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Evaluation of Magnetic Dipolar Terms: F_2^- Molecule-Ion*

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We have evaluated the magnetic dipolar parameter b for several values of the internuclear distance in the molecule F_2^-. The difficulties appearing in the calculations are discussed and a way to overcome them is presented.

Calculou-se o parâmetro dipolar magnético b para vários valores da distância internuclear da molécula F_2^-. As dificuldades que aparecem nesses cãlculos são discutidas e uma forma de superá-las é apresentada.

1. INTRODUCTION

Typical difficulties involved in the calculation of magnetic dipolar parameters for molecules has been recently discussed by Bufáiçal et al.[1]. In that work, the authors considered the evaluation of

$$b(R) = k \int_V \frac{3z^2 - r^2}{r^5} |3\sigma_u(R)|^2 dV \qquad (1)$$

for the F_2^- molecule, where $\vec{r}$ is the position vector of the electron with respect to the nucleus for which the calculation is performed, k is a conveniently defined constant and $3\sigma_u$ is the relevant one-electron an-

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tibonding molecular orbital obtained by Gilbert and Wahl[2] for several values of the internuclear distance R.

To avoid spurious results associated with the possible existence of a numerical pole in the integrand of the above integral, Bufãiçal et al.[1] suggested that the calculation should be performed taking

$$b = k(\langle \phi'_{\sigma_u}(\vec{r}_A,\vec{r}_B)\,|\,b_z^{(A)}\,|\,\phi'_{\sigma_u}(\vec{r}_A,\vec{r}_B)\rangle + 2\langle s(\vec{r}_A)\,|\,b_z^{(A)}\,|\,\phi'_{\sigma_u}(\vec{r}_A,\vec{r}_B)\rangle \quad , \tag{2}$$

where

$$|3\sigma_u(\vec{r}_A,\vec{r}_B)\rangle = |s(\vec{r}_A) + \phi'_{\sigma_u}(\vec{r}_A,\vec{r}_B)\rangle \quad , \tag{3}$$

$$b_z^{(A)} = \frac{3z_A^2 - r_A^2}{r_A^5} \quad , \tag{4}$$

A and B denoting the two fluorine nuclei.

This procedure eliminates improper numerical contributions arising from s-type wavefunctions, explicitly appearing in the LCAO-MO $3\sigma_u$, centered at the origin A, that is, terms like $\langle s(\vec{r}_A)\,|\,b_z^A\,|\,s(\vec{r}_A)\rangle$. It is well known that such terms give zero if the angular integral is performed first and diverges otherwise.

It should be noticed that this procedure does not avoid all spurious contributions since $\phi'_{\sigma_u}(\vec{r}_A,\vec{r}_B)$ still has s-type components centered at A. The purpose of the present work is to review this problem and to present a manner of handling it.

2. METHOD AND RESULTS

Writing the dipolar constant as

$$b = 2\sqrt{\frac{\pi}{5}}\, k\langle\phi_{\sigma_u}(\vec{r}_A) + \phi_{\sigma_u}(\vec{r}_B)\,\Big|\,\frac{Y_2^0(\theta_A)}{r_A}\,\Big|\,\phi_{\sigma_u}(\vec{r}_A) + \phi_{\sigma_u}(\vec{r}_B)\rangle$$

$$\equiv 2\sqrt{\frac{\pi}{5}}\, k(T_1 + T_2 + 2T_3)\ , \tag{5}$$

where, as defined by Gilbert and Wahl[2],

$$\phi_{\sigma_u}(\vec{r}_A) = \sum_{s=1}^{9} f^{(A)}_{\sigma_u,s}\, r_A^{n_s-1}\, e^{-\xi_s r_A}\, Y^0_{\ell_s}(\theta_A)\ , \tag{6}$$

$$\phi_{\sigma_u}(\vec{r}_B) = \sum_{s=1} f^{(B)}_{\sigma_u,s}\, r_B^{n_s-1}\, e^{-\xi_s r_B}\, Y^0_{\ell_s}(\theta_B) \tag{7}$$

$$f^{(A)}_{\sigma_u,s} = \left[(2n_s)!\right]^{-1/2} C_{\sigma_u,s}(2\xi_s)^{n_s+1/2}\ , \tag{8}$$

$$f^{(B)}_{\sigma_u,s} = (-)^{\ell_s - 1} f^{(A)}_{\sigma_u,s}\ ; \tag{9}$$

explicit forms for T_1, T_2 and T_3 are obtained below.

T_1 is readily obtained:

$$T_1 \equiv \langle\phi_{\sigma_u}(\vec{r}_A)\ \Big|\ \frac{Y_2^0(\theta_A)}{r_A^3}\Big|\ \phi_{\sigma_u}(\vec{r}_A)\rangle = \sum_{s,s'} f^{(A)}_{\sigma_u,s}\, f^{(A)}_{\sigma_u,s'} \times$$

$$\times \left[\frac{5}{4\pi}(2\ell_s+1)(2\ell_{s'}+1)\right]^{1/2} \begin{pmatrix} \ell_s & 2 & \ell_{s'} \\ 0 & 0 & 0 \end{pmatrix}^2 \frac{(n_s + n_{s'} - 3)!}{(\xi_s+\xi_{s'})^{n_s+n_{s'}-2}}\ , \tag{10}$$

where $\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$ is a Wigner 3-j symbol.

