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 cálculos 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 Bufáïçal et al.

In that work, the authors considered the evaluation of

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

(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 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, Bufáčal et al. suggested that the calculation should be performed taking

\[ b = k \langle \phi_{\sigma u} (r_A^+, r_B^+) | \phi_{\sigma u} (r_A^+, r_B^+) \rangle + 2 \langle \phi_{\sigma u} (r_A^+) | \phi_{\sigma u} (r_A^+, r_B^+) \rangle, \]  

where

\[ |3\sigma_{\sigma u} (r_A^+, r_B^+)\rangle = |s (r_A^+) + \phi_{\sigma u} (r_A^+, r_B^+)\rangle, \]

\[ b_{\sigma u} (A) = \frac{3s_A^2 - r_A^2}{r_A^2}. \]

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 \(3\sigma_{\sigma u}\), centered at the origin A that is, terms like \( \langle s (r_A^+) | b_{\sigma u} (A) | s (r_A^+) \rangle \). 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 \( \phi_{\sigma u} (r_A^+, r_B^+) \) 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

\[ b = 2 \sqrt{\frac{\pi}{5}} k \left< \phi_\sigma^{(A)} (\mathbf{r}_A) + \phi_\sigma^{(B)} (\mathbf{r}_R) \right| \frac{y^0(\theta)}{r_A} \left| \phi_\sigma^{(A)} (\mathbf{r}_A) + \phi_\sigma^{(B)} (\mathbf{r}_B) \right> \]

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

(5)

where, as defined by Gilbert and Wahl\(^2\),

\[ \phi_\sigma^{(A)} (\mathbf{r}_A) = \sum_{s=1}^9 f_\sigma^{(A)} (u_A, s) n_s^{-1} \varepsilon^{n_A} r_s^{y^0(\theta_A)} , \]  

(6)

\[ \phi_\sigma^{(B)} (\mathbf{r}_R) = \int f_\sigma^{(B)} (u_B, s) n_s^{-1} \varepsilon^{n_B} r_s^{y^0(\theta_B)} , \]  

(7)

\[ f_\sigma^{(A)} = \left[ (2n_s) \right]^{-1/2} c_{\sigma u,s} (2\varepsilon_s)^{n_s + 1/2} , \]  

(8)

\[ f_\sigma^{(B)} = (-1)^{n_s - 1} \]  

(9)

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

\( T_1 \) is readily obtained:

\[ T_1 \equiv \left< \phi_\sigma^{(A)} (\mathbf{r}_A) \right| \frac{y^0(\theta_A)}{r_A^3} \left| \phi_\sigma^{(A)} (\mathbf{r}_A) \right> = \sum_{s,s'} f_\sigma^{(A)} (u_A, s) f_\sigma^{(A)} (u_A, s') \times \]

\[ \times \left[ \frac{5}{4\pi} (2s + 1)(2s' + 1) \right]^{1/2} \left\{ \begin{array}{ccc} \frac{1}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 0 \end{array} \right\} ^{2} \frac{(n_s + n_{s'} - 3)!}{(\varepsilon_s + \varepsilon_{s'})^{n_s + n_{s'} - 2}} , \]

(10)
where \( \{j_1 j_2 j_3 \} \) is a Wigner 3-j symbol.

On the other hand, \( T_i \equiv \langle \phi_{\sigma_i} (r_i) | \sum_{r_B} \frac{Y^0_2 (\theta_A) / r_A^3}{\sum_{r_B} \phi_{\sigma_i} (r_B)} \rangle \) can be obtained expanding \( \frac{Y^0_2 (\theta_A)}{r_A^3} \) on site B, Ref.3, placing the nuclei on the \( z \)-axis:

for \( r_B < R \),

\[
Y^0_2 (\theta_A) / r_A^3 = \sum_{\ell=0}^{\infty} f^{<}_{\ell} r_B^\ell Y^0_\ell (\theta_B),
\]

with

\[
f^{<}_{\ell} = (-)^{\ell} \frac{(2 + \ell)!}{2! \ell!} \left[ \frac{5}{2\ell + 1} \right]^{1/2} \frac{1}{R^{\ell+3}},
\]

and for \( r_B > R \),

\[
Y^0_2 (\theta_A) / r_A^3 = \sum_{\ell=0}^{\infty} f^{>}_{\ell} \frac{1}{r_B^{\ell+3}} Y^0_\ell (\theta_B),
\]

with

\[
f^{>}_{\ell} = (-)^{\ell} \frac{(2 + \ell)!}{2! \ell!} \left[ \frac{5}{2\ell + 1} \right]^{1/2} r_B^{\ell}.\]

