Additive Nature of Correlation and Relativistic Effects in Atomic Hyperfine Structure

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(Received 29 January 1973)

In the calculation of atomic hyperfine structure, it is generally assumed that core polarization effects and relativistic effects can be calculated separately. We examine in detail the validity of this assumption and obtain the lowest-order corrections to such an approach. This correction is described by new operators to be added to the hyperfine Hamilionian, as well as second-order perturbation terms. The systematic effects of the second-order terms are investigated using the effective-operator approach.

I. INTRODUCTION

The Hamiltonian which describes the interaction between the N electrons of an atom and its nucleus is given by, in nonrelativistic form,[1]

$$\mathcal{H}_{\rm hfs} = \mathcal{H}_D + \mathcal{H}_Q ,$$

$$\mathcal{H}_D = \frac{2\mu_0\mu_I}{I}\left\{\sum_{i=1}^{N}\left[\frac{[2(2l+1)]^{1/2}}{3}\frac{\delta(r_i)}{r_i^2}\vec{w}_i^{(10)1} + \frac{[6l(l+1)(2l+1)]^{1/2}}{3}\frac{1}{r_i^3}\vec{w}_i^{(01)1} + \left(\frac{l(l+1)(2l+1)}{(2l+3)(2l-1)}\right)^{1/2}\frac{1}{r_i^3}\vec{w}_i^{(12)1}\right]\cdot\vec{I}^{(1)}\right\}, \tag{1}$$

$$\mathcal{H}_Q = e\sum_{i=1}^{N}\left(\frac{2l(l+1)(2l+1)}{5(2l+3)(2l-1)}\right)^{1/2}\frac{1}{r_i^3}(\vec{w}_i^{(02)2}\cdot\vec{F}^{(2)}) .$$

Here, $\vec{F}^{(2)}$ is a tensor of rank 2 in the nuclear space, related to the nuclear quadrupole moment Q by

$$Q = (2/e)\langle I M_I = I | F_0^{(2)} | I M_I = I\rangle ;$$

μ_I is the magnetic dipole moment of the nucleus; I is the spin of the nucleus; and $\vec{w}^{(kk)}$ is the double tensor of Judd.[2] We have, of course, neglected terms arising from interactions between the electrons and higher-order nuclear multipoles.

In practice, one calculates expectation values of $\mathcal{H}_{\rm hfs}$ with wave functions obtained using some type of central potential or modified Hartree-Fock potential. Comparison of expectation values calculated in this way with experimentally determined values has shown that this procedure is generally not sufficiently sophisticated to provide accurate results. The two main sources of error which arise in this approach are well known: First, the use of central-field wave functions rather than wave functions obtained using the correct interelectron potential may lead to important perturbation effects ("correlation" and "core polarization"); second, the energy of the electrons involved may be such that relativistic effects are important.

There are many techniques available for calculating core-polarization and correlation effects[3] (CP-C effects); in general, they involve use of some form of sophisticated many-body theory. The effects of relativity on hyperfine structure have been well known, of course, for many years[4]; the theory was relatively recently put into a very convenient and useful form by Sandars and Beck.[5]

In the determination of relativistic wave functions, it is even more difficult to use the correct interelectron potential than in the nonrelativistic case, and one is almost always forced to use some type of central-field approximation to the correct potential. Thus, one should, in principle, calculate both the first-order hyperfine structure and the CP-C effects using relativistic wave functions, thus compensating for both of the major failings of the simple theory. However, owing to the complexity of the relativistic wave functions and relativistic interactions, such a complete program is not feasible at this time. The compromise which is most often made is to treat the effects as "additive"; that is, to calculate the relativistic hyperfine structure using relativistic wave functions obtained in a central field, and to add to that the CP-C effects which are calculated using nonrelativistic wave functions.

The sophistication of the nonrelativistic CP-C calculations has reached such high levels, however, that one can consider possible corrections to this additive approach. As we shall show, the first corrections are of order $(Z\alpha)^2$ smaller than the hyperfine structure itself. Although small, this correction can compare in magnitude with the results of some CP-C calculations.