On the other hand, $T_{\sigma_u} \equiv \langle \phi_{\sigma_u}(\vec{r}_B) | [Y_2^0(\theta_A)]/r_A^3 | \phi_{\sigma_u}(\vec{r}_B) \rangle$ can be obtained expanding $[Y_2^0(\theta_A)]/r_A^3$ on site B, Ref.3, placing the nuclei on the z-axis:

for $r_B < R$,

$$Y_2^0(\theta_A)/r_A^3 = \sum_{\ell=0}^{\infty} f_\ell^< \, r_B^\ell \, Y_\ell^0(\theta_B) \quad , \tag{11}$$

with

$$f_\ell^< = (-)^\ell \frac{(2+\ell)!}{2!\ \ell!} \left[\frac{5}{2\ell+1}\right]^{\frac{1}{2}} \frac{1}{R^{\ell+3}} \quad , \tag{12}$$

and for $r_B > R$,

$$Y_2^0(\theta_A)/r_A^3 = \sum_{\ell=0}^{\infty} f_\ell^> \frac{1}{r_B^{\ell+3}} \, Y_{\ell+2}^0(\theta_B) \quad , \tag{13}$$

with

$$f_\ell^> = (-)^\ell \frac{(2+\ell)!}{2!\ \ell!} \left[\frac{5}{2\ell+1}\right]^{\frac{1}{2}} R^\ell \quad . \tag{14}$$

Therefore, T_{σ_u} is given by the sum of the two following terms:

for $r_B < R$,

$$\sum_s f_{\sigma_u,s}^{(B)} \sum_{s'} f_{\sigma_u,s'}^{(B)} \sum_{\ell=|\ell_s-\ell_{s'}|}^{\ell_s+\ell_{s'}} f_\ell^< \left[\frac{(2\ell_s+1)(2\ell+1)(2\ell_{s'}+1)}{4\pi}\right]^{\frac{1}{2}} \times$$

$$\times \begin{pmatrix} \ell_s & \ell & \ell_{s'} \\ 0 & 0 & 0 \end{pmatrix}^2 \int_0^R r^{n_s+n_{s'}+\ell} \, e^{-(\xi_s+\xi_{s'})r_B} \, dr_B \quad , \tag{15}$$

and for $r_B > R$,

$$\sum_s f^{(B)}_{\sigma_u,s} \sum_{s'} f^{(B)}_{\sigma_u,s'} \sum_{\ell=|\ell_s-\ell_{s'}|-2}^{\ell_s+\ell_{s'}-2} f^{>}_{\ell} \left[\frac{(2\ell_s+1)(2L+1)(2\ell_{s'}+1)}{4\pi}\right]^{\frac{1}{2}}$$

$$\times \begin{pmatrix} \ell_s & L & \ell_{s'} \\ 0 & 0 & 0 \end{pmatrix}^2 \int_R^{\infty} r_B^{n_s+n_{s'}-\ell-3} e^{-(\xi_s+\xi_{s'})r_B} dr_B \ , \qquad (16)$$

where $L = 2+R$ and the radial integrals (incomplete Γ functions) are obtained analytically.

Finally, $T_3 \equiv \langle \phi_{\sigma_u}(\vec{r}_A) | [Y^0_2(\theta_A)]/r_A^3 | \phi_{\sigma_u}(\vec{r}_B) \rangle$ is calculated expanding $\phi_{\sigma_u}(\vec{r}_B)$ on site A. We have used the method suggested by Jette[4] taking the Löwdin a-functions[5], generalized by Sharma[6] adapted by Duff[7]:

$$\phi_{\sigma_u}(\vec{r}_B) = \sum_{s'} f^{(B)}_{\sigma_u,s'} \sum_{\omega=0}^{\infty} \frac{\Lambda_\omega(s',R,r_A)}{r_A} Y^0_\omega(\theta_A) \ , \qquad (17)$$

where

$$\Lambda_\omega(s',R,r_A) = \sum_{s=0}^{\ell_{s'}} \sum_{\Delta(s,\omega,\ell)} \frac{(-)^{\ell_{s'}-s}\, \ell_{s'}!}{(\ell_{s'}-s)!\ s!} \left[(2\ell_{s'}+1)(2\ell+1)(2\omega+1)\right]^{1/2} \times$$

$$\times \begin{pmatrix} s & \ell & \omega \\ 0 & 0 & 0 \end{pmatrix}^2 R^{\ell_{s'}-s} r_A^s \alpha_\ell(s',R,r_A) \qquad (18)$$

and the a-functions $\alpha_\ell(s',R,r_A)$ are defined by Jette[4], conveniently adapted for Slater - type functions. Therefore, we obtain:

