# Calculation of Two-Center Zero-Field Splitting Integrals

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Two-center zero-field splitting (ZFS) integrals have been calculated by numerical integration of Coulomb repulsion integrals which are evaluated over basic charge distributions as defined by Roothaan in terms of Slater atomic orbitals. The method is applied to the calculation of the ZFS integrals for $\pi$-$\pi$, $\sigma$-$\pi$ and $\sigma$-$\sigma$ electron interactions on C, N and $N^+$ centers. Numerical results are given.

Zweizentren ZFS-Integrale sind mittels numerischer Integration von Coulombintegralen berechnet worden, und zwar die $\pi$-$\pi$-, $\sigma$-$\pi$- und $\sigma$-$\sigma$-Integrale an C-, N- und $N^+$-Zentren. Die numerischen Resultate werden mitgeteilt.

Les intégrales bi-centriques de séparation à champ nul (ZFS) ont été calculées par intégration numérique des intégrales de répulsion coulombiennes évaluées pour les distributions de charge fondamentales définies par Roothan en termes d'orbitales atomiques de Slater. La méthode est appliquée au calcul des intégrales ZFS pour les interactions $\pi - \pi$, $\sigma - \pi$ et $\sigma - \sigma$ sur les centres C, N et $N^+$. Résultats numériques.

## Introduction

In order to calculate the ZFS parameters $D$ and $E$, describing the energy splitting of a triplet state at zero-field due to magnetic dipolar interaction between the two unpaired electron spins, numerical values of the two-center contributions to $D$ and $E$ are required.

$D$ and $E$ are defined as [1]

$$D = \frac{3}{4}(g\beta)^2 \left\langle \psi_T(1,2) \left| \frac{r_{12}^2 - 3z_{12}^2}{r_{12}^5} \right| \psi_T(1,2) \right\rangle$$

and

$$E = \frac{3}{4}(g\beta)^2 \left\langle \psi_T(1,2) \left| \frac{y_{12}^2 - x_{12}^2}{r_{12}^5} \right| \psi_T(1,2) \right\rangle$$

where $\psi_T(1,2)$ stands for an antisymmetrical space function of the unpaired electrons in the triplet state.

In the calculations of two-center ZFS integrals the greatest difficulty is the treatment of the operators which involve an inverse power of third degree of the interelectronic distance $r_{12}$. In the literature several attempts concerning the evaluation of the integrals have been described. Pitzer *et al.* [2] computed the necessary integrals by direct expansion of the operators in solid spherical harmonics, using the Gaussian transform technique. A similar method has been used by Boorstein and Gouterman [3] in calculations on ZFS parameters of phosphorescent aromatic molecules. Prosser and Blanchard [4] and Lounsbury [5] applied a Fourier transform technique. The latter expanded the ZFS integrals in one-center representations, using Slater-type orbitals. Geller [6] succeeded to

extend the Fourier convolution theorem to two-electron two-center integrals and expressed these integrals in closed analytical form. The integrals were evaluated over basic charge distributions as defined by Roothaan [7]. Geller's method has been employed by Capello and Pullman [8] in calculations of $D$ values for $\pi$-$\pi$ interactions on carbon and nitrogen nuclei. Because of the use of the rather complicated Fourier transform technique, Geller's method demands much effort in compiling the necessary integrals. To avoid this difficulty we want to introduce here a less laborious technique. Taking advantage of an alternative formulation of the $D$ and $E$ operators, the ZFS integrals are reduced directly to two-center repulsion integrals.

The method has been used for the calculations of dipolar interactions between $\pi$-$\pi$, $\sigma$-$\pi$ and $\sigma$-$\sigma$ electrons on carbon and nitrogen nuclei.

