

## Electronic $g$ -Factor and the Structure of $F$ -Centers\*

F. J. ADRIAN

*Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland*

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A study is made of the small electronic  $g$ -factor shifts observed in complex paramagnetic substances. In most cases there is a simple connection between the contribution of a given ion or atom to  $\Delta g$  and the anisotropic part of the magnetic hyperfine interaction of its nucleus with the electron. This connection is useful now that a double-spin-resonance technique developed recently by Feher can give experimental values for such hyperfine interaction constants.

The theory is applied to the case of the  $F$ -center. It is shown that a central  $F$ -center wave function need not have a large  $g$ -state component to account for the order of magnitude of the observed  $\Delta g$ , provided that the function used is orthogonal to the ion-core orbitals. Both the positive and negative ions contribute to  $\Delta g$ . With the aid of Feher's hyperfine-structure measurements in KCl, one gets:  $\Delta g$  (theory) =  $-0.0053$  as compared with  $\Delta g$  (exp) =  $-0.0070$ .

Exchange interactions between the  $F$ -electron and the ion-core electrons are offered as a possible explanation of the positive  $\Delta g$  found for LiF. Such interactions could polarize the nearest-neighbor halide ions, effectively creating a hole. It is estimated that a 0.5–1% polarization of the  $F^- 2p$  orbitals would be required.

### INTRODUCTION

ONE of the quantities obtained from an electron-spin-resonance experiment is the electronic  $g$ -factor. This quantity often deviates from the free-electron value, the deviation being the result of the interaction between the electron spin moment and the magnetic field created by the motion of the electron in the electric field of its environment. In complex systems, such as organic free radicals and solids, the  $g$ -factor shift  $\Delta g$  is usually quite small ( $\approx 10^{-2}$  to  $10^{-3}$ ). The reason for this is that the strong, nonspherically symmetric, electric fields present in such systems prohibit orbital degeneracy, with the result that the first-order spin-orbit interaction is either zero or so small that the electron spin is virtually independent of the orbital motion. Nonetheless, such  $g$ -factor shifts are interesting, because they can provide an estimate of the departure of the unpaired-electron wave function from spherical symmetry, or give a measure of the separation between the ground and lowest excited state.

The usefulness of the  $g$ -factor shift in structure investigations is limited, because its calculation requires a knowledge of the quantities  $\langle 1/r^3 \rangle$  about the various nuclei and an estimate of the energy separation  $\Delta E$  between the ground and lowest excited states. Calculation of  $\langle 1/r^3 \rangle$  is quite difficult, although limited success has been obtained for the  $F$ -center.<sup>1</sup> Fortunately, the double-spin-resonance technique developed recently by Feher<sup>2</sup> gives a means of determining  $\langle 1/r^3 \rangle$  from the experimental value of the anisotropic part of the magnetic hyperfine interaction. This new development should increase the value of  $\Delta g$  measurements.

Our primary interest in this paper will be the  $F$ -center which exhibits small, usually negative  $\Delta g$  values.<sup>3</sup> Kahn

and Kittel<sup>4</sup> have calculated  $\Delta g$  for  $F$ -electrons in KCl using two different wave functions: an LCAO-MO function (i.e., a wave function for a molecular orbital model, constructed as a linear combination of atomic orbitals centered on the six nearest-neighbor alkali ions) gave a  $\Delta g$  value which was of the correct order of magnitude. Using a central wave function,<sup>5</sup> they concluded that a relatively high ratio of  $g$  to  $s$  state would be required to explain the observed effect. However, extensive admixture of this high-angular-momentum function with the spherically symmetric  $s$ -function seemed unlikely from energy considerations.

A solution to this difficulty has been pointed out by Dexter<sup>6</sup> and Krumhansl<sup>7</sup> in connection with the calculation of hyperfine structure constants. They claim that the central  $F$ -center wave function  $\psi_{F0}$  should be regarded as the coefficient of a Bloch-type function  $u_0$  associated with the bottom of the conduction band, i.e.,

$$\varphi_{F0}(\mathbf{r}) = \psi_{F0}(\mathbf{r})u_0(\mathbf{r}). \quad (1)$$

Since  $u_0$  is large at the nuclei it increased the  $F$ -electron density at these points by a factor of 100, bringing the computed hyperfine interaction constants into line with experiment. They, along with Seitz,<sup>8</sup> suggested that similar considerations would explain the observed electronic  $g$ -factor without the necessity of a large  $g$ -component in  $\psi_{F0}$ .

