Theory of Electric-Field Effects on Electron-Spin-Resonance Hyperfine Couplings

Shashi P. Karna*
U.S. Air Force Phillips Laboratory, Space Mission Technologies Division,
3550 Aberdeen Ave, SE, Kirtland AFB, New Mexico 87117-5776

(Received 26 December 1996)

A quantum mechanical theory of the effects of a uniform electric field on electron-spin-resonance hyperfine couplings is presented. The electric-field effects are described in terms of perturbation coefficients which can be used to probe the local symmetry as well as the strength of the electric field at paramagnetic sites in a solid. Results are presented for the first-order perturbation coefficients describing the Bloembergen effect (linear electric-field effect on hyperfine coupling tensor) for the O atom and the OH radical. [S0031-9007(97)03633-8]

PACS numbers: 31.30.Gs, 31.15.Md, 32.10.Fn, 33.15.Kr

In 1961 Bloembergen [1] predicted that a paramagnetic site lacking inversion symmetry will experience linear shift in its electron spin resonance (ESR) spectrum by a uniform external electric field. Using second-order perturbation theory, Bloembergen [2] also showed that the magnetic hyperfine interactions, either isotropic or anisotropic, can be linear functions of the applied external field. Bloembergen's predictions were soon verified through independent experiments by Kushida and Saiki [3], by Ludwig and Woodbury [4], and by Pershan and Bloembergen [5]. Since these early experiments, the Bloembergen effect or the *linear-electric-field effect* (LEFE) *on hyperfine interaction* has been observed in a number of crystalline materials [6,7]. The Bloembergen effect provides detailed information on local symmetry [6] and can be also used to determine the strength of electric field at paramagnetic centers in solids.

While attention to date has been focused on the LEFE, there are also reports in the literature of nonlinear electric field effects (NLEFE) on the hyperfine coupling (HFC) of paramagnetic systems [8,9]. The NLEFE are considered to be especially important for issues related to the atomic clock [10].

Theoretical treatments of the electric field effects on the ESR HFC have been limited to phenomenological description [2,11,12] or *ad hoc* quantum mechanical approximations [13]. In view of the importance and broad range of applications of the electric field effects on ESR hyperfine interaction, we present in this Letter a general quantum mechanical theory of the effects of a uniform electric field on HFC within the framework of the coupled perturbation approach [14]. By treating the external electric field as a perturbation, analytical expressions are derived to calculate the corrections to HFC in terms of the matrix elements of the hyperfine interaction operator ($\mathbf{S}\cdot\mathbf{I}$) and electric-field-perturbed spin density matrix [($\rho(\mathbf{E})$]. The spin density matrix formulation allows a self-consistent determination of the perturbation coefficients from the ground state wave function. Test results from *ab initio* calculations are presented for the first-order coefficients describing the Bloembergen effect for the O atom and the OH radical.

The Hamiltonian operator describing the hyperfine interaction between the magnetic moments associated with the electron spin **S** and nuclear spin **I** in a system containing N magnetic nuclei is given by [15]

$$\mathcal{H}_{hf} = \sum_N \mathbf{S}\cdot\mathbf{A}_N\cdot\mathbf{I}_N\,, \tag{1}$$

where **A**, a second-rank traceless tensor, is called the HFC tensor. **A** can be resolved into an *isotropic* (scalar) part a_N and an *anisotropic* (tensor) part $\mathbf{T}_N$ as [15]

$$\mathbf{A}_N = a_N + \mathbf{T}_N\,, \tag{2}$$

where a_N describes the interaction of electron-spin magnetic moment with nuclear-spin magnetic moment at the site of the nucleus, and $\mathbf{T}_N$ describes the interaction between electron-spin dipole and nuclear-spin dipole.