## Evaluation of ZFS Integrals over Basic Charge Distributions

Using a coordinate system according to Roothaan [7] ($z$-axis as internuclear axis), the $D$ and $E$ operators can be formulated, in conformity with the suggestions of Schrader [9] and Oosterhoff (cited in Ref. [10]), as follows

$$D_{op} = -\frac{3}{4}(g\beta)^2 \frac{\partial}{\partial x_1} \frac{\partial}{\partial x_2} \frac{1}{r_{12}}$$

and

$$E_{op} = -\frac{1}{4}(g\beta)^2 \left( \frac{\partial}{\partial y_1} \frac{\partial}{\partial y_2} + \frac{\partial}{\partial z_1} \frac{\partial}{\partial z_2} \right) \frac{1}{r_{12}}.$$

Using this formulation of the operators, the LCAO approximation of the triplet wave function gives rise to one-, two-, three- and four-center contributions to the ZFS parameters. The one-center integrals need not to be regarded here, the three- and four-center integrals are neglected. The computational procedure will be demonstrated by calculating the two-center $D$ values for $\pi$-electrons, which will further be denoted by $D_{12}$. In the calculation of $D_{12}$ only repulsion integrals of Coulomb-type will be taken into account, the exchange integrals may be neglected [11].

After integration by parts $D_{12}$ is given by

$$D_{12} = \frac{3}{4}(g\beta)^2 \int \int \frac{1}{r_{12}} \frac{\partial}{\partial x_1} \frac{\partial}{\partial x_2} [p_a(1)\, p_b(2)]^2 \, dr_1 \, dr_2 \,.$$

The atomic orbitals $p_a$ and $p_b$ can be written as

$$p_a = N_a x_a e^{-\alpha r_a} \quad \text{and} \quad p_b = N_b x_b e^{-\beta r_b}$$

where $N_a$ and $N_b$ are normalization constants and $\alpha$ and $\beta$ Slater exponents on the centers $a$ and $b$, respectively.

Expanding $D_{12}$ it follows that

$$D_{12} = \frac{3}{4}(g\beta)^2 \cdot 4N_a^2\, N_b^2 \iint \left( x_a(1)\, e^{-2\alpha r_a} - \alpha\, \frac{x_a^2(1)}{r_a}\, e^{-2\alpha r_a} \right) \left| \frac{1}{r_{12}} \right|$$

$$\left( x_b(2)\, e^{-2\beta r_b} - \beta\, \frac{x_b^2(2)}{r_b}\, e^{-2\beta r_b} \right) d\tau_1 \, d\tau_2$$

which can be written as

$$D_{12} = 3(g\beta)^2 \cdot N_a^2\, N_b^2 (I_1 + I_2 + I_3 + I_4)$$

where $I_1 - I_4$ are Coulomb integrals following from the integral part of $D_{12}$. These have to be expressed in basic charge distributions $[N, L, M]$ as defined by Roothaan [7]; they are given by the expression

$$[N, L, M] = \left(\frac{2L+1}{4\pi}\right)^{\frac{1}{2}} \frac{2^L (2\alpha)^{N+2}}{(N+L+1)!}\, r_a^{N-1}\, e^{-2\alpha r_a}\, S_{L,M}(\vartheta, \varphi)$$

where the functions $S_{L,M}(\vartheta, \varphi)$ represent normalized real spherical harmonics.
Making use of this formulation the integrals $I_1 - I_4$ can be written as

$$I_1 = \left(x_a e^{-2\alpha r_a} \left|\frac{1}{r_{12}}\right| x_b e^{-2\beta r_b}\right) = (N_{2P\pi_a}^{bcd} \cdot N_{2P\pi_b}^{bcd})^{-1}\, [2P\pi_a | 2P\pi_b],$$

$$I_2 = -\left(x_a e^{-2\alpha r_a} \left|\frac{1}{r_{12}}\right| \beta \frac{x_b^3}{r_b} e^{-2\beta r_b}\right)$$

$$= -\frac{3}{5}(N_{2P\Pi_a}^{bcd} \cdot N_{3P\Pi_b}^{bcd})^{-1}\, \beta\, [2P\Pi_a | 3P\Pi_b]$$

$$+ \frac{3}{20}(N_{2P\Pi_a}^{bcd} \cdot N_{3F\Pi_b}^{bcd})^{-1}\, \beta\, [2P\Pi_a | 3F\Pi_b],$$

$$I_3 = -\left(\alpha \frac{x_a^3}{r_a} e^{-2\alpha r_a} \left|\frac{1}{r_{12}}\right| x_b e^{-2\beta r_b}\right)$$