Recently, Gourary and the author<sup>9</sup> have proposed another central wave function suitable for hyperfine-structure calculations. This wave function is constructed by orthogonalizing  $\psi_{F0}$  to all the ion-core orbitals by

<sup>4</sup> A. Kahn and C. Kittel, Phys. Rev. **89**, 315 (1953).

<sup>5</sup> By central  $F$ -center wave function, we denote an expansion in spherical harmonics about the center of the vacancy.

<sup>6</sup> D. L. Dexter, Phys. Rev. **93**, 244 (1954).

<sup>7</sup> J. A. Krumhansl, Phys. Rev. **93**, 245 (1954).

<sup>8</sup> F. Seitz, Revs. Modern Phys. **26**, 7 (1954).

<sup>9</sup> B. S. Gourary and F. J. Adrian, Phys. Rev. **105**, 1180 (1957).

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<sup>1</sup> F. Adrian, Phys. Rev. **106**, 1357(L) (1957).

<sup>2</sup> G. Feher, Phys. Rev. **103**, 834 (1956).

<sup>3</sup> Kip, Kittel, Levy, and Portis, Phys. Rev. **91**, 1066 (1953).

the Schmidt process:

$$\varphi_{F0} = N[\psi_{F0} - \sum_i (F|i)\psi_i]. \quad (2)$$

The results obtained for the isotropic part of the hyperfine interaction with the above function, which is equivalent to using  $\psi_{F0}$  in a determinantal wave function, are comparable with those of Dexter and Krumhansl. However, the orthogonalized wave function has the advantage that it contains both  $s$  and  $p$  core orbitals, whereas, further refinement of Eq. (1) is required to give the proper admixture of  $p$  core orbitals.

It will be shown that the  $p$  core orbitals which are admixed with  $\psi_{F0}$  give the major contribution to  $\Delta g$  in KCl. However, the ion-core orbitals, when looked at from the center of the vacancy, correspond to a series of high-angular-momentum components in the expansion of  $\varphi_{F0}$ .

### $g$ -FACTOR SHIFT IN COMPLEX SYSTEMS

In calculating  $g$ -factor shifts in complex systems, one uses the fact that the spin-orbit Hamiltonian is a short-range interaction which is negligible everywhere except near the nuclei of the system. Thus, the contribution of each ion or atom to  $\Delta g$  can be treated separately, by expansion about the nucleus in question. Previous calculations have assumed that the spin-orbit Hamiltonian for each atom or ion had the simple form  $\xi(r)\mathbf{L}\cdot\mathbf{S}$ .

The above process can be justified by using the gauge-invariance properties of the complete Hamiltonian. If the unpaired electron moves in the field of an effective electrostatic potential  $U$ , and a magnetic field of vector potential  $\mathbf{A}$ , the Schrödinger equation is:

$$(\mathcal{H} + \mathcal{H}_{s.o.})\varphi = E\varphi, \quad (3)$$

where

$$\mathcal{H} = (1/2m)[\mathbf{p} - (e/c)\mathbf{A}]^2 + eU - (e\hbar/mc)\mathbf{H}\cdot\mathbf{S} + (e\hbar^2/8m^2c^2)\nabla^2 U \quad (4)$$

$$\mathcal{H}_{s.o.} = (e\hbar/2m^2c^2)\mathbf{S}\cdot\nabla U \times [\mathbf{p} - (e/c)\mathbf{A}]. \quad (5)$$

