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The Use of Improved Atomic Orbitals in the Evaluation of Zero-Field Splitting Integrals*

DIANA CAPELLO and ALBERTE PULLMAN

Institut de Biologie Physico-Chimique, Laboratoire de Biochimie Théorique, associé au CNRS,
13 rue P. Curie, Paris 5e

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The effect of improving the $2p_z$-atomic orbital representation on the values of molecular zero-field splitting integrals is assessed on the example of the two-center Coulomb integral involving the $(r^2 - 3z^2)/r^5$ operator in the cases of nitrogen and carbon. The results suggest that the use of the classical Slater orbital or its Gaussian equivalent may be misleading.

Ein spezielles, bei der Berechnung der molekularen Nullfeldaufspaltung von Tripletts auftretendes Zweizentrenintegral wird in Abhängigkeit von der Güte der $2p_z$-Orbitale des Kohlenstoff- bzw. Stickstoffatoms untersucht. Offenbar sind die üblichen Slaterorbitale und deren Approximation durch Gaußfunktionen ungeeignet.

On a étudié l'effet de l'amélioration de la base d'orbitales atomiques $2p_z$ sur les valeurs des intégrales qui interviennent dans le calcul de la séparation des niveaux d'un triplet moléculaire en l'absence de champ magnétique. L'utilisation de l'orbitale de Slater classique ou de son équivalent en Gaussienne peut conduire à des conclusions appréciablement erronées.

1. Introduction

The splitting of the triplet state energy levels in the absence of a magnetic field, through spin-spin interaction, has first been observed by electron-spin resonance measurements on molecules oriented in single crystals [1], and subsequently on randomly oriented molecules in rigid glasses [2, 3]. Further refinements of the ESR techniques [4, 5], and the analysis of the observed spectra [3, 6, 7, 8] allow the determination of the energies of the split levels in terms of two *ad hoc* parameters D and E.

The theory of the splitting has been developed on the basis of a perturbation Hamiltonian [9]

$$\mathcal{H}' = \frac{g^2\beta^2}{r^3}\left\{\vec{S}(1)\,\vec{S}(2) - \frac{3\,[\vec{S}(1)\cdot\vec{r}]\,[\vec{S}(2)\cdot\vec{r}]}{r^2}\right\} \tag{1}$$

where $\vec{S}(1)$ and $\vec{S}(2)$ are the spin operators for electrons (1) and (2) [with components $S_x(1)$, $S_y(1)$, $S_z(1)$ and $S_x(2)$, $S_y(2)$, $S_z(2)$], r is the distance between electrons (1) and (2) (with components x, y, z), g is the gyromagnetic ratio and β the Bohr magneton. The use of this Hamiltonian in a first order perturbation treatment yields [10] the theoretical expression of the split levels. When the unperturbed wave function is written as the simplest combination of two Slater deter-

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minants built on one-electron molecular orbitals, the theoretical expression of the zero-field splitting parameters reduces to:

$$D = \tfrac{3}{4}\, g^2\beta^2 \left\langle\varphi \left| \frac{r^2 - 3z^2}{r^5} \right| \varphi\right\rangle \tag{2}$$

$$E = \tfrac{3}{4}\, g^2\beta^2 \left\langle\varphi \left| \frac{y^2 - x^2}{r^5} \right| \varphi\right\rangle \tag{3}$$

where φ represents the antisymetric combination of the two orbitals occupied by the uncoupled electrons [11]:

$$\varphi(1{,}2) = \frac{1}{\sqrt{2}}\left[\varphi_i(1)\,\varphi_j(2) - \varphi_j(1)\,\varphi_i(2)\right] \tag{4}$$

and if the molecular orbitals are expressed as linear combinations of atomic orbitals:

$$\varphi_i = \sum_r c_{ir}\,\chi_r \tag{5}$$

the calculation of D and E reduces to the summation:

$$\tfrac{3}{4}\, g^2\beta^2 \sum_{p,q,r,s} c_{ip}\, c_{jq}\, c_{ir}\, c_{js}\left[\langle pr \mid qs\rangle - \langle ps \mid qr\rangle\right] \tag{6}$$

with the definition:

$$\langle pr \mid qs\rangle = \langle \chi_p(1)\,\chi_r(1) \mid \Omega \mid \chi_q(2)\,\chi_s(2)\rangle \tag{7}$$

where Ω is one of the spin-spin operators involved in expressions (2) and (3).

