{P}$$

introduced in Chapter 10 ($\hat{P}$ is the permutation operator, and p is its parity).

[1] That is, of a Slater determinant built of acceptor and donor orbitals.

Case $c_0(DA)$

The $c_0(DA)$ coefficient means the contribution of the structure $n^2\chi^2$, i.e.

$$\Psi(DA) = (4!)^{-\frac{1}{2}} \det[n\bar{n}\chi\bar{\chi}] = (4!)^{\frac{1}{2}} \hat{A}[n\bar{n}\chi\bar{\chi}]$$

in the ground-state Slater determinant

$$\Psi_0 = (4!)^{-\frac{1}{2}} \det[\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2] = (4!)^{\frac{1}{2}} \hat{A}[\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2].$$

We have to calculate

$$\begin{aligned}
c_0(DA) &= \langle Y_k|X_i\rangle = \langle\Psi(DA)\big|\Psi_0\rangle \\
&= 4!\langle\hat{A}[n\bar{n}\chi\bar{\chi}]\big|\hat{A}[\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2]\rangle \\
&= 4!\langle[n\bar{n}\chi\bar{\chi}]\big|\hat{A}^2[\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2]\rangle \\
&= 4!\langle[n\bar{n}\chi\bar{\chi}]\big|\hat{A}[\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2]\rangle \\
&= 4!\langle\big[n(1)\bar{n}(2)\chi(3)\bar{\chi}(4)\big]\big|\hat{A}\big[\varphi_1(1)\bar{\varphi}_1(2)\varphi_2(3)\bar{\varphi}_2(4)\big]\rangle,
\end{aligned}$$

where we have used $\hat{A}$ as Hermitian and idempotent. Next, we have to write all the 24 permutations $[\varphi_1(1)\bar{\varphi}_1(2)\varphi_2(3)\bar{\varphi}_2(4)]$ (taking into account their parity) and then perform integration over the coordinates of all the four electrons (together with summation over the spin variables):

$$\begin{aligned}
c_0(DA) = \int \mathrm{d}\tau_1\,\mathrm{d}\tau_2\,\mathrm{d}\tau_3\,\mathrm{d}\tau_4\,\big[n(1)\bar{n}(2)\chi(3)\bar{\chi}(4)\big]^* \\
\times \sum_P (-1)^p P\big[\varphi_1(1)\bar{\varphi}_1(2)\varphi_2(3)\bar{\varphi}_2(4)\big].
\end{aligned}$$

The integral to survive *has* to have perfect matching of the spin functions between $[n(1)\bar{n}(2)\chi(3)\bar{\chi}(4)]$ and $\hat{P}[\varphi_1(1)\bar{\varphi}_1(2)\varphi_2(3)\bar{\varphi}_2(4)]$. This makes 20 of these permutations vanish. Only four integrals will survive:

$$\begin{aligned}
&c_0(DA) \\
&\quad= \int \mathrm{d}\tau_1\,\mathrm{d}\tau_2\,\mathrm{d}\tau_3\,\mathrm{d}\tau_4\,\big[n(1)\bar{n}(2)\chi(3)\bar{\chi}(4)\big]^*\big[\varphi_1(1)\bar{\varphi}_1(2)\varphi_2(3)\bar{\varphi}_2(4)\big] \\
&\qquad- \int \mathrm{d}\tau_1\,\mathrm{d}\tau_2\,\mathrm{d}\tau_3\,\mathrm{d}\tau_4\,\big[n(1)\bar{n}(2)\chi(3)\bar{\chi}(4)\big]^*\big[\varphi_1(1)\bar{\varphi}_1(4)\varphi_2(3)\bar{\varphi}_2(2)\big] \\
&\qquad- \int \mathrm{d}\tau_1\,\mathrm{d}\tau_2\,\mathrm{d}\tau_3\,\mathrm{d}\tau_4\,\big[n(1)\bar{n}(2)\chi(3)\bar{\chi}(4)\big]^*\big[\varphi_1(3)\bar{\varphi}_1(2)\varphi_2(1)\bar{\varphi}_2(4)\big] \\
&\qquad+ \int \mathrm{d}\tau_1\,\mathrm{d}\tau_2\,\mathrm{d}\tau_3\,\mathrm{d}\tau_4\,\big[n(1)\bar{n}(2)\chi(3)\bar{\chi}(4)\big]^*\big[\varphi_1(3)\bar{\varphi}_1(4)\varphi_2(1)\bar{\varphi}_2(2)\big]
\end{aligned}$$