The above Hamiltonian is the expanded form of a result obtained by Frosch and Foley<sup>10</sup> by applying a transformation due to Foldy and Wouthuysen<sup>11</sup> to the Dirac equation. Here,  $e$  is the electronic charge and  $\mathbf{S}$  is the electron spin in units of  $\hbar$ . To determine the contribution of ion or atom  $\alpha$  to  $\Delta g$ , one evaluates the spin-orbit Hamiltonian  $\mathcal{H}_{s.o.\alpha}$ , which is given by Eq. (5) with  $U$  replaced by  $U_\alpha$ , using the ground state eigenfunction of  $\mathcal{H}$ . Since both  $\mathcal{H}$  and  $\mathcal{H}_{s.o.\alpha}$  satisfy the gauge-invariance condition, e.g.,

$$T\mathcal{H}(\mathbf{A})T^{-1} = \mathcal{H}(\mathbf{A} + \nabla\chi),$$

under the gauge transformation generated by the unitary operator

$$T = \exp[ie\chi(\mathbf{r})/c\hbar],$$

the matrix elements of  $\mathcal{H}_{s.o.\alpha}$  will be independent of the choice of gauge. Since  $U_\alpha$  is spherically symmetric in the region of importance close to the nucleus, the simplest choice for a static field is:

$$\mathbf{A} = \frac{1}{2}\mathbf{H} \times \mathbf{r}. \quad (6)$$

With  $\mathbf{A}$  given by Eq. (6), the expressions for  $\mathcal{H}$  and  $\mathcal{H}_{s.o.\alpha}$  are, effectively,

$$\mathcal{H} = \mathbf{p}^2/2m + eU - (e\hbar/mc)\mathbf{H}\cdot\mathbf{S} - (e\hbar/2mc)\mathbf{H}\cdot\mathbf{L},$$

$$\mathcal{H}_{s.o.\alpha} = (e\hbar^2/2m^2c^2)r^{-1}(dU_\alpha/dr)\mathbf{L}\cdot\mathbf{S},$$

where  $\mathbf{L}$  is the orbital angular momentum in units of  $\hbar$ . The terms in  $\mathbf{A}^2$  and  $\nabla^2 U$  have been omitted from  $\mathcal{H}$  because they do not contribute to the  $g$ -factor shift. The component in  $\mathbf{S}\cdot\nabla U_\alpha \times \mathbf{A}$  has been omitted from  $\mathcal{H}_{s.o.\alpha}$ . If  $\mathbf{A}$  is given by Eq. (6) the combined contributions of this term from all potential centers is of the order  $V/mc^2 \approx 10^{-6}$ , where  $V$  is the potential energy of the electron.

The  $g$ -factor shift due to  $\alpha$  can be calculated either variationally or by perturbation theory. First-order terms vanish,<sup>12</sup> so the energy is, in second order,

$$E_{0\alpha}' - E_0 = \sum_k (E_0 - E_k)^{-1} \langle 0 | \mathcal{H}_{\alpha'} | k \rangle \langle k | \mathcal{H}_{\alpha'} | 0 \rangle,$$

where

$$\mathcal{H}_{\alpha'} = - (e\hbar/2mc)\mathbf{H}\cdot\mathbf{L} + (e\hbar^2/2m^2c^2)r^{-1}(dU_\alpha/dr)\mathbf{L}\cdot\mathbf{S},$$

and the zero-order Hamiltonian is  $\mathbf{p}^2/2m + eU$ . The quantity  $\Delta g_\alpha$  is given by that part of  $E_{0\alpha}' - E_0$  which is linear in  $M_S$  and  $H$ . With the assumption of a constant average excitation energy,

$$\Delta E = E_0 - E_k, \quad (7)$$

for all excited states, standard matrix multiplication gives the result:

$$\Delta g_\alpha = (e\hbar^2/m^2c^2\Delta E) \langle 0 | r^{-1}(dU_\alpha/dr)L_z^2 | 0 \rangle. \quad (8)$$

Here, the  $z$  axis is in the direction of  $\mathbf{H}$ . The integration over the spin, which is strongly quantized along  $\mathbf{H}$ , has been carried out. Since the major contribution to the integral comes from the region very close to the nucleus, one can use the following simplification<sup>13</sup>:  $\langle r^{-1}(dU_\alpha/dr) \rangle = eZ_{i\alpha} \langle 1/r^3 \rangle$ , where  $Z_{i\alpha}$  (the effective atomic number for ion  $\alpha$ ) is slightly less than the atomic number of the nucleus. Equation (8) becomes

$$\Delta g_\alpha = (4Z_{i\alpha}\beta^2/\Delta E) \langle 0 | L_z^2/r^3 | 0 \rangle, \quad (9)$$

where  $\beta$  is the Bohr magneton.