Since the energy differences between the split levels are very small (of the order of 0.1 cm^{-1} in conjugated hydrocarbons), it is clear that the calculation of D and E values provide a severe test on the accuracy of the wave function used to represent the triplet state. Improvement over the single-configuration representation by configuration mixing has soon been recognized to be necessary if any agreement with experimental values is to be obtained [12—16], while the inadequacy of projected unrestricted Hartree-Fock wave functions was attributed to the exclusion by spin projection of components which are important contributors to the ZFS parameters [17]. Triplet wave functions of the open-shell type supplemented by extensive configuration mixing have also been investigated [18].

All these improvements have been mainly concerned with the molecular wave function. Very little attention has been paid to the atomic orbitals used as the LCAO basis and which occur in the ZFS integrals (7). It is generally assumed that they are Slater $2p_z$-orbitals*. On account of computational difficulties, the zero-field splitting integrals (7) are frequently calculated by approximating the Slater orbitals by Gaussian functions [13, 14, 16] and the emphasis has recently been put on the importance of the usually neglected multicenter and exchange integrals [16]. One may perhaps question, however, the utility of refining the molecular wave function and introducing all atomic integrals, insofar as the atomic orbital basis is made of single Slater orbitals. It has been known for a good many years that even a full configuration interaction calculation with accurate values of the electron-repulsion integrals gives a poor representation of π-electron systems and that this is, at least partly, to be blamed on the inaccuracy of a basis of single Slater p_z-orbitals. This is generally taken care of together with the other "built-in"

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* One specific example of the use of SCF atomic orbitals in carbon compounds can be found in Ref. [19].

approximations of the method [20] by an empirical adjustment of the repulsion integrals between atomic orbitals.

An empirical fitting of the zero-field splitting integrals has been suggested recently [18] which would at the same time correct for the inadequacy of the atomic orbitals and for other effects like $\sigma - \pi$ interactions, but no systematic investigation of the improvment of the atomic orbital basis on the calculation of the ZFS integrals has been performed.

This paper is concerned with the influence of the use of refined atomic functions on the two-center integral:

$$D_I = \frac{3\,g^2\,\beta^2}{4\,hca_0^3} \left\langle \chi_p(1)\,\chi_p(1) \left| \frac{r^2 - 3z^2}{r^5} \right| \chi_q(2)\,\chi_q(2) \right\rangle \tag{8}$$

(atomic units are used and the unit of D_I is the cm^{-1}), taken as an illustrative example.

II. Computations and Choice of Atomic Basis

Geller [21] has shown that the integrals (8) over Slater orbitals could be computed exactly by using the Fourier convolution theorem, and Boorstein and Gouterman [22] have used his method to obtain the expression of D_I in closed analytical form for Slater orbitals with the same orbital exponent ζ. Furthermore, the corresponding general expressions in terms of auxiliary polynomials have become available for Slater orbitals with different exponents [23]. This has been programmed, in Fortran IV, on an IBM 1130* computer allowing the easy obtention of accurate values of D_I for any combination of Slater $2p_z$ atomic orbitals with the same or different exponents.

Thus, we have choosen the $2p_z$-orbital on each center as follows:

a) One Slater orbital with orbital exponent given by Slater's rules (Slater ζ).

b) One single Slater orbital with optimization of the ζ value in a minimal basis set self-consistent-field atomic calculation [24] (Best Single ζ).

c) Linear combination of two Slater-type orbitals with exponents and coefficients optimized in a self-consistent calculation [25] (Double ζ).

d) Similar combination obtained with four Slater-type orbitals. This last combination is advocated to be an excellent representation of accurate Hartree-Fock atomic orbitals [26] (Four ζ).

e) Accessorily, comparison will be given with a basis of one Gaussian function obtained by the criterium of the maximum overlap with the Slater orbital [22, 27]**.