$$
\begin{aligned}
&= \int \mathrm{d}\tau_1\, n(1)^* \varphi_1(1) \int \mathrm{d}\tau_2\, \bar{n}(2)^* \bar{\varphi}_1(2) \int \mathrm{d}\tau_3\, \chi(3)^* \varphi_2(3) \int \mathrm{d}\tau_4\, \bar{\chi}(4)^* \bar{\varphi}_2(4) \\
&\quad - \int \mathrm{d}\tau_1\, n(1)^* \varphi_1(1) \int \mathrm{d}\tau_2\, \bar{n}(2)^* \bar{\varphi}_2(2) \int \mathrm{d}\tau_3\, \chi(3)^* \varphi_2(3) \int \mathrm{d}\tau_4\, \bar{\chi}(4)^* \bar{\varphi}_1(4) \\
&\quad - \int \mathrm{d}\tau_1\, n(1)^* \varphi_2(1) \int \mathrm{d}\tau_2\, \bar{n}(2)^* \bar{\varphi}_1(2) \int \mathrm{d}\tau_3\, \chi(3)^* \varphi_1(3) \int \mathrm{d}\tau_4\, \bar{\chi}(4)^* \bar{\varphi}_2(4) \\
&\quad + \int \mathrm{d}\tau_1\, n(1)^* \varphi_2(1) \int \mathrm{d}\tau_2\, \bar{n}(2)^* \bar{\varphi}_2(2) \int \mathrm{d}\tau_3\, \chi(3)^* \varphi_1(3) \int \mathrm{d}\tau_4\, \bar{\chi}(4)^* \bar{\varphi}_1(4) \\
&= (a_1)^2(-b_2)^2 - a_1 a_2 (-b_2) b_1 - a_2 a_1 b_1 (-b_2) + (a_2)^2 (b_1)^2 \\
&= (a_1)^2 (b_2)^2 + a_1 a_2 b_2 b_1 + a_2 a_1 b_1 b_2 + (a_2)^2 (b_1)^2 \\
&= a_1 b_2 (a_1 b_2 + a_2 b_1) + a_2 b_1 (a_1 b_2 + a_2 b_1) \\
&= (a_1 b_2 + a_2 b_1)^2 = \begin{vmatrix} a_1 & a_2 \\ b_1 & -b_2 \end{vmatrix}^2 .
\end{aligned}
$$

Hence,

$$
c_0(DA) = \begin{vmatrix} a_1 & a_2 \\ b_1 & -b_2 \end{vmatrix}^2
$$

which agrees with the formula on p. 805.

Case $c_2(DA)$

The $c_2(DA)$ represents the contribution of the structure $\Psi(DA) = (4!)^{\frac{1}{2}} \hat{A}[n\bar{n}\chi\bar{\chi}]$ in the Slater determinant corresponding to the double excitation $\Psi_{2d} = (4!)^{\frac{1}{2}} \hat{A}[\varphi_1\bar{\varphi}_1\varphi_3\bar{\varphi}_3]$. We are interested in the integral

$$
\begin{aligned}
c_2(DA) &= \langle \Psi(DA) | \Psi_{2d} \rangle \\
&= 4! \langle [n(1)\bar{n}(2)\chi(3)\bar{\chi}(4)] | \hat{A}[\varphi_1(1)\bar{\varphi}_1(2)\varphi_3(3)\bar{\varphi}_3(4)] \rangle.
\end{aligned}
$$

This case is very similar to the previous one, the only difference is the substitution $\varphi_2 \to \varphi_3$. Therefore, everything goes the same way as before, but this time we obtain:

$$
\begin{aligned}
&c_2(DA) \\
&= \int \mathrm{d}\tau_1\, n(1)^* \varphi_1(1) \int \mathrm{d}\tau_2\, \bar{n}(2)^* \bar{\varphi}_1(2) \int \mathrm{d}\tau_3\, \chi(3)^* \varphi_3(3) \int \mathrm{d}\tau_4\, \bar{\chi}(4)^* \bar{\varphi}_3(4) \\
&\quad - \int \mathrm{d}\tau_1\, n(1)^* \varphi_1(1) \int \mathrm{d}\tau_2\, \bar{n}(2)^* \bar{\varphi}_3(2) \int \mathrm{d}\tau_3\, \chi(3)^* \varphi_3(3) \int \mathrm{d}\tau_4\, \bar{\chi}(4)^* \bar{\varphi}_1(4) \\
&\quad - \int \mathrm{d}\tau_1\, n(1)^* \varphi_3(1) \int \mathrm{d}\tau_2\, \bar{n}(2)^* \bar{\varphi}_1(2) \int \mathrm{d}\tau_3\, \chi(3)^* \varphi_1(3) \int \mathrm{d}\tau_4\, \bar{\chi}(4)^* \bar{\varphi}_3(4)
\end{aligned}
$$