II. RELATIVISTIC INTERACTIONS

The Hamiltonian most often used to describe the interaction between N relativistic electrons and a fixed nucleus of charge Ze is given by

$$\mathcal{H}=\sum_{i=1}^{N}\left(c(\vec{\alpha}_i\cdot\vec{p}_i)+\beta_i mc^2-\frac{Ze^2}{r_i}\right)+\sum_{i>j}\frac{e^2}{r_{ij}}+\mathcal{H}_B, \quad (2)$$

where $\mathcal{H}_B$ is the Breit interaction[6]

$$\mathcal{H}_B=-\frac{e^2}{2}\sum_{i>j}\left(\frac{\vec{\alpha}_i\cdot\vec{\alpha}_j}{r_{ij}}+\frac{(\vec{\alpha}_i\cdot\vec{r}_{ij})(\vec{\alpha}_j\cdot\vec{r}_{ij})}{r_{ij}^3}\right) \quad (3)$$

and $\vec{r}_{ij}=\vec{r}_i-\vec{r}_j$, $r_{ij}=|\vec{r}_{ij}|$; $\vec{\alpha}$ is a 4×4 matrix related to the usual Pauli spin matrices $\vec{\sigma}$ by

$$\vec{\alpha}=\begin{pmatrix}0 & \vec{\sigma}\\ \vec{\sigma} & 0\end{pmatrix}.$$

The presence of an external field modifies this interaction through the addition of a term depending on the scalar potential Φ of the field $e\sum_i\Phi(\vec{r}_i)$ and a term depending on the vector potential $\vec{A}$ of the field $e\sum_i\vec{\alpha}_i\cdot\vec{A}(\vec{r}_i)$. This Hamiltonian is, of course, neither covariant nor exact; its limitations have, however, been discussed in detail elsewhere[7] and shall not be considered here.

Unfortunately, the eigenvalue equation for $\mathcal{H}$,

$$\mathcal{H}|\psi)=E|\psi), \quad (4)$$

is much too complicated to be solved directly. One can, of course, utilize perturbation theory at this point to obtain approximate solutions to Eq. (4). That is, one can write

$$\mathcal{H}=\mathcal{H}_C+\mathcal{H}_P+\mathcal{H}_B, \quad (5)$$

where

$$\mathcal{H}_C=\sum_{i=1}^{N}[c(\vec{\alpha}_i\cdot\vec{p}_i)+\beta_i mc^2+U(r_i)]=\sum_{i=1}^{N}\mathcal{H}_c(i),$$

$$\mathcal{H}_P=\sum_{i=1}^{N}\left(-\frac{Ze^2}{r_i}-U(r_i)\right)+\sum_{i>j}\frac{e^2}{r_{ij}}.$$

The quantity $U(r)$, the "central field," is chosen so as to make $\mathcal{H}_P$ small. Then, one can solve the eigenvalue equation

$$\mathcal{H}_C|\varphi)=E_C|\varphi) \quad (6)$$

and use perturbation theory to obtain approximate values of $|\psi)$ and E. This approach is somewhat limited, however, because the Breit interaction can be treated only to first order in the perturbation expansion.[7] This limitation complicates greatly the application of the perturbation solutions to studies of hyperfine structure.

A procedure which circumvents the complications of the relativistic-perturbation approach is obtained by using the Foldy-Wouthuysen (FW) transformation.[8] In order to apply this technique to a study of hyperfine structure in the following sections, we will need to have FW expansions for both $\mathcal{H}$ and $\mathcal{H}_C$. These expansions are well known[8,9]; one obtains, approximately to order $(Z\alpha)^4mc^2$,

$$\mathcal{H}\to\mathcal{H}'=\sum_{i=1}^{N}\left(mc^2+\frac{(\vec{\sigma}_i\cdot\vec{p}_i)^2}{2m}-\frac{Ze^2}{r_i}+\frac{\hbar}{2m^2c^2}\left\{\left[\vec{\nabla}_i\left(-\frac{Ze^2}{r_i}+\sum_{j\neq i}\frac{e^2}{r_{ij}}\right)\vec{p}_i\right]\cdot\vec{s}_i\right\}\right.$$
$$\left.-\frac{(\vec{\sigma}_i\cdot\vec{p}_i)^4}{8m^3c^2}+\frac{\hbar^2}{8m^2c^2}\nabla_i^2\left(-\frac{Ze^2}{r_i}+\sum_{j\neq i}\frac{e^2}{r_{ij}}\right)\right)+\sum_{i>j}\frac{e^2}{r_{ij}}+\mathcal{H}_{BP}, \quad (7)$$