Therefore, \( T_i \) is given by the sum of the two following terms:

for \( r_B < R \),

\[
\sum_{s} \sum_{\sigma_i u, s'} \sum_{s} \sum_{\sigma_i u', s''} \sum_{\ell=0}^{\ell_s+\ell_{s'}} f^{(B)}(s, s') f^{(B)}(s', s) f^{<}_{\ell} \left[ \frac{(2\ell_s + 1)(2\ell_{s'} + 1)(2\ell_{s'} + 1)}{4\pi} \right]^{1/2} \times
\]

\[
\times \left\{ \begin{array}{ccc} \ell_s & \ell_s & \ell_{s'} \\ 0 & 0 & 0 \end{array} \right\}^2 \int_0^R r_B^{\ell_s + \ell_{s'} + \ell_{s'}} e^{-\xi_{s'} \xi_{s'}} j_{\ell_s + \ell_{s'}} \, dr_B,
\]

500
and for $r_B > R$, 

$$
\sum_s \sum_s' f_{\sigma u, s}^{(B)} \sum_{s'} f_{\sigma u, s'}^{(B)} \frac{l_{s} + l_{s'} - 2}{l_{s} - l_{s'}} \frac{(2l_{s} + 1)(2L+1)(2l_{s} + 1)}{4\pi} \left[ \begin{array}{c} \alpha \cr \beta \cr \gamma \cr \delta \cr \end{array} \right]
$$

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

Finally, $T_3 \equiv \langle \sum \phi_{\sigma u}^{(A)}(r_A) | \sum \phi_{\sigma u}^{(A)}(r_A) \rangle$ is calculated expanding $\phi_{\sigma u}^{(A)}(r_B)$ 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$^7$:

$$
\phi_{\sigma u}^{(A)}(r_B) = \sum_{s} f_{S}^{(B)} \sum_{s'} \frac{\Lambda_\omega(s', R, r_A)}{r_A^n} y_\omega(\theta_A),
$$

where

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

$$
\begin{bmatrix} 0 & 0 & 0 \end{bmatrix}
$$

and the $a$-functions $\alpha_{\lambda}(s', R, r_A)$ 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.
\[
T_3 = \sqrt{\frac{5}{4\pi}} \sum_{s} f_{\sigma}^{(A)} u_{s}^{(A)} \sqrt{(2\lambda+1)} \sum_{s'} f_{\sigma}^{(B)} u_{s'}^{(B)} \sum_{\omega=|l_s-2|}^{l_s+2} \sqrt{(2\omega+1)} \times \\
\times \left( \begin{array}{ccc} l_s & 2 & \omega \\ 0 & 0 & 0 \end{array} \right)^2 \int_{0}^{\infty} \rho_{A}^{s-3} e^{-\rho_{A}^{s}} \Lambda_{\omega}(s',R,r_{A}) (19)
\]

and the radial integral was numerically evaluated by the Simpson-Newton-Cote method\textsuperscript{8}.

It is clear, from the expressions for \( T_1, T_2 \) and \( T_3 \), that the symmetry properties involving the \( 3-j \) symbols eliminate 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 Buifáićal et al.\textsuperscript{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 Buifáićal et al.\textsuperscript{1} the cross terms of the type

\[
\langle s | \hat{r}_{A}^{\vec{r}} | b_{z}^{(A)} | \phi_{U}^{(A)} \hat{r}_{A}^{\vec{r}} | \hat{r}_{B}^{\vec{r}} \rangle
\]

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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REFERENCES