$$= -\frac{3}{5}(N_{3P\Pi_a}^{bcd} \cdot N_{2P\Pi_b}^{bcd})^{-1}\, \alpha\, [3P\Pi_a | 2P\Pi_b]$$

$$+ \frac{3}{20}(N_{3F\Pi_a}^{bcd} \cdot N_{2P\Pi_b}^{bcd})^{-1}\, \alpha\, [3F\Pi_a | 2P\Pi_b]$$

and

$$I_4 = \left(\alpha \frac{x_a^3}{r_a} e^{-2\alpha r_a} \left|\frac{1}{r_{12}}\right| \beta \frac{x_b^3}{r_b} e^{-2\beta r_b}\right)$$

$$= \frac{1}{16}(N_{3F\phi_a}^{bcd} \cdot N_{3F\phi_b}^{bcd})^{-1}\, \alpha\beta\, [3F\phi_a | 3F\phi_b]$$

$$+ \frac{9}{100}(N_{3F\Pi_a}^{bcd} \cdot N_{3F\Pi_b}^{bcd})^{-1}\, \alpha\beta\, [3F\Pi_a | 3F\Pi_b]$$

$$+ \frac{9}{25}(N_{3P\Pi_a}^{bcd} \cdot N_{3P\Pi_b}^{bcd})^{-1}\, \alpha\beta\, [3P\Pi_a | 3P\Pi_b]$$

$$- \frac{9}{100}(N_{3F\Pi_a}^{bcd} \cdot N_{3P\Pi_b}^{bcd})^{-1}\, \alpha\beta\, [3F\Pi_a | 3P\Pi_b]$$

$$- \frac{9}{100}(N_{3P\Pi_a}^{bcd} \cdot N_{3F\Pi_b}^{bcd})^{-1}\, \alpha\beta\, [3P\Pi_a | 3F\Pi_b]$$

where the coefficients $N_{NLM}^{bcd}$ are defined as

$$N_{NLM}^{bcd} = \left(\frac{2L+1}{4\pi}\right)^{\frac{1}{2}} \cdot \frac{2^L(2\alpha)^{N+2}}{(N+L+1)!} N_{L,M}^{rs}$$

in which $N_{L,M}^{s}$ is the normalization constant of a real spherical harmonic.

All other terms occurring in the expansion of $D_{12}$ vanish due to ortho-normality of the spherical harmonics used.

In the evaluation of $D(\sigma, \pi)$, $D(\sigma, \sigma)$, $E(\pi, \pi)$, $E(\sigma, \pi)$ and $E(\sigma, \sigma)$ integrals similar combinations of repulsion integrals appear.

A survey of the expansion coefficients of the repulsion integrals to be used in the calculations of the ZFS integrals is given in Table 1. In this table the reciprocal values of the constants $N_{NLM}^{bcd}$ and the normalization factors of the Slater orbitals used, have been included in the integrals $[NLM_a|NLM_b]$. To express the $D$ integrals in $cm^{-1}$, the linear combinations of the repulsion integrals have to be multiplied by

$$\frac{3(g\beta)^2 \alpha\beta}{4hc\, a_0^3} = 8.785426\,\alpha\beta$$

and those for the $E$ integrals by $2.928475\,\alpha\beta$.

Some of the repulsion integrals have been given by Roothaan [7] in analytical form; the expressions in which a $3F$ term occurs have not been reported, however. Following Roothaan's method for the determination of these integrals, it appears necessary to calculate first the potential $[a|3F\Sigma]$.

Using spheroidal coordinates $(\xi, \eta, \varphi)$ for the positions of the centers $a$ and $b$, we find for the potential of the charge distribution $3F\Sigma$ on $b$

$$[a|3F\Sigma_b] = \frac{\beta}{\varrho 4}\left\{1 - \left(1 + 2\varrho + 2\varrho^2 + \frac{4}{3}\varrho^3 + \frac{2}{3}\varrho^4 + \frac{4}{15}\varrho^5 + \frac{4}{45}\varrho^6\right)e^{-2\varrho}\right\}$$

in which $\varrho = \beta r_b$. With help of this expression the potentials $U_{3F\Sigma}$, $U_{3F\Pi}$, $U_{3F\Delta}$ and $U_{3F\phi}$ can be deduced. Using polar coordinates $(r, \vartheta, \varphi)$, the result is

$$U_{3FM}(r_a, \vartheta_a, \varphi_a) = \left(\frac{4\pi}{7}\right)^{\frac{1}{2}} S_{3M}(\vartheta_b, \varphi_b)\, [a|3F\Sigma_b]\,.$$