where $\mathcal{H}_{BP}$ is the Breit-Pauli operator

$$\mathcal{H}_{BP}=\sum_{i\neq j}\left\{2\mu_0^2\left(\frac{\vec{s}_i\cdot\vec{s}_j}{r_{ij}^3}-\frac{3(\vec{r}_{ij}\cdot\vec{s}_i)(\vec{r}_{ij}\cdot\vec{s}_j)}{r_{ij}^5}-\frac{8\pi}{3}(\vec{s}_i\cdot\vec{s}_j)\delta^{(3)}(\vec{r}_{ij})\right)\right.$$
$$\left.+\frac{\hbar}{m^2c^2}\left[\left(\vec{\nabla}_i\frac{e^2}{r_{ij}}\vec{p}_i\right)\cdot\vec{s}_j\right]-\frac{e^2}{4m^2c^2}\left(\frac{\vec{p}_i\cdot\vec{p}_j}{r_{ij}}+\frac{\vec{r}_{ij}(\vec{r}_{ij}\cdot\vec{p}_{ij})\cdot\vec{p}_j}{r_{ij}^3}\right)\right\}, \quad (8)$$

$$\mathcal{H}_C\to\mathcal{H}_C'=\sum_{i=1}^{N}\left(mc^2+\frac{(\vec{\sigma}_i\cdot\vec{p}_i)^2}{2m}+U(r_i)+\frac{\hbar}{2m^2c^2}\{[\vec{\nabla}_iU(r_i)\vec{p}_i]\cdot\vec{s}_i\}-\frac{(\vec{\sigma}_i\cdot\vec{p}_i)^4}{8m^3c^2}+\frac{\hbar^2}{8m^2c^2}\nabla_i^2U(r_i)\right). \quad (9)$$

Of course, both $\mathcal{H}'$ and $\mathcal{H}_C'$ are too complicated for one to solve the resulting eigenvalue equations exactly. In the following sections, we shall use solutions of the nonrelativistic central-field equation

$$\mathcal{H}_{nr}|\varphi\rangle=\sum_{i=1}^{N}\left(\frac{p_i^2}{2m}+U(r_i)\right)|\varphi\rangle=E_{nr}|\varphi\rangle \quad (10)$$

to construct perturbation solutions for the eigenvalue equations for the operators $\mathcal{H}'$ and $\mathcal{H}_C'$.

III. MAGNETIC-DIPOLE HYPERFINE INTERACTION

In this section, we wish to consider the effects of adding a term

$$e\sum_{i=1}^{N}\vec{\alpha}_i\cdot\vec{A}(\vec{r}_i)$$

to the Hamiltonians of Sec. II, where

$$\vec{A}(r)=\frac{\mu_I}{I}(\vec{I}\times\vec{r})\frac{1}{r^3}. \quad (11)$$

The "additive" approach of Sec. I can, in this case, be described in terms of the complete wave function $|\psi)$ and the central-field wave functions $|\varphi)$ and $|\varphi\rangle$ of Sec. II as

$$(\psi|e\sum_{i=1}^{N}\vec{\alpha}_i\cdot\vec{A}(\vec{r}_i)|\psi)=(\varphi|e\sum_{i=1}^{N}\vec{\alpha}_i\cdot\vec{A}(\vec{r}_i)|\varphi)$$
$$+\left(\sum_K\frac{\langle\varphi|\mathcal{H}_D|\varphi_K\rangle\langle\varphi_K|\mathcal{H}_P|\varphi\rangle}{E-E_K}+\text{c.c.}\right), \quad (12)$$

where all higher-order terms left unspecified involve one interaction with $\mathcal{H}_D$ and multiple interactions with $\mathcal{H}_P$. We will essentially make FW transformations of both sides of this equation in order to determine what terms have been neglected.