For a molecular wave function Ψ built up from one-electron basis functions ϕ_μ, a_N, and $\mathbf{T}_N$ are obtained as [16]

$$a_N = \frac{4\pi}{3} g_e\beta_e g_N\beta_N\hbar\langle S_z\rangle^{-1}\sum_{\mu\nu}\rho_{\mu\nu}\langle\phi_\mu|\delta(\mathbf{r}_N)|\phi_\nu\rangle\,, \tag{3}$$

$$T_{Nij} = \frac{1}{2} g_e\beta_e g_N\beta_N\hbar\langle S_z\rangle^{-1} \times\sum_{\mu\nu}\rho_{\mu\nu}\langle\phi_\mu|r_N^{-5}(3r_{N_i}r_{N_j} - r_N^2\delta_{ij})|\phi_\nu\rangle\,. \tag{4}$$

In the above equations, g_e is the electronic g factor, often taken as the free electron g factor ($g_0 = 2.002\,319\,3$), β_e is the Bohr magneton, g_N is the nuclear g factor, β_N is the nuclear magneton, S_z is the eigenvalue of the z component of the spin angular moment operator, $\mathbf{r}_N$ is the position vector of the spinning electron relative to nucleus N, and $\delta(\mathbf{r}_N)$ is the Dirac delta function of $\mathbf{r}_N$.

Summation indices μ, ν run over one-electron functions and $i, j (= x, y, z)$ represent the Cartesian coordinates. $\rho_{\mu\nu}$ is an element of the spin density matrix defined at a point P in space as [16,17]

$$\rho(P) = \langle \Psi | \sum_k 2\mathbf{S}_{zk} \delta(r_k) | \Psi \rangle . \tag{5}$$

Here $\mathbf{S}_{zk}$ is the z component of the spin angular momentum for electron k and $\delta(r_k)$ is the Dirac delta function of the distance r_k between electron k and point P. For the sake of brevity, we drop the subscript N from a_N and $\mathbf{T}_N$ henceforth and also use the following definition:

$$G_d = (1/2) g_e \beta_e g_N \beta_N \langle S_z \rangle^{-1}, \qquad G_c = (8\pi/3) G_d;$$
$$V^c_{\mu\nu} = \langle \phi_\mu | \delta(\mathbf{r}_N) | \phi_\nu \rangle ,$$
$$V^{ij}_{\mu\nu} = \langle \phi_\mu | r_N^{-5} (3 r_{N_i} r_{N_j} - r_N^2 \delta_{ij}) | \phi_\nu \rangle .$$

Now we can write Eqs. (3) and (4) in a matrix form as

$$a = G_c \, \mathrm{tr}[\mathbf{V}^c \rho] , \tag{6}$$

$$T_{ij} = G_d \, \mathrm{tr}[\mathbf{V}^{ij} \rho] . \tag{7}$$

Here, tr stands for *trace* and ρ is the spin density matrix defined by Eq. (5). In the above derivation it is assumed that the system is free from external perturbation.

Let us now assume that this system is placed in a uniform external electric field represented by $\mathbf{E}(\mathbf{r}, t) = E(r) \cos \omega t$. For the sake of generality, we have chosen an optical field of arbitrary frequency. Let us further assume that this field is large enough to polarize the unpaired electron spin distribution, so that its effects can be treated as a perturbation to the hyperfine tensor. The perturbation Hamiltonian in this case can be written as

$$\mathcal{H}' = \mathbf{E}(\mathbf{r}, t) \cdot (\mathbf{I} . \mathbf{A}' \cdot \mathbf{S}) . \tag{8}$$

Here, $\mathbf{A}'$ represents the electric-field-perturbed hyperfine (a summation of the operator over all N magnetic nuclei is assumed). We can now write the hyperfine tensor $\mathbf{A}(E) = \mathbf{A} + \mathbf{A}'$ as a Taylor series expansion in terms of the perturbing field $\mathbf{E}(\mathbf{r}, t)$ as

$$\mathbf{A}(E) = \mathbf{A}^{(0)} + \mathbf{A}^{(1)} \cdot \mathbf{E} + \frac{1}{2!} \mathbf{A}^{(2)} : \mathbf{E}\mathbf{E} + \ldots , \tag{9}$$

where the arguments of the electric field have been dropped for the sake of simplicity. In Eq. (9), $\mathbf{A}^{(0)}$ is the hyperfine tensor in the absence of the external field, and $\mathbf{A}^{(n)}$ $(n \geq 1)$ represents the nth-order correction to it. The nth-order coefficient $\mathbf{A}^{(n)}$ is a tensor of rank $m = (n + 2)$ and has, in general, $3^{(n+2)}$ elements. From Eqs. (2) and (9), we can write

$$a(E) = a^{(0)} + \sum_k a^{(1)}_k E_k + \frac{1}{2} \sum_k \sum_l a^{(2)}_{kl} E_k E_l + \ldots , \tag{10}$$

$$T_{ij}(E) = T^{(0)}_{ij} + \sum_k T^{(1)}_{ijk} E_k + \frac{1}{2} \sum_k \sum_l T^{(2)}_{ijkl} E_k E_l + \ldots . \tag{11}$$