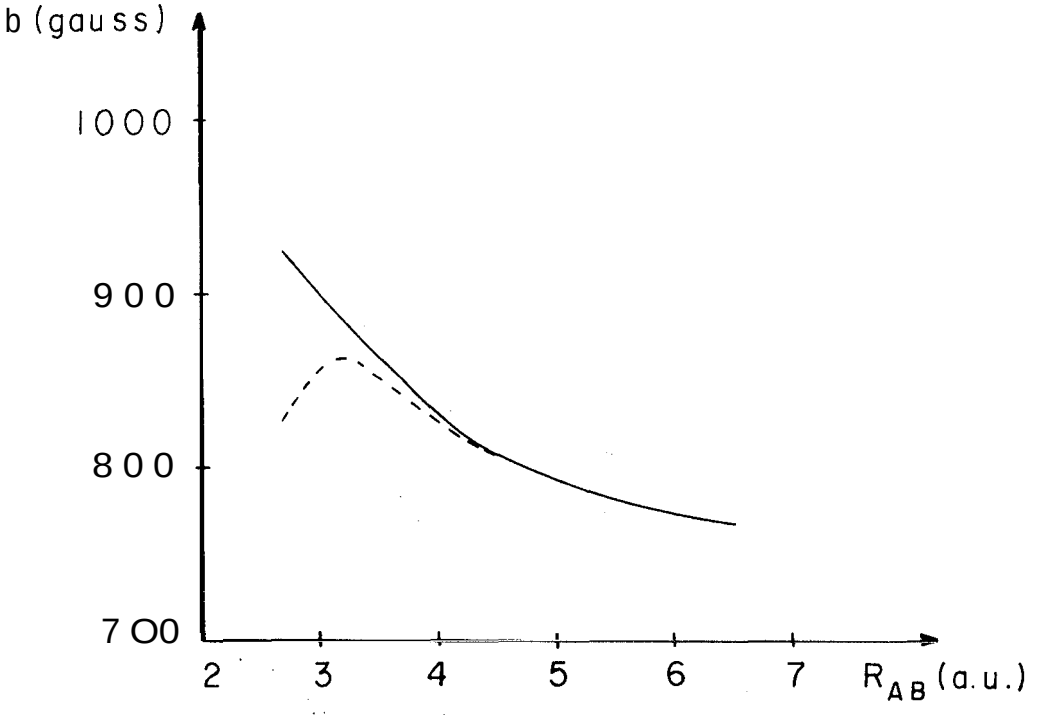

Fig. 1 - Magnetic dipolar constant versus internuclear distance. Full curve: results of the calculation using the method presented in this work. Dashed curve: results of the calculation using the method presented in Ref. 1.

$$T_3 = \sqrt{\frac{5}{4\pi}} \sum_s f^{(A)}_{\sigma_u,s} \sqrt{(2\ell+1)} \sum_{s'} f^{(B)}_{\sigma_u,s'} \sum_{\omega=|\ell_s-2|}^{\ell_s+2} \sqrt{(2\omega+1)} \times$$

$$\times \begin{pmatrix} \ell_s & 2 & \omega \\ 0 & 0 & 0 \end{pmatrix}^2 \int_0^\infty dr_A \, r_A^{n_s-3} \, e^{-\xi_s r_A} \, \Lambda_\omega(s', R, r_A) \qquad (19)$$

and the radial integral was nurnerically evaluated by the Simpson-Newton -Cote rnethod[8].

It is clear, from the expressions for T_1, T_2 and T_3, that thesymrnetry properties involving the 3-j syrnbols elirninate the possible numerical divergence in the evaluation of the dipolar parameter b. The presence of these 3-j reflects the fact that for T_1, T_2 and T_3 we have first performed the angular integrals analytically.

In Fig.1, the full curve shows the results of the calculations using the method presented above.

We have also calculated b as a function of R following the suggestions of Buifãiçal *et al.*[1]; the result is the dashed curve of Figure 1. We point out that there is a disagreement between this curve and the final result of Ref.1; we have verified that in the work by Bufãiçal et *al.*[1] the cross terms of the type

$$\langle s(\vec{r}_A) | b_z^{(A)} | \phi'_{\sigma_u}(\vec{r}_A, \vec{r}_B) \rangle$$

were improperly evaluated and neglected. For small values of R, these terms are not negligible and lead to physically incorrect results since we can expect that b increases for decreasing values of R.

In conclusion, we should remark that the difficulties arising in the evaluation of magnetic dipolar parameters in molecules are due to the fact that functions centered on one nucleus have non zero values on other nuclei. In the case of the F_2^- molecule, we have shown that this

is relevant only for internuclear distances smaller than 3.5 a.u.. Generally, a proper manner of eliminating the spurious contributions due to the existence of s-type functions is essential to a realistic calculation of magnetic dipolar parameters in molecules.

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