One can easily make a FW expansion of the Hamiltonian

$$\mathcal{H}_1=\mathcal{H}+e\sum_{i=1}^{N}\vec{\alpha}_i\cdot\vec{A}(\vec{r}_i)=\mathcal{H}+\mathcal{H}_A\,.$$

It is well known[10] that the resulting FW expansion of $\mathcal{H}_1$, which we denote as $\mathcal{H}_1'$, is equivalent to $\mathcal{H}'$ with $\vec{p}_i$ replaced by $\vec{\pi}_i$, where

$$\vec{\pi}_i=\vec{p}_i+(e/c)\vec{A}(\vec{r}_i)\,. \quad (13)$$

As in Sec. II, we cannot solve the eigenvalue equation for $\mathcal{H}_1'$, but must find a perturbation solution using $|\varphi\rangle$ [Eq. (10)]. From the resulting expansion of the energy, we pick out those terms depending linearly on $\vec{A}$; this set, which we shall call $E_{\rm hf}$, allows one to calculate the hyperfine structure through terms of magnitude roughly $(Z\alpha)^4E_{\rm nr}$ using the nonrelativistic central-field wave function $|\varphi\rangle$:

$$E_{\rm hf}=\langle\varphi|\mathcal{H}_D|\varphi\rangle+\left(\sum_K\frac{\langle\varphi|\mathcal{H}_D|\varphi_K\rangle\langle\varphi_K|\mathcal{H}_P+\mathcal{H}_{\rm so}+\mathcal{H}_{\rm BP}|\varphi\rangle}{E-E_K}+\text{c.c.}\right)$$
$$+\langle\varphi|\sum_{i=1}^{N}\Bigg(\frac{e\hbar}{2m^2c^3}\left\{\left[\vec{\nabla}_i\left(-\frac{Ze^2}{r_i}+\sum_{j\neq i}\frac{e^2}{r_{ij}}\right)\vec{A}_i\right]\cdot\vec{s}_i\right\}+\frac{e\hbar}{m^2c^3}\left\{\left[\vec{\nabla}_i\left(\sum_{j\neq i}\frac{e^2}{r_{ij}}\right)\vec{A}_i\right]\cdot\vec{s}_j\right\}$$
$$-\frac{e^3}{2m^2c^3}\sum_{j\neq i}\left(\frac{\vec{A}_i\cdot\vec{p}_j}{r_{ij}}+\frac{(\vec{r}_{ij}\cdot\vec{A}_j)(\vec{r}_{ij}\cdot\vec{p}_i)}{r_{ij}^3}\right)-\frac{p_i^2}{2m^2c^2}\mathcal{H}_D(i)\Bigg)|\varphi\rangle\,, \quad (14)$$

where $\mathcal{H}_{\rm so}$ is the spin-orbit operator[1]

$$\mathcal{H}_{\rm so}=\sum_{\text{all }nl}\left(\sum_{i\neq j}A(n_1l_1n_2l_2;n_3l_3n_4l_4)[\vec{w}_i^{(00)0}(n_1l_1,n_3l_3)\cdot\vec{w}_j^{(11)0}(n_2l_2,n_4l_4)]+\sum_{i=1}^{N}B(n_2l_2,n_4l_4)w_i^{(11)0}(n_2l_2,n_4l_4)\right),$$

with

$$A(n_1l_1n_2l_2;n_3l_3n_4l_4)=-\frac{\hbar^2}{2m^2c^2}\left[l_2(l_2+1)(2l_2+1)(2l_1+1)\right]^{1/2}\delta(l_2,l_4)\delta(l_1,l_3)$$
$$\times\iint R_2(r_2)R_4(r_2)\frac{1}{r_2}\frac{1}{dr_2}\left(e^2\frac{R_1(r_1)R_3(r_1)}{r_>}\right)dr_1\,dr_2\,, \quad (15)$$

$$B(n_2l_2,n_4l_4)=-\frac{\hbar^2}{2m^2c^2}\delta(l_2,l_4)\left(\frac{l_2(2l_2+1)(l_2+1)}{2}\right)^{1/2}\iint R_2R_4\frac{1}{r}\frac{d}{dr}\left(-\frac{Ze^2}{r}\right)dr\,,$$

and $\vec{w}^{(k_k)}(n_1l_1,n_2l_2)$ is the double tensor of Feneuille.[10] Clearly, to order $(Z\alpha)^4E_{\rm nr}$, $E_{\rm hf}$ corresponds to the first-order hyperfine structure calculated using the complete relativistic wave function

$$(\psi|e\sum_{i=1}^{N}\vec{\alpha}_i\cdot\vec{A}(\vec{r}_i)|\psi)=(\psi|\mathcal{H}_A|\psi)\,,$$

and thus includes both relativistic and CP-C effects.