At this stage of the evaluation all basic elements needed for the derivation of the two-center repulsion integrals are known. Integration over $\varphi$ can easily be carried out. Integration over the other two variables looks to be troublesome. For that reason we have evaluated the basic repulsion integrals which were not given by Roothaan, by numerical integration. For the practical realization of this method of computation, Roothaan's coordinates have been transferred into cylindrical ones.

In the execution of the numerical integrations two standard techniques have been used, i.e. the method according to Gauss-Legendre (GaLe) and that to Gauss-Laguerre (GaLa) [12]. The GaLe method has been employed for the integration over the closed $z$-interval of the interatomic distance and over a part

Table 1. Expansion coefficients of repulsion integrals

| | $[2P\Sigma\vert2P\Sigma]$ | $[2P\Sigma\vert3P\Sigma]$ | $[2P\Sigma\vert3F\Sigma]$ | $[2P\Pi\vert2P\Pi]$ | $[2P\Pi\vert3P\Pi]$ | $[2P\Pi\vert3F\Pi]$ | $[3P\Sigma\vert2P\Sigma]$ | $[3P\Sigma\vert3P\Sigma]$ | $[3P\Sigma\vert3F\Sigma]$ | $[3P\Pi\vert2P\Pi]$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $D(\pi,\pi)$ | | | | $+\,4$ | $-\,6$ | $+\,9\sqrt{\tfrac{3}{2}}$ | | | | $-\,6$ |
| $D(\sigma,\pi)$ | | | | | | | | | | $-\,2$ |
| $D(\sigma,\sigma)$ | | | | | | | | | | |
| $E(\pi,\pi)$ | | | | | | | | $+\,1$ | $-\,\tfrac{9}{2}$ | |
| $E(\sigma,\pi)$ | | $-\,2$ | $+\,9$ | | | | | $+\,3$ | $-\,\tfrac{27}{2}$ | |
| $E(\sigma,\sigma)$ | $+\,4$ | $-\,6$ | $-\,18$ | | | | | $+\,9$ | $+\,27$ | $-\,6$ |

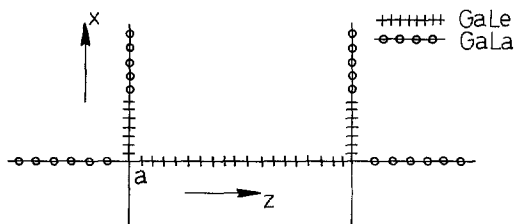| | $[3P\Pi\vert3P\Pi]$ | $[3P\Pi\vert3F\Pi]$ | $[3F\Sigma\vert2P\Sigma]$ | $[3F\Sigma\vert3P\Sigma]$ | $[3F\Sigma\vert3F\Sigma]$ | $[3F\Pi\vert2P\Pi]$ | $[3F\Pi\vert3F\Pi]$ | $[3F\Pi\vert3P\Pi]$ | $[3F\Delta\vert3F\Delta]$ | $[3F\Phi\vert3\Phi]$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $D(\pi,\pi)$ | $+\,9$ | $-\,\tfrac{27}{2}\sqrt{\tfrac{3}{2}}$ | | | | $+\,9\sqrt{\tfrac{3}{2}}$ | $-\,\tfrac{27}{2}\sqrt{\tfrac{3}{2}}$ | $+\,\tfrac{243}{8}$ | | $+\,\tfrac{405}{8}$ |
| $D(\sigma,\pi)$ | $+\,3$ | $-\,\tfrac{9}{2}\sqrt{\tfrac{3}{2}}$ | | | | $-\,12\sqrt{\tfrac{3}{2}}$ | $+\,18\sqrt{\tfrac{3}{2}}$ | $-\,\tfrac{81}{2}$ | | |
| $D(\sigma,\sigma)$ | $+\,1$ | $+\,6\sqrt{\tfrac{3}{2}}$ | | | | | $+\,6\sqrt{\tfrac{3}{2}}$ | $+\,54$ | | |
| $E(\pi,\pi)$ | $+\,1$ | $-\,\tfrac{3}{2}\sqrt{\tfrac{3}{2}}$ | | $-\,\tfrac{9}{2}$ | $+\,\tfrac{81}{4}$ | | $-\,\tfrac{3}{2}\sqrt{\tfrac{3}{2}}$ | $+\,\tfrac{27}{8}$ | $+\,\tfrac{135}{4}$ | $+\,\tfrac{405}{8}$ |
| $E(\sigma,\pi)$ | $+\,1$ | $-\,\tfrac{3}{2}\sqrt{\tfrac{3}{2}}$ | | $+\,9$ | $-\,\tfrac{81}{2}$ | | $+\,6\sqrt{\tfrac{3}{2}}$ | $-\,\tfrac{27}{2}$ | | |
| $E(\sigma,\sigma)$ | $+\,1$ | $+\,6\sqrt{\tfrac{3}{2}}$ | $-\,18$ | $+\,27$ | $+\,81$ | | $+\,6\sqrt{\tfrac{3}{2}}$ | $+\,54$ | | |