### APPLICATION TO $F$ -CENTERS

The magnetic field, which determines the  $z$  axis, may, without loss of generality in the isotropic  $F$ -center, be taken along one of the  $[100]$  axes. Then, if  $\mathbf{R}_\alpha$  is the

<sup>10</sup> R. A. Frosch and H. M. Foley, Phys. Rev. **88**, 1337 (1952).

<sup>11</sup> L. I. Foldy and S. A. Wouthuysen, Phys. Rev. **78**, 29 (1950).

<sup>12</sup> This statement, when applied to systems with strong asymmetrical electric fields, is true in general and for  $F$ -centers in particular. However, it should be verified for the system at hand.

<sup>13</sup> R. G. Barnes and W. V. Smith, Phys. Rev. **93**, 95 (1954).

position vector of ion  $\alpha$  with respect to the center of the vacancy, the  $s$  and  $p$  components of the  $F$ -electron wave function  $\varphi_{F0}$  expanded about  $\alpha$  are, respectively,

$$\begin{aligned}\varphi_{F0s} &= U_{\alpha s}(r)Y_0^0(\theta, \varphi), \\ \varphi_{F0p} &= -U_{\alpha p}(r)[(X_{\alpha}/R_{\alpha})Y_1^x \\ &\quad + (Y_{\alpha}/R_{\alpha})Y_1^y + (Z_{\alpha}/R_{\alpha})Y_1^z].\end{aligned}$$

We have neglected  $d$  and higher components because the core orbitals of ion  $\alpha$  provide the large contributions to  $|\varphi_{F0}|^2$  close to  $\alpha$ , and the ions being studied here do not have  $d$  core orbitals. Using the above components of  $\varphi_{F0}$ , Eq. (9) becomes

$$\Delta g_{\alpha} = \frac{4Z_{i\alpha}\beta^2}{\Delta E} \left( \frac{X_{\alpha}^2 + Y_{\alpha}^2}{R_{\alpha}^2} \right) \langle U_{\alpha p} | 1/r^3 | U_{\alpha p} \rangle. \quad (10)$$

A wave function of the type described in Eq. (2) has been used to calculate the above matrix elements for KCl.<sup>1</sup> It was found that  $\langle 1/r^3 \rangle_{K^+} = 0.68 \times 10^{24} \text{ cm}^{-3}$ . It was felt that the present  $F$ -center wave function was not accurate enough far away from the vacancy to calculate  $\langle 1/r^3 \rangle_{Cl^-}$ . However, in principle, the calculation would proceed along the same lines with the core orbitals of the ion making the chief contribution. Feher's results for the anisotropic hfs constants<sup>14</sup> have been used to determine the values of  $\langle 1/r^3 \rangle$  for both the positive and negative ions. The results are:  $\langle 1/r^3 \rangle_{K^+} = 0.64 \times 10^{24} \text{ cm}^{-3}$  and  $\langle 1/r^3 \rangle_{Cl^-} = 0.16 \times 10^{24} \text{ cm}^{-3}$ .