In order to determine what terms must be added to the additive approach, we must also have a nonrelativistic expansion for the matrix element $(\varphi|\mathcal{H}_A|\varphi)$. This is easily obtained by replacing $\vec{p}_i$ by $\vec{\pi}_i$ in Eq. (9), and by making once again a perturbation in terms of $|\varphi\rangle$. If we denote the resulting energy terms linear in $\vec{A}$ by $E_{\rm hf}^c$, we find

$$E_{\rm hf}^c=\langle\varphi|\mathcal{H}_D|\varphi\rangle+\left(\sum_K\frac{\langle\varphi|\mathcal{H}_D|\varphi_K\rangle\langle\varphi_K|\mathcal{H}_{\rm soc}|\varphi\rangle}{E-E_K}+\text{c.c.}\right)+\langle\varphi|\sum_{i=1}^{N}\left(\frac{\hbar e}{2m^2c^3}\{[\vec{\nabla}_iU(r_i)\,\vec{A}_i]\cdot\vec{s}_i\}-\frac{p_i^2}{2m^2c^2}\mathcal{H}_D(i)\right)|\varphi\rangle,$$

where

$$\mathcal{H}_{\rm soc} = \frac{\hbar^2}{2m^2c^2} \sum_{\text{all } n_l} \sum_{i=1}^{N} \delta(l_1, l_2) \left(\frac{l_1(l_1+1)(2l_1+1)}{2} \right)^{1/2} \int R_1 R_2 \frac{1}{r} \frac{dU}{dr} dr \, \vec{\mathbf{w}}_i^{(11)0}(n_1 l_1, n_2 l_2) . \tag{16}$$

To an accuracy of roughly $(Z\alpha)^4 E_{\rm nr}$, $E_{\rm hf}^c$ is equal to $(\varphi | e \sum_i \vec{\alpha}_i \cdot \vec{\mathbf{A}}_i | \varphi)$.

Comparing Eqs. (14) and (16), we see that, keeping terms of size roughly $(Z\alpha)^4 E_{\rm nr}$, we can write

$$(\psi | \mathcal{H}_A | \psi) = (\varphi | \mathcal{H}_A | \varphi) + \left(\sum_K \frac{\langle \varphi | \mathcal{H}_D | \varphi_K \rangle \langle \varphi_K | \mathcal{H}_P | \varphi \rangle}{E - E_K} + \text{c.c.} \right) + \Delta_D , \tag{17}$$

$$\begin{aligned} \Delta_D = \langle \varphi | \Bigg[& \frac{e\hbar}{2m^2c^3} \Bigg(\sum_{i=1}^{N} \left\{ \left[\vec{\nabla}_i \left(-\frac{Ze^2}{r_i} - U(r_i) \right) \vec{\mathbf{A}}_i \right] \cdot \vec{\mathbf{s}}_i \right\} \\ & + \sum_{i \neq j} \left[\left(\vec{\nabla}_i \frac{e^2}{r_{ij}} \vec{\mathbf{A}}_i \right) \cdot (\vec{\mathbf{s}}_i + 2\vec{\mathbf{s}}_j) \right] \Bigg) - \frac{e^3}{2m^2c^3} \sum_{i \neq j} \left(\frac{\vec{\mathbf{A}}_i \cdot \vec{\mathbf{p}}_j}{r_{ij}} + \frac{(\vec{\mathbf{r}}_{ij} \cdot \vec{\mathbf{A}}_i)(\vec{\mathbf{r}}_{ij} \cdot \vec{\mathbf{p}}_j)}{r_{ij}^3} \right) \Bigg] | \varphi \rangle \\ & + \left(\sum_K \frac{\langle \varphi | \mathcal{H}_D | \varphi_K \rangle \langle \varphi_K | \mathcal{H}_{\rm so} - \mathcal{H}_{\rm soc} | \varphi \rangle}{E - E_K} + \sum_K \frac{\langle \varphi | \mathcal{H}_D | \varphi_K \rangle \langle \varphi_K | \mathcal{H}_{\rm BP} | \varphi \rangle}{E - E_K} + \text{c.c.} \right) . \end{aligned} \tag{18}$$

The second-order term in Eq. (17) is, of course, the familiar leading term in the CP-C effect; the first two terms in Eq. (17) are thus the leading terms in the additive approach, and Δ_D is the first correction to this approach.