Fig. 1. Illustration of the intervals for numerical calculation

of the $x$-interval. For integration over all other parts of space the GaLa technique was used, as illustrated in Fig. 1.

The number of quadrature points was fixed on eighteen, twelve points for the GaLe integration and six for the GaLa one. The values of the numerically calculated $[2P\Pi|2P\Pi]$, $[2P\Pi|3P\Pi]$, $[3P\Pi|2P\Pi]$ and $[3P\Pi|3P\Pi]$ integrals did not deviate more than one millionth from those obtained from Roothaan's analytical formulae [7]. Increase of the number of integration points to twenty-four did not change the integral values.

Applying different grids to the integration, the best results were obtained by using a GaLe interval in the $x$-direction of 1.5 a.u. and a scaling factor of $2(\alpha + \beta)$ for the GaLa integration.

For unequal basic charge distributions the values of the basic integrals have been checked by interchanging the two nuclei under consideration, in which case other potentials are involved.

## Results

The method of the numerical integration as outlined above, has been applied to the calculation of $D(\pi, \pi)$, $D(\sigma, \pi)$, $D(\sigma, \sigma)$, $E(\pi, \pi)$, $E(\sigma, \pi)$ and $E(\sigma, \sigma)$ integrals on carbon (C) and nitrogen (N and $N^+$) nuclei as well as on combinations of these centers. The Slater exponents for C, N and $N^+$ were taken to be 1.59, 1.915 and 2.09, respectively. The carbon exponent of 1.59 has been chosen to be able to compare the integral values with the corresponding ones as derived by van der Waals and ter Maten [10]. In order to obtain ZFS values needed for the extension of van der Waals' semi-empirical method to nitrogen containing molecules, the values of 1.915 for aza- and 2.09 for amino-nitrogen have been chosen, in conformity with Slater's rules (see e.g. Ref. [13]).

The calculated two-center ZFS integrals for intramolecular distances in naphthalene have been listed in Table 2.

## Discussion

The $D(\pi, \pi)$ and $E(\pi, \pi)$ values for carbon can be compared with those obtained by van der Waals and ter Maten [10], and the $D(\pi, \pi)$ values for carbon-carbon and nitrogen-nitrogen interactions with those obtained by Capello and Pullman [8]. In the former case the $D(\pi, \pi)$ values agree very well, the $E(\pi, \pi)$ values deviate at most by five percent. In the other case a good agreement