Calculations of D_I with the different atomic basis have been performed for carbon-carbon and nitrogen-nitrogen interactions. The Double ζ and Four ζ functions of Clementi [28] have been used for nitrogen $1s^2 2s^2 2p^3\,{}^4S$ and for divalent carbon $1s^2 2s^2 2p^2\,{}^3P$. The corresponding functions for the $1s^2 2s\,2p^3\,V_4$ valence-state of carbon have been taken in Ref. [29].

III. Results and Discussion

Tabs. 1, 2, 3 summarize the values of D_I for different distances of the two atomic centers in the five approximations mentioned above for nitrogen, divalent

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* We would like to thank Dr. Geller for so kindly rechecking some of his polynomial expressions and part of our programming. Thanks are also due to Dr. Gouterman for a helpful correspondence about a typographical error.

** The D_I integrals in the Gaussian approximation were kindly calculated by E. Kochanski.

Table 1. *Values of the integral D_I for Nitrogen* $1s^2\,2s^2\,2p^3$, (^4S)

R(Å)	R(a.u.)	D_I(cm^{-1})					
		Gaussian	One Slater $\zeta = 1{,}95$	Best Slater $\zeta = 1{,}917$	Double-ζ	Four-ζ	One Slater $\zeta = 1{,}68$
0.0000	0.0000	—	−0.3102	−0.2947	−0.4748	−0.4739	—
0.5000	0.9449	0.3149	0.2773	0.2554	0.1402	—	—
0.8000	1.5118	0.3804	0.4019	0.3822	0.2720	—	—
1.0000	1.8898	0.3569	0.3614	0.3483	0.2616	0.2620	0.2528
1.2550[a]	2.3716	0.2820	0.2748	0.2679	0.2148	0.2134	0.2141
1.3810[a]	2.6097	0.2411	0.2344	0.2295	0.1897	0.1879	0.1900
1.5000	2.8346	0.2053	0.2009	0.1972	0.1674	0.1655	0.1678
2.0000	3.7795	0.1050	0.1076	0.1064	0.0972	0.0961	0.0964
2.5000	4.7244	0.0604	0.0626	0.0620	0.0586	0.0581	0.0577
3.5000	6.6141	0.0254	0.0260	0.0259	0.0250	0.0249	0.0247

[a] These interatomic distances are found in the molecule of 5-aminotetrazole monohydrate [31], and are included as an example of nitrogen-nitrogen distances in conjugated molecules.

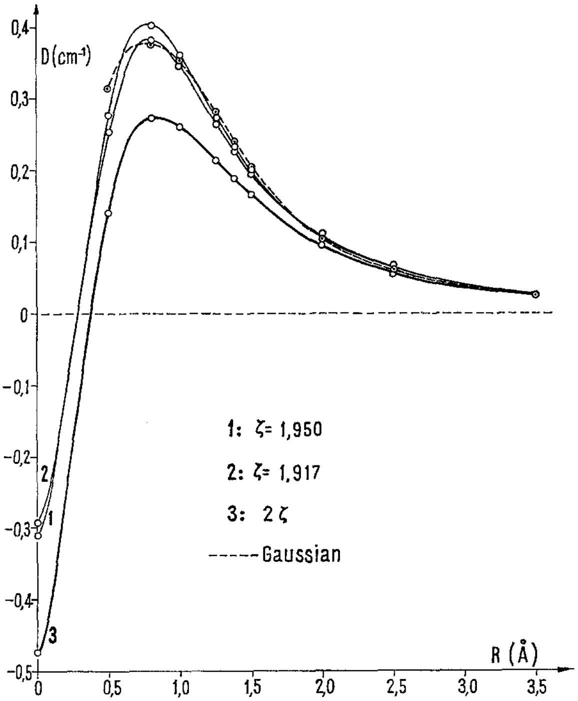

Fig. 1. Curves D_I versus R for nitrogen $1s^2 2s^2 2p^3$ (^4S)

carbon and quadrivalent carbon respectively. This results are plotted in Figs. 1, 2, and 3. A few interesting comments can be made on these data:

