APPENDIX Z

Acceptor-Donor Structure Contributions in the MO Configuration

In Chapter 14, the Slater determinants have been constructed in three different ways using the following:

- Molecular orbitals (MO picture)
- Acceptor and donor orbitals (AD picture)
- Atomic orbitals (VB picture).

Then, a problem appeared: how do you express one picture by another? In particular, this has been important for expressing the MO picture in the AD one. 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 MOs 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) that contains exclusively the donor and the acceptor orbitals:

$$X_i = \sum_j C_i\left(Y_j\right) Y_j,$$

where the coefficient $C_i\left(Y_k\right) = \langle Y_k | X_i \rangle$ 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 $\hat{A} = \frac{1}{N!}\sum_P \left(-1\right)^p \hat{P}$ introduced in Chapter 10 ($\hat{P}$ is the permutation operator, and p is its parity).

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

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Case $C_0\left(DA\right)$

The $C_0\left(DA\right)$ coefficient means a contribution of the structure $n^2\chi^2$; i.e.,
$\Psi\left(DA\right) = (4!)^{-\frac{1}{2}} \det\left[n\bar{n}\chi\bar{\chi}\right] = \left(4!\right)^{\frac{1}{2}}\hat{A}\left[n\bar{n}\chi\bar{\chi}\right]$ in the ground-state Slater determinant
$\Psi_0 = \left(4!\right)^{-\frac{1}{2}} \det\left[\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\right] = \left(4!\right)^{\frac{1}{2}}\hat{A}\left[\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\right]$. We have to calculate

$$\begin{aligned}
C_0\left(DA\right) &= \langle Y_k|X_i\rangle = \left\langle \Psi\left(DA\right)|\Psi_0\right\rangle = 4!\left\langle \hat{A}\left[n\bar{n}\chi\bar{\chi}\right]|\hat{A}\left[\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\right]\right\rangle \\
&= 4!\left\langle\left[n\bar{n}\chi\bar{\chi}\right]|\hat{A}^2\left[\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\right]\right\rangle = 4!\left\langle\left[n\bar{n}\chi\bar{\chi}\right]|\hat{A}\left[\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\right]\right\rangle \\
&= 4!\left\langle\left[n(1)\bar{n}(2)\chi(3)\bar{\chi}(4)\right]|\hat{A}\left[\varphi_1(1)\bar{\varphi}_1(2)\varphi_2(3)\bar{\varphi}_2(4)\right]\right\rangle,
\end{aligned}$$

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

$$C_0\left(DA\right) = \int d\tau_1 d\tau_2 d\tau_3 d\tau_4 \left[n(1)\bar{n}(2)\chi(3)\bar{\chi}(4)\right]^* \sum_P (-1)^p\, P\left[\varphi_1(1)\bar{\varphi}_1(2)\varphi_2(3)\bar{\varphi}_2(4)\right].$$

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

$$\begin{aligned}
C_0\left(DA\right) = &\int d\tau_1 d\tau_2 d\tau_3 d\tau_4 \left[n(1)\bar{n}(2)\chi(3)\bar{\chi}(4)\right]^* \left[\varphi_1(1)\bar{\varphi}_1(2)\varphi_2(3)\bar{\varphi}_2(4)\right] \\
&- \int d\tau_1 d\tau_2 d\tau_3 d\tau_4 \left[n(1)\bar{n}(2)\chi(3)\bar{\chi}(4)\right]^* \left[\varphi_1(1)\bar{\varphi}_1(4)\varphi_2(3)\bar{\varphi}_2(2)\right] \\
&- \int d\tau_1 d\tau_2 d\tau_3 d\tau_4 \left[n(1)\bar{n}(2)\chi(3)\bar{\chi}(4)\right]^* \left[\varphi_1(3)\bar{\varphi}_1(2)\varphi_2(1)\bar{\varphi}_2(4)\right] \\
&+ \int d\tau_1 d\tau_2 d\tau_3 d\tau_4 \left[n(1)\bar{n}(2)\chi(3)\bar{\chi}(4)\right]^* \left[\varphi_1(3)\bar{\varphi}_1(4)\varphi_2(1)\bar{\varphi}_2(2)\right] \\
= &\int d\tau_1 n(1)^*\varphi_1(1) \int d\tau_2 \bar{n}(2)^*\bar{\varphi}_1(2) \int d\tau_3 \chi(3)^*\varphi_2(3) \int d\tau_4 \bar{\chi}(4)^*\bar{\varphi}_2(4) \\
&- \int d\tau_1 n(1)^*\varphi_1(1) \int d\tau_2 \bar{n}(2)^*\bar{\varphi}_2(2) \int d\tau_3 \chi(3)^*\varphi_2(3) \int d\tau_4 \bar{\chi}(4)^*\bar{\varphi}_1(4) \\
&- \int d\tau_1 n(1)^*\varphi_2(1) \int d\tau_2 \bar{n}(2)^*\bar{\varphi}_1(2) \int d\tau_3 \chi(3)^*\varphi_1(3) \int d\tau_4 \bar{\chi}(4)^*\bar{\varphi}_2(4) \\
&+ \int d\tau_1 n(1)^*\varphi_2(1) \int d\tau_2 \bar{n}(2)^*\bar{\varphi}_2(2) \int d\tau_3 \chi(3)^*\varphi_1(3) \int d\tau_4 \bar{\chi}(4)^*\bar{\varphi}_1(4)
\end{aligned}$$

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

Hence,

$$C_0(DA) = \begin{vmatrix} a_1 & a_2 \\ b_1 & -b_2 \end{vmatrix}^2 ,$$

which agrees with the formula on p. 925.