Table 2. *Two-center ZFS-integrals* (cm$^{-1}$)

| | $r$(Å) | $D(\pi,\pi)$ | $E(\pi,\pi)$ | $D(\pi,\sigma)$ | $E(\pi,\sigma)$ | $D(\sigma,\pi)$ | $E(\sigma,\pi)$ | $D(\sigma,\sigma)$ | $E(\sigma,\sigma)$ |
|---|---|---|---|---|---|---|---|---|---|
| CC | 1.390 | 0.2268 | 0.2347 | 0.2161 | 0.2369 | 0.2161 | 0.2369 | 0.7430 | 0.2297 |
| | 2.408 | 0.0616 | 0.0735 | 0.0826 | 0.0967 | 0.0826 | 0.0967 | 0.1672 | 0.1393 |
| | 2.780 | 0.0433 | 0.0503 | 0.0572 | 0.0647 | 0.0572 | 0.0647 | 0.0988 | 0.0918 |
| | 3.678 | 0.0213 | 0.0234 | 0.0261 | 0.0278 | 0.0261 | 0.0278 | 0.0353 | 0.0351 |
| | 4.170 | 0.0152 | 0.0164 | 0.0180 | 0.0189 | 0.0180 | 0.0189 | 0.0227 | 0.0226 |
| | 4.815 | 0.0103 | 0.0109 | 0.0117 | 0.0122 | 0.0117 | 0.0122 | 0.0139 | 0.0139 |
| | 5.012 | 0.0092 | 0.0097 | 0.0104 | 0.0108 | 0.0104 | 0.0108 | 0.0121 | 0.0121 |
| CN | 1.390 | 0.2345 | 0.2631 | 0.1916 | 0.2785 | 0.3227 | 0.3032 | 0.8194 | 0.3076 |
| | 2.408 | 0.0642 | 0.0758 | 0.0782 | 0.0931 | 0.0948 | 0.1048 | 0.1580 | 0.1417 |
| | 2.780 | 0.0451 | 0.0516 | 0.0546 | 0.0618 | 0.0630 | 0.0682 | 0.0927 | 0.0893 |
| | 3.678 | 0.0219 | 0.0237 | 0.0252 | 0.0268 | 0.0273 | 0.0285 | 0.0337 | 0.0336 |
| | 4.170 | 0.0156 | 0.0166 | 0.0175 | 0.0183 | 0.0186 | 0.0193 | 0.0218 | 0.0218 |
| | 4.815 | 0.0105 | 0.0110 | 0.0115 | 0.0119 | 0.0120 | 0.0123 | 0.0135 | 0.0135 |
| | 5.012 | 0.0094 | 0.0098 | 0.0102 | 0.0105 | 0.0107 | 0.0109 | 0.0118 | 0.0118 |
| CN$^+$ | 1.390 | 0.2334 | 0.2729 | 0.1808 | 0.2915 | 0.3730 | 0.3346 | 0.8450 | 0.3464 |
| | 2.408 | 0.0651 | 0.0765 | 0.0767 | 0.0913 | 0.0995 | 0.1078 | 0.1538 | 0.1412 |
| | 2.780 | 0.0457 | 0.0520 | 0.0536 | 0.0606 | 0.0650 | 0.0695 | 0.0902 | 0.0878 |
| | 3.678 | 0.0221 | 0.0239 | 0.0249 | 0.0265 | 0.0278 | 0.0288 | 0.0331 | 0.0330 |
| | 4.170 | 0.0157 | 0.0167 | 0.0173 | 0.0181 | 0.0189 | 0.0194 | 0.0215 | 0.0215 |
| | 4.815 | 0.0106 | 0.0110 | 0.0114 | 0.0118 | 0.0121 | 0.0124 | 0.0134 | 0.0134 |
| | 5.012 | 0.0094 | 0.0098 | 0.0101 | 0.0104 | 0.0107 | 0.0109 | 0.0117 | 0.0117 |
| NN | 1.390 | 0.2573 | 0.2976 | 0.2984 | 0.3538 | 0.2984 | 0.3538 | 0.8866 | 0.4105 |
| | 2.408 | 0.0682 | 0.0785 | 0.0892 | 0.0999 | 0.0892 | 0.0999 | 0.1475 | 0.1399 |
| | 2.780 | 0.0474 | 0.0530 | 0.0597 | 0.0648 | 0.0597 | 0.0648 | 0.0866 | 0.0854 |
| | 3.678 | 0.0226 | 0.0242 | 0.0263 | 0.0274 | 0.0263 | 0.0274 | 0.0322 | 0.0322 |
| | 4.170 | 0.0160 | 0.0169 | 0.0181 | 0.0187 | 0.0181 | 0.0187 | 0.0211 | 0.0211 |
| | 4.815 | 0.0107 | 0.0111 | 0.0118 | 0.0120 | 0.0118 | 0.0120 | 0.0131 | 0.0132 |
| | 5.012 | 0.0095 | 0.0099 | 0.0104 | 0.0106 | 0.0114 | 0.0106 | 0.0116 | 0.0116 |
| NN$^+$ | 1.390 | 0.2629 | 0.3098 | 0.2864 | 0.3683 | 0.3486 | 0.3888 | 0.9052 | 0.4583 |
| | 2.408 | 0.0696 | 0.0794 | 0.0872 | 0.0977 | 0.0933 | 0.1024 | 0.1430 | 0.1378 |
| | 2.780 | 0.0482 | 0.0535 | 0.0586 | 0.0634 | 0.0616 | 0.0658 | 0.0842 | 0.0835 |
| | 3.678 | 0.0229 | 0.0243 | 0.0260 | 0.0271 | 0.0267 | 0.0277 | 0.0316 | 0.0316 |
| | 4.170 | 0.0161 | 0.0169 | 0.0179 | 0.0185 | 0.0183 | 0.0188 | 0.0208 | 0.0208 |
| | 4.815 | 0.0108 | 0.0112 | 0.0117 | 0.0119 | 0.0119 | 0.0121 | 0.0130 | 0.0130 |
| | 5.012 | 0.0096 | 0.0099 | 0.0103 | 0.0106 | 0.0105 | 0.0107 | 0.0114 | 0.0115 |
| N$^+$N$^+$ | 1.390 | 0.2716 | 0.3229 | 0.3359 | 0.4038 | 0.3359 | 0.4038 | 0.9194 | 0.5086 |
| | 2.408 | 0.0712 | 0.0804 | 0.0911 | 0.0999 | 0.0911 | 0.0999 | 0.1384 | 0.1351 |
| | 2.780 | 0.0491 | 0.0540 | 0.0603 | 0.0644 | 0.0603 | 0.0644 | 0.0820 | 0.0815 |
| | 3.678 | 0.0231 | 0.0245 | 0.0264 | 0.0273 | 0.0264 | 0.0273 | 0.0311 | 0.0311 |
| | 4.170 | 0.0163 | 0.0170 | 0.0181 | 0.0186 | 0.0181 | 0.0186 | 0.0205 | 0.0205 |
| | 4.815 | 0.0108 | 0.0112 | 0.0118 | 0.0120 | 0.0118 | 0.0120 | 0.0129 | 0.0129 |
| | 5.012 | 0.0097 | 0.0100 | 0.0104 | 0.0106 | 0.0104 | 0.0106 | 0.0113 | 0.0114 |