The values of D_I calculated with one Slater-type atomic function do not differ very much as one goes from the Slater-rules ζ to the optimized ζ. It is clear, however, that for both atoms, the use of the double ζ functions as an atomic orbital brings about a significant decrease in the values of D_I, except in the region

Table 2. *Values of the integral D_I for Carbon* $1s^2\,2s^2\,2p^2$ (^3P)

R(Å)	R(a.u.)	D_I(cm^{-1})				
		Gaussian	One Slater $\zeta = 1.625$	Best Slater $\zeta = 1{,}5679$	Double-ζ	Four-ζ
0.0000	0.0000	—	−0.1795	−0.1612	−0.2579	−0.2574
0.5000	0.9449	0.1813	0.1049	0.0841	0.0218	—
0.8000	1.5118	0.2353	0.2228	0.1956	0.1326	—
1.0000	1.8898	0.2405	0.2310	0.2088	0.1512	0.1527
1.3000	2.4567	0.2070	0.1933	0.1803	0.1395	0.1397
1.5000	2.8346	0.1720	0.1600	0.1515	0.1222	0.1217
2.0000	3.7795	0.0963	0.0937	0.0908	0.0798	0.0790
2.5000	4.7244	0.0559	0.0565	0.0553	0.0510	0.0505
3.5000	6.6141	0.0240	0.0244	0.0241	0.0231	0.0229

Table 3. *Values of D_I for Carbon* $1s^2\,2s\,2p^3$ (V_4)

R(Å)	R(a.u.)	D_I(cm^{-1})				
		Gaussian	One Slater $\zeta = 1.625$	Best Slater $\zeta = 1{,}59$	Four-ζ	One Slater $\zeta = 1{,}37$
0.0000	0.0000	—	−0.1795	−0.1682	−0.2563	—
0.5000	0.9449	0.1813	0.1049	0.0918	—	—
0.8000	1.5118	0.2353	0.2228	0.2059	—	—
1.0000	1.8898	0.2405	0.2310	0.2173	0.1469	0.1368
1.3000	2.4567	0.2070	0.1933	0.1854	0.1355	0.1336
1.3970[a]	2.6400	0.1904	0.1771	0.1706	0.1276	0.1273
1.5000	2.8346	0.1720	0.1600	0.1548	0.1186	0.1193
2.0000	3.7795	0.0963	0.0937	0.0919	0.0776	0.0788
2.5000	4.7244	0.0559	0.0565	0.0558	0.0499	0.0501
3.5000	6.6141	0.0240	0.0244	0.0242	0.0228	0.0226

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[a] Interatomic distance between two neighbour carbon atoms in benzene.

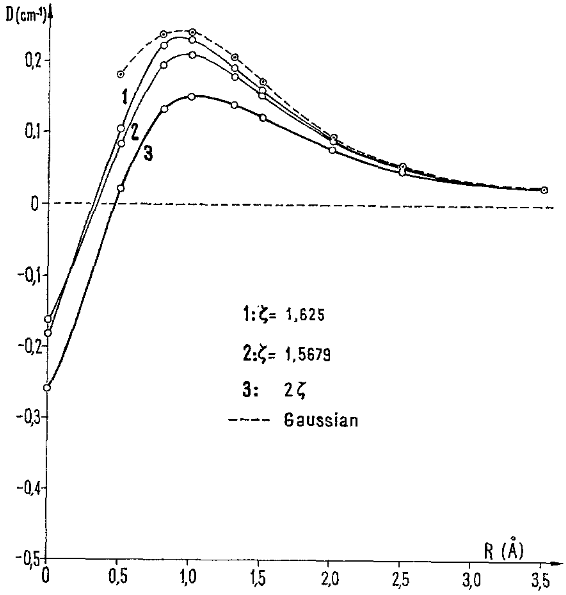

Fig. 2. Curves D_I versus R for carbon $1s^2 2s^2 2p^2$ (^3P)