The first of the components of Δ_D, which is a first-order term, is similar to an operator which appears in the calculation of the Zeeman effect.[11] One of the second-order correction terms results from the use of the central potential rather than the correct potential in the relativistic wave equation for $|\varphi)$. The other second-order correction term simply describes perturbations produced by the Breit-Pauli interaction.

These correction terms are roughly of order $(Z\alpha)^2$ times the usual CP-C term. It must be recognized, of course, that because of differences in angular and radial dependence between the operators involved, the ratio between the CP-C term and Δ_D may differ greatly from $(Z\alpha)^2$, depending upon the atom considered. We shall discuss Δ_D further in Secs. V and VI.

IV. ELECTRIC-QUADRUPOLE HYPERFINE INTERACTION

We can, of course, carry out a calculation similar to that of Sec. III in order to determine corrections to the additive approach when the perturbation is $\mathcal{H}_Q$ of Eq. (1). In this case, we compare the developments of the two Hamiltonians

$$\mathcal{H}_2 = \mathcal{H} + \mathcal{H}_Q$$

and (19)

$$\mathcal{H}_3 = \mathcal{H}_C + \mathcal{H}_Q .$$

Following exactly the procedure used in Sec. III, we obtain a correction which we denote by Δ_Q,

$$\begin{aligned} \Delta_Q = & \left(\sum_K \frac{\langle \varphi | \mathcal{H}_{\rm so} - \mathcal{H}_{\rm soc} | \varphi_K \rangle \langle \varphi_K | \mathcal{H}_Q | \varphi \rangle}{E - E_K} + \text{c.c} \right) \\ & + \left(\sum_K \frac{\langle \varphi | \mathcal{H}_{\rm BP} | \varphi_K \rangle \langle \varphi_K | \mathcal{H}_Q | \varphi \rangle}{E - E_K} + \text{c.c} \right) . \end{aligned} \tag{20}$$

Once again, Δ_Q is of order $(Z\alpha)^2$ times the usual CP-C correction to the quadrupole interaction. We shall discuss Δ_Q further in Secs. V and VI.

V. EFFECTIVE OPERATORS

In order to better understand the effects of the second-order operators discussed in Secs. III and IV, we can consider their formulation in terms of effective operators. This formulation, in which a second-order perturbation term is approximated by a first-order operator, can be used when the energy denominator of the second-order term, $E - E_k$, is approximately constant ($E - E_k \simeq \Delta E$) for all states of each of the perturbing configurations. This technique has been used with considerable success to understand the systematic variations of, among other things, the leading term in the CP-C effect.[12] We shall use this technique to consider in some detail the general form of the perturbation depending on the operator $\mathcal{H}_{\rm so} - \mathcal{H}_{\rm soc}$. This is a term which can be calculated reasonably easily, using the same techniques used to evaluate CP-C effects, and is thus of practical interest. We shall not consider in this section the term depending on $\mathcal{H}_{\rm BP}$, as this term, which is probably too small to justify the very complicated calculation involved in its evaluation using CP-C techniques, is not of much practical interest. We shall, however, outline the general effects of this term in Sec. VI.

We consider the case in which N electrons are

in the nl shell ($N \leq 4l+2$), and all others are in filled shells. In order to obtain explicit results, we must explicitly define the central field $U(r)$ to be used; we choose the central field proposed by Judd[13]:

$$\langle \alpha | U(r) + \frac{Ze^2}{r} | \alpha' \rangle = \sum_\beta f(\beta) \left(\langle \alpha_1 \beta_2 | \frac{e^2}{r_{12}} | \alpha_1' \beta_2 \rangle - \langle \alpha_1 \beta_2 | \frac{e^2}{r_{12}} | \beta_1 \alpha_2' \rangle \right), \tag{21}$$

where α and β represent the single-electron quantum numbers $nlm_s m_l$. The sum over β runs over all possible values, and

$$f(\beta) = N_\beta / (4l_\beta + 2),$$

where N_β is the number of electrons present in the $n_\beta l_\beta$ shell.