Since the field-free isotropic HFC $a^{(0)}$ is a scalar, its first-order electric-field correction $\mathbf{a}^{(1)}$ is a vector with components $a^{(1)}_x$, $a^{(1)}_y$, and $a^{(1)}_z$. The higher-order correction terms $\mathbf{a}^{(n)} (n > 1)$ are tensor quantities of rank n. Unlike $a^{(0)}$, the zeroth-order dipolar term $\mathbf{T}^{(0)}$ is a tensor of rank 2. Therefore, the nth-order correction to $\mathbf{T}$ is a tensor of rank $m = (n + 2)$. The first-order terms $\mathbf{a}^{(1)}$ and $\mathbf{T}^{(1)}$ together describe the Bloembergen effect [1,2] and vanish for a paramagnetic center at a site with a center of inversion. It is important to note that it is *the symmetry at the location of the individual nucleus that counts rather than the symmetry of the entire system* [18]. Thus, from Eq. (2), for a nucleus located at a site with center of inversion,

$$\mathbf{A}^{(1)} = 0 . \tag{12}$$

This is true for all odd rank $\mathbf{A}$ tensors ($\mathbf{A}^{(1)}$, $\mathbf{A}^{(3)}$, etc.) in Eq. (9). The even rank tensors $\mathbf{A}^{(0)}$, $\mathbf{A}^{(2)}$, $\mathbf{A}^{(4)}$, etc., on the other hand, do not have this inversion symmetry restriction. However, the following trace relation [18]

$$\sum_i A^{(0)}_{ii} = \sum_i A^{(1)}_{iij} = \sum_i A^{(2)}_{iijk} = 0; \qquad i, j, k = x, y, z \tag{13}$$

exists for the $\mathbf{A}$ tensor in all orders.

The magnitude of the perturbation coefficients $\mathbf{a}^{(n)}$ and $\mathbf{T}^{(n)}$ will depend on the strength of the electric field, the symmetry of charge distribution at the site of the nucleus, and the "spin polarizability" of the system. We wish to distinguish the term spin polarizability from spin polarization: Spin polarization is used in the ESR literature [15,16] to describe a preferential alignment of the spin vectors in an otherwise perfectly paired shell due to the magnetic field of unpaired electron(s). Thus spin polarization is an intrinsic effect in a paramagnetic system. Spin polarizability, on the other hand, is the electrical polarizability of individual spins induced by an external field.

The expansion coefficients $\mathbf{a}^{(n)}$ and $\mathbf{T}^{(n)}$ [Eqs. (10) and (11)] describing the effects of electric field on HFC can be evaluated from a perturbative treatment of Eqs. (6) and (7), respectively. A Taylor series expansion of Eq. (6) in terms of the electric field **E** and collection of the terms with same coefficients yield, to second order,

$$a^{(0)} = G_c \operatorname{tr}[\mathbf{V}^c \rho^{(0)}], \qquad a_i^{(1)} = G_c \operatorname{tr}[\mathbf{V}^c \rho_i^{(1)}], \qquad a_{ij}^{(2)} = G_c \operatorname{tr}[\mathbf{V}^c \rho_{ij}^{(2)}]. \tag{14}$$

A similar treatment to Eq. (7) yields

$$T_{ij}^{(0)} = G_d \operatorname{tr}[\mathbf{V}^{ij} \rho^{(0)}], \qquad T_{ijk}^{(1)} = G_d \operatorname{tr}[\mathbf{V}^{ij} \rho_k^{(1)}], \qquad T_{ijkl}^{(2)} = G_d \operatorname{tr}[\mathbf{V}^{ij} \rho_{kl}^{(2)}]. \tag{15}$$

Expressions for coefficient with ($n > 2$) can be derived in an analogous manner. In deriving Eqs. (14) and (15), use has been made of the fact that the matrix elements $V_{\mu\nu}^{c}$ and $V_{\mu\nu}^{ij}$ of the Dirac delta operator and electric field gradient operator, respectively, are not affected by the external electric field.