The selection of the effective excitation energy  $\Delta E$  should be fairly reliable for  $F$ -centers since the extra energy associated with higher excited states is offset by the increased polarization of the medium. For example, the first excited state in the  $F$ -center is only slightly below the conduction band.<sup>15</sup> Use of the  $F$ -band energy gives  $\Delta E = -2.31 \text{ ev}$ .<sup>16</sup> The effective charges are  $(Z_i)_{K^+} = 15$ ,  $(Z_i)_{Cl^-} = 14$ .<sup>18</sup> Thus, the  $g$ -factor shifts due to the nearest-neighbor positive and negative ions are

$$\Delta g(K^+) = -0.0036, \quad \Delta g(Cl^-) = -0.0017.$$

The net theoretical and experimental<sup>3</sup> results are

$$\Delta g(\text{theory}) = -0.0053, \quad \Delta g(\text{exp}) = -0.0070.$$

Thus, it is seen that the usual  $F$ -center wave function, either as an LCAO-MO or central-field function, can account for the order of magnitude of most of the observed  $\Delta g$  values.<sup>17</sup> There is one exception, namely,

<sup>14</sup> G. Feher, Phys. Rev. **105**, 1122 (1957).

<sup>15</sup> N. F. Mott and M. J. Littleton, Trans. Faraday Soc. **34**, 485 (1938).

<sup>16</sup> C. A. Russell and C. C. Klick, Phys. Rev. **101**, 1473 (1956).

<sup>17</sup> T. Kojima (private communication to B. S. Gourary) has obtained, as part of a detailed study of the  $F$ -center, an expression for  $\Delta g$ . He uses a variational solution of our Eq. (4). He states that rough estimates of the required matrix elements, using a LCAO-MO wave function, indicate that  $\Delta g \approx 10^{-3}$ .

LiF for which  $\Delta g = 0.0006$ .<sup>18</sup> The usual  $F$ -electron wave function which pictures the electron as moving solely outside the closed ion cores will predict a negative  $\Delta g$ .

The usual explanation of a positive  $\Delta g$ , which seems to be the most likely one, is a hole or missing electron in a closed shell. The negative ions are the most likely places to look for such a hole since their outer core electrons are far more loosely bound than are those of the positive ions. Formally, one might describe the presence of such a hole in terms of configuration interaction between the usual  $F$ -center wave function and a function containing excited states of the ions. If it is to produce a positive  $\Delta g$ , the hole must have the same spin as the  $F$ -electron. Thus, the interaction which mixes the two configurations must be selective in the spin. Exchange and overlap interactions between the  $F$ -electron and the  $F^- 2p\sigma$  orbital<sup>19</sup> with the same spin are one possibility. These interactions, which are most likely repulsive, might polarize this orbital somewhat, effectively creating a hole. If this were true, the  $F$ -center wave function for LiF would be:

$$\varphi(F) + \epsilon \sum_{\alpha} \langle F, F_{\alpha}' \rangle,$$

where  $\varphi(F)$  denotes the usual  $F$ -center wave function and  $\langle F, F_{\alpha}' \rangle$  describes a configuration involving an excited state of the  $\alpha$ th  $F^-$  ion. Using Eq. (10), one can make the following rough estimate of the contribution of the holes in the halide ion cores to  $\Delta g$ :

$$\Delta g = - (32\beta^2/\Delta E) (Z_i)_{F^-} \langle 1/r^3 \rangle_{2pF^-} \epsilon^2.$$

We have  $(Z_i)_{F^-} \langle 1/r^3 \rangle_{2pF^-} = 3.10 \times 10^{26} \text{ cm}^{-3}$ ,<sup>13</sup> and the  $F$ -band energy for LiF gives  $\Delta E = -4.87 \text{ ev}$ .<sup>20</sup> Thus, if we neglect the direct contribution of  $\varphi(F)$ ,  $\Delta g = 0.0006$  requires that  $\epsilon^2 = 0.0054$ . This result, which indicates that the exchange polarization of each  $F^-$  ion is roughly 0.5 to 1%, is of reasonable size. Moreover, such an effect is likely to be largest in LiF because of its small interionic distance, and large ratio of anion effective radius to cation effective radius. On the other hand, this point is still quite speculative, and further study will be required before any definite conclusion can be reached.

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<sup>18</sup> Norman W. Lord, Phys. Rev. **105**, 756 (1957).

<sup>19</sup>  $p\sigma$  denotes the  $p$  orbital directed along the line joining the nucleus and the center of the vacancy.

<sup>20</sup> We have used the  $F$ -band energy predicted by the formulas of H. Ivey, Phys. Rev. **72**, 341 (1947).