Calculation of Magnetic Hyperfine Constants: Integration Method for the Dipolar Term*

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The Gauss-Legendre method of integration is applied to calculate the hyperfine magnetic dipolar term for the F_2^- molecule-ion. The difficulties appearing in the numerical calculations and the proper manner of avoid them are discussed in detail.

Aplica-se o método de Gauss-Legendre ao cálculo do termo de estrutura hiperfina dipolar magnética, para o caso do íon molecular F_2^-. Discutem-se em detalhe as dificuldades que surgem nos cálculos numéricos, assim como maneira de evitá-las.

1. INTRODUCTION

The basic understanding for any phenomenological calculation of V_k and H centers in ionic crystals is intrinsically related to the F_2^- molecule-ion, as indicated by Electron Spin Resonance (ESR) measurements of $\tilde{g}$ tensors and hyperfine parameters for these defects[1-5].

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The idea underlying this type of calculation is to use the F_2^- molecule-ion as the basic model for a V_k or an H center, and then try to reproduce magnetic hyperfine tensors determined by ESR measurements, and Electron Nuclear Double Resonance (ENDOR). This kind of calculation furnishes a better description of the defect as a whole, allowing the determination of approximate values for relaxations of the ions neighboring the central molecule, and suggesting possible improvements for the electronic description of the center, as well. Furthermore, these phenomenological calculations can be most relevant when one is interested in proposing an *ab initio* formulation for the problem.

Because of the specific form of the dipole-dipole interaction operator, it is wellknown that a certain care must be taken when numerically evaluating the dipolar constants. In the present paper, we intend to describe in detail the method which we deemed convenient in handling these calculations, discussing also the difficulties and the proper manner to bypass them. The rnain reason in presenting a complete discussion of the method is that is has been successfully employed in a number of papers concerning defects in solids[6,7]. To better understand these calculations, we apply them to the simplest case, which is the evaluation of the dipolar hyperfine constant for the F_2^- molecule-ion.

The monoelectronic wave functions for the F_2^- molecule-ion have been calculated by Gilbert and Wahl[8] who made use of appropriate linear combinations of Slater type functions, centered on the nuclei, within a Restricted Hartree-Fock LCAO-MO scheme. In such a scheme, the only wave function of interest in describing the magnetic properties of the molecule-ion is the one associated with the unpaired electron, that is $3\sigma_u$. Such wave functions were obtained for several values of the internuclear distance R, and, therefore, by varying R, we are able to fit the calculated results with the experimental ones.

2. METHOD OF CALCULATIONS AND RESULTS

In order to calculate, for the F_2^- molecule-ion, the magnetic hyperfine dipolar constant, one has to compute an integral of the form:

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

corresponding to the dipolar interaction of the unpaired electron with the magnetic moment of one of the two equivalent nuclei of the molecule-ion. In Eq.1, $\vec{r}$ is the position vector of the electron with respect to the nucleus for which the calculation is performed, and k is a conveniently defined constant. The integral is evaluated using the coordinate axes defined in Fig.1, where V_1 and V_2 are the molecule-ion nuclei, and R the internuclear distance. The 30_u axial symmetry makes it convenient the use of cylindrical coordinates (cf.Fig.1), and then the ϕ integration can be performed at once.

Since the 30_{u_g} wave function is given in analytical form, the Gauss-Legendre method can be conveniently used for numerical integration. One of the advantages of using this procedure is the eventual saving. of computer memory.

After integrating over ϕ, we calculate the following integral:

$$B = \int_{-\infty}^{+\infty} dz \int_0^{\infty} \left| \rho \left| \frac{3z^2}{(\rho^2+z^2)^{5/2}} - \frac{1}{(\rho^2+z^2)^{3/2}} \right| \right| |f(z,\rho)|^2 d\rho \ , \qquad (2)$$

where (cf.Fig.1), $(\rho^2+z^2)^{1/2} = r$. In the integrand, we have a term which varies as the inverse of a length square, and, therefore, depending on the form $f(z,\rho)$, there could exist a numerical pole that might be a source of difficulties. The integral in Eq.2 is evaluated by writing