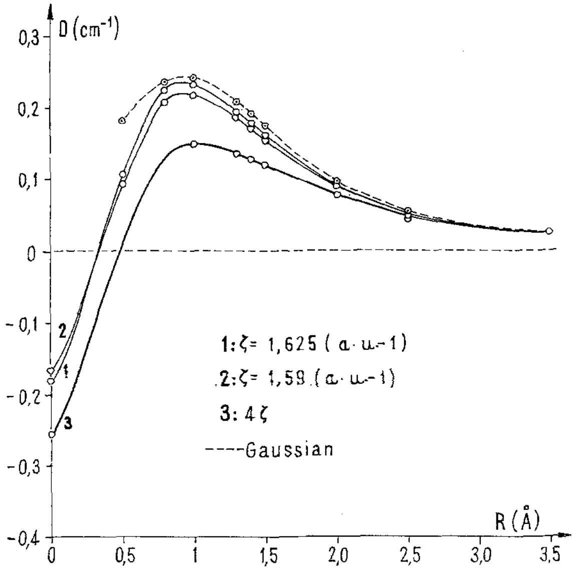

Fig. 3. Curves D_I versus R for carbon $1s^2 2s 2p^3$ (V_4)

of large interatomic distances. Calculations using a combination of four Slater-type functions for each atomic orbital show that practically no improvement is achieved from the two Slater-type functions basis, as the values only differ slightly on the third decimal. Configuration interaction with upper-shell excited configurations in the atomic functions [30] would perhaps bring about a new variation, but it would seriously increase the computation time, which is already large for the Four ζ basis set.

On the other hand, the computation time for the D_I integrals over a two Slater-type basis set is quite reasonable. In a molecular calculation, in principle, the same atomic basis would have to be employed to find the molecular wavefunctions. As this may enlarge significantly the computation time, a value of a single ζ for nitrogen is given which reproduces in the best possible way the curve D_I versus R of the Double ζ atomic basis, in the region where are found most interatomic distances in conjugated molecules (Tab. 1). This value of ζ is 1.68, considerably lower than 1.95 (Slater's rules) or 1.917 (best single ζ). A similar fit for the Four ζ function of the valence-state of carbon yields an *ad hoc* ζ of 1.37 (Tab. 3)*. This would correspond to $D_I = 0.127$ cm^{-1} for adjacent carbon atoms in benzene against 0.177 cm^{-1} obtained with the usual Slater orbital, corresponding to a lowering of D_I of 0.05 cm^{-1}. This is larger than the empirical lowering of 15% suggested in Ref. [18] to fit the experimental data. Interesting, in this connection, is the fact that the use of the empirically lowered integral has yielded D-values somewhat larger than experimental values [32] in a number of aromatic hydrocarbons.

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* Notice that the use of the valence-state functions instead of the ^3P functions for carbon changes very little the D_I-values, a feature which could be expected from the comparison of the functions themselves.

IV. Conclusion

It is clear from this study that the zero-field splitting atomic integrals are very sensitive to the precise form of the atomic orbital basis and that conclusions based on the use of accurate values of all the non-vanishing integrals may be misleading if the usual Slater atomic orbitals are used. In the same fashion the calibration of one or more Gaussian orbitals on these same Slater orbitals is certainly not realistic. At least a calibration on a Double ζ basis or on its Single ζ equivalent (*vide supra*) would be more appropriate. More calculations in this direction are being performed in connection with the utilization of similar basis in energy calculations.

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Dr. A. Pullman
Institut de Biologie Physico-Chimique
Laboratoire de Biochimie Théorique
13, Rue Pierre Curie, Paris 5^e, France