Equations (14) and (15) provide a means to analytically calculate $\mathbf{a}^{(n)}$ and $\mathbf{T}^{(n)}$ from a knowledge of the matrix elements of the HFC operators and nth-order spin density matrix $\rho^{(n)}$. Matrix elements $V_{\mu\nu}^{c}$ and $V_{\mu\nu}^{ij}$ can be calculated in a trivial manner from a number of the state-of-the-art *ab initio* quantum mechanical software packages [19]. However, evaluation of the electric-field perturbed spin density matrix $\rho^{(n)}$ is somewhat less trivial. One way to simplify the calculation of $\rho^{(n)}$ is to express it in terms of the density matrix of α- and β-spin electrons. In the notation of the spin-unrestricted Hartree-Fock (UHF) theory [20], the nth-order spin density matrix $\rho^{(n)}$ can be written as

$$\rho^{(n)} = \mathbf{P}^{\alpha(n)} - \mathbf{P}^{\beta(n)}, \tag{16}$$

where $\mathbf{P}^{\alpha(n)}$ ($\mathbf{P}^{\beta(n)}$) represents the nth-order perturbed density matrix for $\alpha(\beta)$-spin electrons. Use of Eq. (16) in Eqs. (14) and (15) yields expressions for $\mathbf{a}^{(n)}$ and $\mathbf{T}^{(n)}$ in terms of $\mathbf{P}^{\sigma(n)}(\sigma = \alpha, \beta)$ that can be conveniently calculated in a self-consistent manner from a recently developed time-dependent (TD) UHF technique [21].

As a test of the present formulation, we performed *ab initio* calculations of zeroth-order hyperfine terms $a^{(0)}$, $T_{ij}^{(0)}$, and their first-order corrections, $a_i^{(1)}$ and $T_{ijk}^{(1)}$, respectively, for O atom and OH radical. The matrix elements of $\mathbf{V^c}$ and $\mathbf{V^{ij}}$ operates were evaluated according to Chandra and Buenker [22]. The perturbed spin-dependent density matrix, $\mathbf{P}^{\sigma(n)}(\sigma = \alpha, \beta)$, was calculated by the *ab initio* TDUHF method as described in Ref. [21]. The atomic basis sets used in the calculations were taken from the work of Sadlej [23]. Calculations on OH radical were performed at an internuclear distance $R(\mathrm{OH}) = 1.95$ bohr. The first-order perturbation coefficients were calculated at a dc electric field ($\hbar\omega = 0$) and also at the ruby laser wavelength ($\lambda = 694.3$ nm, $\hbar\omega = 1.786$ eV). Results of the calculations are listed in Table I.

TABLE I. Hyperfine coupling coefficients for O atom and OH radical. The unit of zero-order coefficients $a^{(0)}$ and $T_{ii}^{(0)}$ is gauss. For the first-order coefficients $a_i^{(1)}$ and $T_{ijk}^{(1)}$, the unit is gauss$/E(5.142 \times 10^{13}$ volts meter$^{-1})$. The first-order coefficients are calculated at static-electric field and at $\lambda = 649.3$ nm (listed inside parentheses).

Nucleus	^{17}O		^{1}H
system	O	OH	OH
$a^{(0)}$	−14.57	−30.30	−44.57
$a_x^{(1)}$	0	0	0
$a_y^{(1)}$	0	0	0
$a_z^{(1)}$	0	−28.43 (−29.34)	18.45 (19.41)
$T_{xx}^{(0)}$	49.50	−96.20	−9.07
$T_{yy}^{(0)}$	−24.75	49.27	−23.74
$T_{zz}^{(0)}$	−24.75	46.93	32.82
$T_{xxz}^{(1)}$	0	2.00 (1.99)	1.34 (1.45)
$T_{yyz}^{(1)}$	0	−4.49 (−4.68)	4.26 (4.37)
$T_{zxx}^{(1)}$	0	10.98 (13.64)	−4.87 (−4.35)
$T_{zyy}^{(1)}$	0	0.77 (0.99)	2.52 (2.60)
$T_{zzz}^{(1)}$	0	2.49 (2.69)	−5.61 (−5.82)