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

$$C_2(DA) = \langle \Psi(DA) | \Psi_{2d} \rangle = 4! \Big\langle [n(1)\bar{n}(2)\chi(3)\bar{\chi}(4)] | \hat{A}[\varphi_1(1)\bar{\varphi}_1(2)\varphi_3(3)\bar{\varphi}_3(4)] \Big\rangle .$$

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

$$\begin{aligned} C_2(DA) = & \int d\tau_1 n(1)^* \varphi_1(1) \int d\tau_2 \bar{n}(2)^* \bar{\varphi}_1(2) \int d\tau_3 \chi(3)^* \varphi_3(3) \int d\tau_4 \bar{\chi}(4)^* \bar{\varphi}_3(4) \\ & - \int d\tau_1 n(1)^* \varphi_1(1) \int d\tau_2 \bar{n}(2)^* \bar{\varphi}_3(2) \int d\tau_3 \chi(3)^* \varphi_3(3) \int d\tau_4 \bar{\chi}(4)^* \bar{\varphi}_1(4) \\ & - \int d\tau_1 n(1)^* \varphi_3(1) \int d\tau_2 \bar{n}(2)^* \bar{\varphi}_1(2) \int d\tau_3 \chi(3)^* \varphi_1(3) \int d\tau_4 \bar{\chi}(4)^* \bar{\varphi}_3(4) \\ & + \int d\tau_1 n(1)^* \varphi_3(1) \int d\tau_2 \bar{n}(2)^* \bar{\varphi}_3(2) \int d\tau_3 \chi(3)^* \varphi_1(3) \int d\tau_4 \bar{\chi}(4)^* \bar{\varphi}_1(4) \end{aligned}$$

or

$$\begin{aligned} C_2(DA) &= (a_1)^2 (b_3)^2 - a_1(-a_3) b_3 b_1 - (-a_3) a_1 b_1 b_3 + (-a_3)^2 (b_1)^2 \\ &= (a_1)^2 (b_3)^2 + a_1 a_3 b_3 b_1 + a_3 a_1 b_1 b_3 + (a_3)^2 (b_1)^2 \\ &= (a_1 b_3 + a_3 b_1)^2 = \begin{vmatrix} a_1 & b_1 \\ -a_3 & b_3 \end{vmatrix}^2 . \end{aligned}$$

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. 925.

Case $C_3\left(DA\right)$

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

$$C_2\left(DA\right)=\left\langle\Psi\left(DA\right)|\Psi_{3d}\right\rangle=4!\left\langle\left[n(1)\bar{n}(2)\chi(3)\bar{\chi}(4)\right]|\hat{A}\left[\varphi_2(1)\bar{\varphi}_2(2)\varphi_3(3)\bar{\varphi}_3(4)\right]\right\rangle.$$

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

$$\begin{aligned}C_3\left(DA\right)=&\int d\tau_1 n(1)^*\varphi_2(1)\int d\tau_2\bar{n}(2)^*\bar{\varphi}_2(2)\int d\tau_3\chi(3)^*\varphi_3(3)\int d\tau_4\bar{\chi}(4)^*\bar{\varphi}_3(4)\\&-\int d\tau_1 n(1)^*\varphi_2(1)\int d\tau_2\bar{n}(2)^*\bar{\varphi}_3(2)\int d\tau_3\chi(3)^*\varphi_3(3)\int d\tau_4\bar{\chi}(4)^*\bar{\varphi}_2(4)\\&-\int d\tau_1 n(1)^*\varphi_3(1)\int d\tau_2\bar{n}(2)^*\bar{\varphi}_2(2)\int d\tau_3\chi(3)^*\varphi_2(3)\int d\tau_4\bar{\chi}(4)^*\bar{\varphi}_3(4)\\&+\int d\tau_1 n(1)^*\varphi_3(1)\int d\tau_2\bar{n}(2)^*\bar{\varphi}_3(2)\int d\tau_3\chi(3)^*\varphi_2(3)\int d\tau_4\bar{\chi}(4)^*\bar{\varphi}_2(4)\end{aligned}$$

or

$$\begin{aligned}C_3\left(DA\right)&=\left(a_2\right)^2\left(b_3\right)^2-a_2\left(-a_3\right)b_3\left(-b_2\right)-\left(-a_3\right)a_2\left(-b_2\right)b_3+\left(-a_3\right)^2\left(-b_2\right)^2\\&=\left(a_2\right)^2\left(b_3\right)^2-a_2a_3b_3b_2-a_3a_2b_2b_3+\left(a_3\right)^2\left(b_2\right)^2\\&=a_2b_3\left[a_2b_3-a_3b_2\right]-a_3b_2\left[a_2b_3-a_3b_2\right]\\&=\left(a_2b_3-a_3b_2\right)^2=\begin{vmatrix}a_2&-b_2\\-a_3&b_3\end{vmatrix}^2.\end{aligned}$$

Finally,

$$C_3\left(DA\right)=\begin{vmatrix}a_2&-b_2\\-a_3&b_3\end{vmatrix}^2,$$

and again, the agreement with the formula on p. 925 is obtained.