$$+\int d\tau_1\, n(1)^*\varphi_3(1)\int d\tau_2\, \bar{n}(2)^*\bar{\varphi}_3(2)\int d\tau_3\, \chi(3)^*\varphi_1(3)\int d\tau_4\, \bar{\chi}(4)^*\bar{\varphi}_1(4),$$

or

$$\begin{aligned}c_2(DA) &= (a_1)^2(b_3)^2 - a_1(-a_3)b_3b_1 - (-a_3)a_1b_1b_3 + (-a_3)^2(b_1)^2\\ &= (a_1)^2(b_3)^2 + a_1a_3b_3b_1 + a_3a_1b_1b_3 + (a_3)^2(b_1)^2 = (a_1b_3 + a_3b_1)^2\\ &= \begin{vmatrix} a_1 & b_1 \\ -a_3 & b_3 \end{vmatrix}^2.\end{aligned}$$

We have

$$c_2(DA) = \begin{vmatrix} a_1 & b_1 \\ -a_3 & b_3 \end{vmatrix}^2$$

which also agrees with the result used on p. 806.

Case $c_3(DA)$

This time we have to calculate the contribution of $\Psi(DA) = (4!)^{\frac{1}{2}}\hat{A}[n\bar{n}\chi\bar{\chi}]$ in the Slater determinant $\Psi_{3d} = (4!)^{\frac{1}{2}}\hat{A}[\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3]$, therefore

$$\begin{aligned}c_2(DA) &= \langle \Psi(DA)|\Psi_{3d}\rangle\\ &= 4!\big\langle \big[n(1)\bar{n}(2)\chi(3)\bar{\chi}(4)\big]\big|\hat{A}\big[\varphi_2(1)\bar{\varphi}_2(2)\varphi_3(3)\bar{\varphi}_3(4)\big]\big\rangle.\end{aligned}$$

This is a similar case to the previous one, but we have to exchange $\varphi_1 \to \varphi_2$. We obtain:

$$\begin{aligned}&c_3(DA)\\ &= \int d\tau_1\, n(1)^*\varphi_2(1)\int d\tau_2\, \bar{n}(2)^*\bar{\varphi}_2(2)\int d\tau_3\, \chi(3)^*\varphi_3(3)\int d\tau_4\, \bar{\chi}(4)^*\bar{\varphi}_3(4)\\ &\quad - \int d\tau_1\, n(1)^*\varphi_2(1)\int d\tau_2\, \bar{n}(2)^*\bar{\varphi}_3(2)\int d\tau_3\, \chi(3)^*\varphi_3(3)\int d\tau_4\, \bar{\chi}(4)^*\bar{\varphi}_2(4)\\ &\quad - \int d\tau_1\, n(1)^*\varphi_3(1)\int d\tau_2\, \bar{n}(2)^*\bar{\varphi}_2(2)\int d\tau_3\, \chi(3)^*\varphi_2(3)\int d\tau_4\, \bar{\chi}(4)^*\bar{\varphi}_3(4)\\ &\quad + \int d\tau_1\, n(1)^*\varphi_3(1)\int d\tau_2\, \bar{n}(2)^*\bar{\varphi}_3(2)\int d\tau_3\, \chi(3)^*\varphi_2(3)\int d\tau_4\, \bar{\chi}(4)^*\bar{\varphi}_2(4),\end{aligned}$$

or

$$\begin{aligned}c_3(DA) &= (a_2)^2(b_3)^2 - a_2(-a_3)b_3(-b_2) - (-a_3)a_2(-b_2)b_3 + (-a_3)^2(-b_2)^2\\ &= (a_2)^2(b_3)^2 - a_2a_3b_3b_2 - a_3a_2b_2b_3 + (a_3)^2(b_2)^2\\ &= a_2b_3[a_2b_3 - a_3b_2] - a_3b_2[a_2b_3 - a_3b_2]\\ &= (a_2b_3 - a_3b_2)^2 = \begin{vmatrix} a_2 & -b_2 \\ -a_3 & b_3 \end{vmatrix}^2.\end{aligned}$$

Finally,

$$c_3(DA) = \begin{vmatrix} a_2 & -b_2 \\ -a_3 & b_3 \end{vmatrix}^2$$

and again agreement with the formula on p. 806 is obtained.