As predicted by Bloembergen [1,2], the first-order corrections to the HFC tensor (Table I) vanish for the O atom but have nonzero values for the OH radical. The former has a center of inversion while the latter does not. In this respect, $\mathbf{a}^{(1)}$ and $\mathbf{T}^{(1)}$ have properties similar to the dipole moment vector μ and the electric hyperpolarizability tensor β, respectively. Both these latter quantities vanish for a system with centrosymmetric charge distribution [24]. However, these is an important distinction between the hyperfine properties and the electrical properties in their requirements of the spatial symmetry of the charge distribution. The electrical properties μ and β are determined by the overall symmetry of the charge distribution in the system. The hyperfine properties $\mathbf{a}^{(1)}$ and $\mathbf{T}^{(1)}$, on the other hand, depend on the *local* symmetry at the site of the paramagnetic nucleus. Another important distinction between $\mathbf{T}^{(1)}$ tensor and β tensor is in the permutational symmetry of their components. In the static-field limit ($\hbar\omega \rightarrow 0$) the elements of β tensor can be freely interchanged [25], i.e., $\beta_{ijk} = \beta_{jik} = \beta_{jki}$, and so on. The same is not true for the elements of $\mathbf{T}^{(1)}$. We note from Table I that in the case of OH radical, $T_{xxz}^{(1)} \neq T_{zxx}^{(1)}$ and $T_{yyz}^{(1)} \neq T_{zyy}^{(1)}$. The calculated components of $\mathbf{T}^{(0)}$ and $\mathbf{T}^{(1)}$ (Table I), however, follow the trace relation given in Eq. (13).

The magnitude of $a_z^{(1)}$ is calculated to be much larger than those of the elements of $\mathbf{T}^{(1)}$ at both magnetic nuclei in OH. An important aspect of the electric field effects on the hyperfine couplings is reflected in the relative sign of $a^{(0)}$ and $a_z^{(1)}$. In OH radical, $a^{(0)}$ and $a^{(1)}$ have the same sign at the O nucleus, but different signs at H. As a consequence, while the magnitude of hyperfine splitting at the O nucleus will experience an increase, that at the H nucleus will experience a decrease in the presence of an external electric field.

The nonzero elements of $\mathbf{a}^{(1)}$ and $\mathbf{T}^{(1)}$ also exhibit substantial dispersion due to the frequency of the external optical field. For example, the value of $a_z^{(1)}(^{17}\mathrm{O})$ in OH radical increases by about 3% in going from a dc electric field ($\hbar\omega = 0$) to the ruby laser frequency ($\hbar\omega = 1.786$ eV). For the same frequency change, the value of $a_z^{(1)}(^1\mathrm{H})$ in the OH radical increases by about 5%. The $T_{ijk}^{(1)}$ terms do not exhibit a systematic change due to frequency, although generally their magnitude shows an increase with the frequency of the optical field. The largest dispersion in going from a dc electric field ($\hbar\omega = 0$) to that corresponding to a ruby laser frequency ($\hbar\omega = 1.786$ eV) is exhibited by $T_{zxx}^{(1)}(^{17}\mathrm{O})$, which increases by about 24%, followed by $T_{zzz}^{(1)}(^{17}\mathrm{O})$ showing an increase of about 8%. Corresponding changes at the ^{1}H nucleus are much smaller.

It is important to note that, for the first-row elements, the UHF method generally overestimates the spin density at the site of the nucleus [26]. Therefore, the results for $a^{(0)}$ and $a_z^{(1)}$ presented here may be somewhat overestimated. Indeed, the calculated $a^{(0)}(^1\mathrm{H})$ is about twice the experimental value of -22.7 G reported by Toriyama and Iwasaki [27] and about 1.6 times the value (-26.7 G) reported by Radford [28]. However, the ratio ($a^{(1)}/a^{(0)}$), which describes the Bloembergen shift in the isotropic hyperfine splitting, should be reasonably accurate.

The UHF method generally gives quite accurate results for the dipolar term $\mathbf{T}$ [26], as is also noted here from a good agreement between the calculated values of $T_{ii}^{(0)}(^1\mathrm{H})$ (Table I) and the corresponding experimental results ($T_{xx} = -6.25$ G, $T_{yy} = -21.52$ G, $T_{zz} = 27.67$ G) obtained by Toriyama and Iwasaki [27]. A similar accuracy is expected in the calculated results for $\mathbf{T}^{(1)}$. Currently, however, we are more concerned about a qualitative description of the electric field effects on hyperfine couplings than the accuracy of the results, which is the subject of a more detailed study [29].