$$B = \int_a^b \int_c^d F(\rho,z) \, d\rho dz = \left| \frac{b-a}{2} \right| \left| \frac{d-c}{2} \right| \sum_{j=1}^n \sum_{i=1}^n W_j^n \, W_i^n \, F(\rho_i',z_j'), \qquad (3)$$

where

$$\rho_i' = \left| \frac{b-a}{2} \right| \rho_i^n + \frac{b+a}{2} \ , \quad z_j' = \left| \frac{d-c}{2} \right| z_j^n + \frac{d+c}{2} \ ;$$
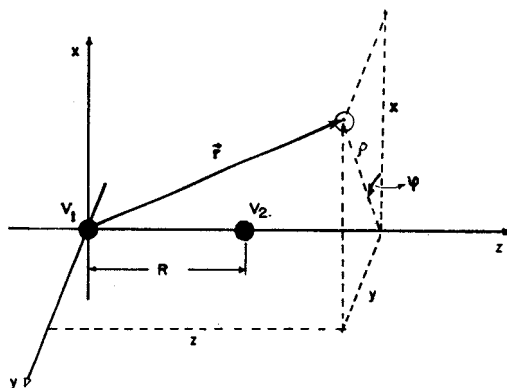
Fig.1 - Coordinate system used in the calculation. V_1 and V_2 are the nuclei of F_2^-.
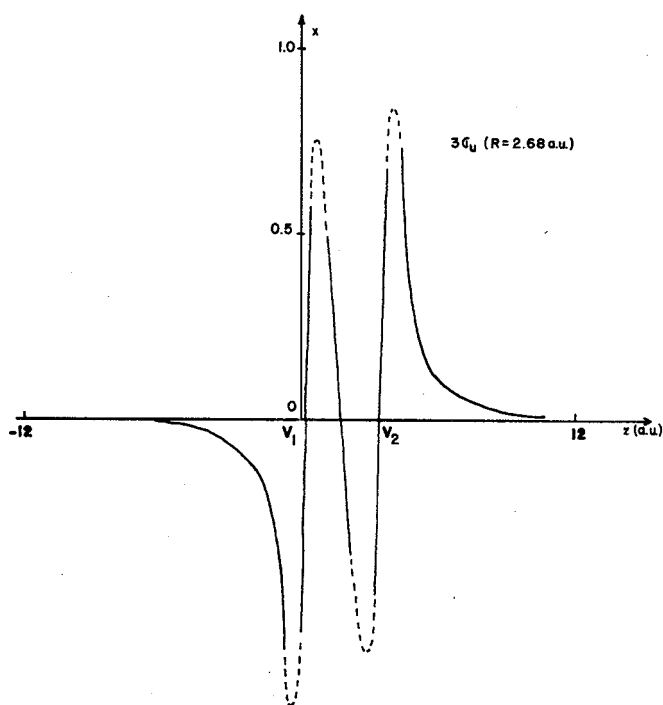

Fig.2 - Plot of $3\sigma_u$ as a function of z for $\rho \approx 0$ and R = 2.68 a.u..

ρ_i^n : i^{th} root of Legendre polynomial of order n,

z^n : j^{th} root of Legendre polynomial of order n, and

W_a^n : weight associated with the αth root.

Let us now discuss a problem which appeared in the calculation . It is clear that the integrand depends on the position of the roots which , in turns, is dependent on the limits of integration, and or the order of the Legendre polynomial. It should also be noticedthat rhese roots are concentrated near the limits of integration. From Fig.2, we see that the behavior of $3\sigma_u$ near the origin, together with the numerical singularity, requires a detailed description of the integrand near this region.

Of course, the first attempt to perform this integration, for different values of R, would be to vary the order of the Legendre polynomials, and to check the convergence of the results. As is clearly shown in Fig.3 (full lines), the convergence is quite poor. In a certain way this result could be expected by the reasons put forward above. In order to obtain results which are independent of the order of the polynomials, and of the limits of integration, as well, it is necessary to divide the interval of integration in subregions so that the roots are concentrated near the origin. Figure 3 (broken line) also shows the results of this procedure: we have made two series of calculations using polynomials of orders 48 and 96, for each subregion. Four subregions were sufficient to assure convergence. We would like to comment that this result can be obtained using polynomials of order smaller than 48. It is worthwhile noticing that the subdivision scheme, taking the origin as one of the limits, automatically excludes the problem that may arise from the existence of a pole, since the integrand will in no case be evaluated at the origin.