exists for the $D(\pi, \pi)$ values of carbon and nitrogen when compared with the integrals obtained from "best Slater" orbitals (Slater exponents 1.59 and 1.917, resp.).

It must be noted, however, that the ortho $D(\pi, \pi)$ values resulting from our calculations are somewhat greater than those presented by the other authors. In van der Waals' semi-empirical method the ortho $D$ and $E$ values have been

reduced owing to $\sigma$-$\pi$ polarization. Using his analytical treatment of the one-center $\sigma$-$\pi$ integrals [14] and taking our $D(\pi, \pi)$, $D(\sigma, \pi)$, $E(\pi, \pi)$ and $E(\sigma, \pi)$ two-center integrals, the ortho $D(\pi, \pi)$ and $E(\pi, \pi)$ values for carbon become $0.151\ \text{cm}^{-1}$ and $0.186\ \text{cm}^{-1}$, respectively, close to those proposed by van der Waals and ter Maten [10].

The $D(\sigma, \sigma)$, $D(\sigma, \pi)$, $E(\sigma, \sigma)$ and $E(\sigma, \pi)$ integrals of Table 2, which have not been published before, were required for the calculations of intermolecular contributions to the ZFS parameters of phosphorescent charge-transfer complexes. They have been applied successfully to the calculation of $D$ and $E$ parameters for the $s$-triazine/N,N-diethylaniline and benzonitrile/N,N-diethylaniline complexes [15, 16].

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