In summary, we have presented a perturbation theory treatment of the effects of electric field on ESR HFC. We have derived quantum mechanical expressions for the expectation values of the perturbation coefficients $a_i^{(1)}$, $a_{ij}^{(2)}$, $T_{ijk}^{(1)}$, and $T_{ijkl}^{(2)}$ in terms of electric-field-perturbed spin-density matrix. The first-order coefficients describing the Bloembergen effect [1,2] provide information about the local symmetry of a paramagnetic center and can be also used to estimate the strength of electric field at a paramagnetic site in solids. We have shown the applicability of the theory by calculating the first-order coefficients in two simple cases, O atom and OH radical. The calculated results follow the symmetry relations predicted by Bloembergen [1,18]. The first-order coefficients also exhibit substantial dispersion due to optical electric field.

The author is indebted to Professor N. Bloembergen for valuable comments and suggestions. Helpful comments by Gerry Lushington, Robert Pugh, John Garth, Joseph Chavez, Prabhat Pandey, Pat Lenahan, and Art Edwards have greatly benifited this work.

---

*Electronic address: karnas@plk.af.mil

[1] N. Bloembergen, Science **133**, 1363 (1961).

[2] N. Bloembergen, Phys. Rev. Lett. **7**, 90 (1961).

[3] T. Kushida and K. Saiki, Phys. Rev. Lett. **7**, 9 (1961).

[4] G.W. Ludwig and H.H. Woodbury, Phys. Rev. Lett. **7**, 240 (1961).

[5] P.S. Pershan and N. Bloembergen, Phys. Rev. Lett. **7**, 165 (1961).

[6] *Encounters in Magnetic Resonances: Selected Papers of N. Bloembergen*, edited by N. Bloembergen (World Science Publishing, River Edge, New Jersey, 1996).

[7] W.B. Mims, *The Linear Electric Field Effect in Paramagnetic Resonance* (Clarendon, Oxford, 1976).

[8] R.D. Haun, Jr. and J.R. Zacharias, Phys. Rev. **107**, 107 (1957).

[9] S.H. Wemple, Bull. Am. Phys. Soc. **8**, 62 (1963).

[10] N. Bloembergen (private communications).

[11] F.S. Ham, Phys. Rev. Lett. **7**, 242 (1961).

[12] A. Kiel, Phys. Rev. **148**, 247 (1966).

[13] B.S. Gerstman and A.S. Brill, Phys. Rev. A **39**, 5903 (1989).

[14] P.W. Langhoff, S.T. Epstein, and M. Karplus, Rev. Mod. Phys. **44**, 602 (1962).

[15] W. Weltner, Jr., *Magnetic Atoms and Molecules* (Dover Publication, New York, 1983).

[16] D.L. Beveridge and J.W. McIver, Jr., J. Chem. Phys. **54**, 4681 (1971).

[17] H.M. McConnel, J. Chem. Phys. **28**, 1188 (1958).

[18] J. Armstrong, N. Bloembergen, and D. Gill, Phys. Rev. Lett. **7**, 11 (1961).

[19] *Modern Techniques in Computational Chemistry,* edited by E. Clementi (ESCOM, Leiden, 1990).

[20] J.A. Pople and R.K. Nesbet, J. Chem. Phys. **22**, 571 (1954).

[21] S.P. Karna, J. Chem. Phys. **104**, 6590 (1996).

[22] P. Chandra and R.J. Buenker, J. Chem. Phys. **79**, 358 (1983).

[23] A.D. Sadlej, Theor. Chem. Acta **79**, 123 (1991).

[24] N. Bloembergen, *Nonlinear Optics* (Benjamin, New York, 1965).

[25] D.A. Kleinman, Phys. Rev. **126**, 1977 (1962).

[26] S.P. Karna and F. Grein, Int. J. Quantum Chem. **36**, 265 (1989).

[27] K. Toriyama and M. Iwasaki, J. Chem. Phys. **55**, 1890 (1971).

[28] H.E. Radford, Phys. Rev. **122**, 114 (1961).

[29] S.P. Karna (to be published).