It is clear that this last result is not physically acceptable, since we should expect, on physical grounds, that the value of b will increase with decreasing R. This rather unexpected behavior can be easily understood by a close analysis of the $3\sigma_u$ wave function. The linear combination for this wave function contains "s" type Slater functions,
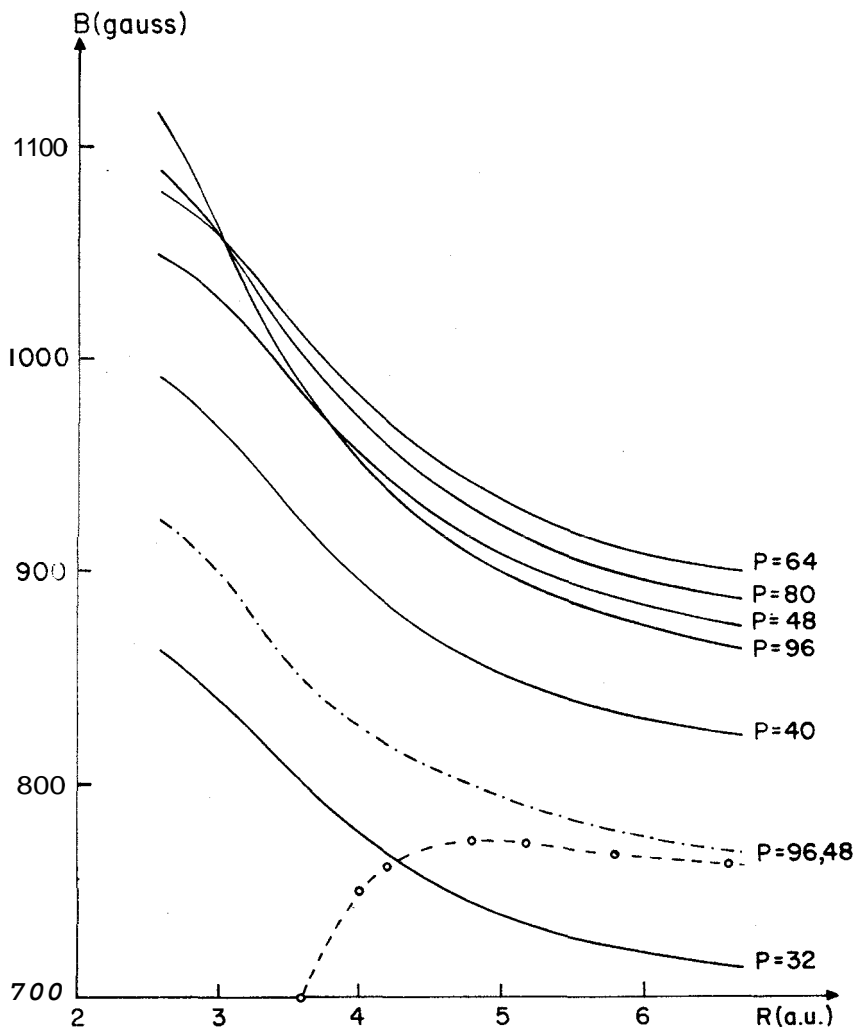
Fig.3 - Plot of the dipolar constant b as a function of R. P indica-
tes the order of the polynominal. Intervals of integration in a.u.:
(-12; +12) for z and (0;8) for ρ.

centered on the origin. Clearly enough, these functions have to be excluded, since they are responsible for the Fermi contact term, and cannot be taken into account in the calculations of the dipolar constant. Only cross terms involving these "s" type functions, centered on the origin, will contribute to this constant; they can be evaluated separately using the same scheme. Calculations have shown that they are usually very small (maximum contribution of the order of 2%). The final result is still shown in Fig.3 (dash-point line), and the agreement with the same kinf of calculations, performed by Jette et al.[10], using a different method, is exact. We have again used polynomials of orders 48 and 96 for each subregion.

We should also mention that the use of this method, when the wave function is given numerically, requires a complex interpolation procedure. We again emphasize that one of the advantages of this scheme is a significant saving on computer memory.

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