Table Z.1. Units of physical quantities

Quantity	Unit	Symbol	Value
light velocity		c	$299792.458\ \frac{\text{km}}{\text{s}}$
Planck constant		h	$6.6260755 \cdot 10^{-34}$ J · s
mass	electron rest mass	m_0	$9.1093897 \cdot 10^{-31}$ kg
charge	element. charge = a.u. of charge	e	$1.60217733 \cdot 10^{-19}$ C
action	$\frac{h}{2\pi}$	$\hbar$	$1.05457266 \cdot 10^{-34}$ J · s
length	bohr = a.u. of length	a_0	$5.29177249 \cdot 10^{-11}$ m
energy	hartree = a.u. of energy	E_h	$4.3597482 \cdot 10^{-18}$ J
time	a.u. of time	$\frac{\hbar}{E_h}$	$2.418884 \cdot 10^{-17}$ s
velocity	a.u. of velocity	$\frac{a_0 E_h}{\hbar}$	$2.187691 \cdot 10^{6}\ \frac{\text{m}}{\text{s}}$
momentum	a.u. of momentum	$\frac{\hbar}{a_0}$	$1.992853 \cdot 10^{-24}\ \frac{\text{kg m}}{\text{s}}$
electr. dipole moment	a.u. of electr. dipole	ea_0	$8.478358 \cdot 10^{-30}$ C · m (2.5415 D)
magn. dipole	Bohr magneton	$\frac{e\hbar}{2m_0 c}$	$0.92731 \cdot 10^{-20}\ \frac{\text{erg}}{\text{gauss}}$
polarizability		$\frac{e^2 a_0^2}{E_h}$	$1.648778 \cdot 10^{-41}\ \frac{\text{C}^2\text{m}^2}{\text{J}}$
electric field		$\frac{E_h}{ea_0}$	$5.142208 \cdot 10^{11}\ \frac{\text{V}}{\text{m}}$
Boltzm. constant		k_B	$1.380658 \cdot 10^{-23}\ \frac{\text{J}}{\text{K}}$
Avogadro constant		N_A	$6.0221367 \cdot 10^{23}$ mol^{-1}

Table Z.2. Conversion coefficients

	a.u.	erg	eV	$\frac{\text{kcal}}{\text{mole}}$	1 cm^{-1}	1 Hz	1 K
1 a.u.	1	$4.35916 \cdot 10^{-11}$	27.2097	627.709	$2.194746 \cdot 10^{5}$	$6.579695 \cdot 10^{15}$	$3.15780 \cdot 10^{5}$
1 erg	$2.29402 \cdot 10^{10}$	1	$6.24197 \cdot 10^{11}$	$1.43998 \cdot 10^{13}$	$5.03480 \cdot 10^{15}$	$1.50940 \cdot 10^{26}$	$7.2441 \cdot 10^{15}$
1 eV	$3.67516 \cdot 10^{-2}$	$1.60206 \cdot 10^{-12}$	1	23.0693	$8.06604 \cdot 10^{3}$	$2.41814 \cdot 10^{14}$	$1.16054 \cdot 10^{4}$
1 $\frac{\text{kcal}}{\text{mol}}$	$1.59310 \cdot 10^{-3}$	$6.9446 \cdot 10^{-14}$	$4.33477 \cdot 10^{-2}$	1	$3.49644 \cdot 10^{2}$	$1.048209 \cdot 10^{13}$	$5.0307 \cdot 10^{2}$
1 cm^{-1}	$4.556336 \cdot 10^{-6}$	$1.98618 \cdot 10^{-16}$	$1.23977 \cdot 10^{-4}$	$2.86005 \cdot 10^{-3}$	1	$2.997930 \cdot 10^{10}$	1.43880
1 Hz	$1.519827 \cdot 10^{-16}$	$6.62517 \cdot 10^{-27}$	$4.13541 \cdot 10^{-15}$	$9.54009 \cdot 10^{-14}$	$3.335635 \cdot 10^{-11}$	1	$4.7993 \cdot 10^{-11}$
1 K	$3.16676 \cdot 10^{-6}$	$1.38044 \cdot 10^{-16}$	$8.6167 \cdot 10^{-5}$	$1.98780 \cdot 10^{-3}$	0.69502	$2.08363 \cdot 10^{10}$	1