With the above approximations, the results for the effective operator can be obtained directly from Armstrong,[1] who showed that the effects of a perturbation of the general type

$$\sum_K \frac{\langle \varphi | \mathcal{H}_{so} - \mathcal{H}_{soc} | \varphi_K \rangle \langle \varphi_K | \vec{\mathbf{T}}^{(SL)J} | \varphi \rangle}{\Delta E} + \text{c.c.} \tag{22}$$

could be reproduced by effective operators of the form

$$\vec{\mathbf{P}}^{(\kappa k)J} = \{[\kappa][k][S][L]\}^{1/2} \begin{Bmatrix} S & 1 & \kappa \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} L & 1 & k \\ l & l & l \end{Bmatrix} \begin{Bmatrix} L & S & J \\ \kappa & k & 1 \end{Bmatrix} f \vec{\mathbf{W}}^{(\kappa k)J} + \{[\kappa][k]\}^{1/2} \begin{Bmatrix} L & S & J \\ \kappa & k & 1 \end{Bmatrix} g \sum_{i \neq j} \tfrac{1}{2} (\vec{\mathbf{w}}_i^{(SL)} \cdot \vec{\mathbf{w}}_j^{(11)})^{(\kappa k)J}, \tag{23}$$

where κ and k take on all values allowed by the 6-j symbols; f and g are functions of radial integrals and ΔE only, i.e., are independent of the quantum numbers L, S, J, κ, and k.

In the case of the quadrupole interaction, we identify the operator $T^{(SL)J}$ of Eq. (22) as

$$\sum_{i=1}^{N} \frac{e}{r_i^3} \left(\frac{2l(l+1)(2l+1)}{5(2l-1)(2l+3)} \right)^{1/2} \vec{\mathbf{w}}_i^{(02)2};$$

that is, we have $S=0$, $L=J=2$. The allowed values of κ and k are then $\kappa=1$ and $k=1, 3$. Thus, we obtain the effective operators

$$\begin{aligned} \vec{\mathbf{P}}^{(11)2} &= \frac{e}{56} f \vec{\mathbf{w}}^{(11)2} + e(\tfrac{3}{20})^{1/2} g \sum_{i \neq j} (\vec{\mathbf{w}}_i^{(02)} \vec{\mathbf{w}}_j^{(11)})^{(11)2}, \\ \vec{\mathbf{P}}^{(13)2} &= -\frac{e}{10} \left(\frac{(2l+4)(2l-2)}{(2l-1)(2l+3)} \right)^{1/2} f \vec{\mathbf{w}}^{(13)2} + e(\tfrac{7}{20})^{1/2} g \sum_{i \neq j} (\vec{\mathbf{w}}_i^{(02)} \vec{\mathbf{w}}_j^{(11)})^{(13)2}. \end{aligned} \tag{24}$$

In the case of the dipole interaction, the results are somewhat more complicated. There, we identify $\vec{\mathbf{T}}^{(SL)J}$ as

$$\sum_{i=1}^{N} \left[\tfrac{2}{3} \mu_0 [2(2l+1)]^{1/2} \frac{\delta(r_i)}{r_i^2} \vec{\mathbf{w}}_i^{(10)1} + \tfrac{2}{3} \mu_0 [6l(l+1)(2l+1)]^{1/2} \frac{1}{r_i^3} \vec{\mathbf{w}}_i^{(01)1} + 2\mu_0 \left(\frac{l(l+1)(2l+1)}{(2l-1)(2l+3)} \right)^{1/2} \frac{1}{r_i^3} \vec{\mathbf{w}}_i^{(12)1} \right].$$

Fortunately, the term transforming as $\vec{\mathbf{w}}^{(10)1}$ does not contribute to the effective operators, as can be seen by considering the general equation of Armstrong. We are thus left with two combinations of S and L: $S=0$, $L=1$, from which one can have $\kappa=1$, $k=0$ and $\kappa=1$, $k=2$; and $S=1$, $L=2$, for which one can have $\kappa=1$, $k=2$ and $\kappa=0$, $k=1$. Substituting into Eq. (23), we then find the effective operators

$$\begin{aligned} \vec{\mathbf{P}}^{(10)1} &= \tfrac{2}{3} \mu_0 [2(2l+1)]^{1/2} \left[\left(\frac{l(l+1)}{6(2l+1)} \right)^{1/2} f \vec{\mathbf{W}}^{(10)1} + [l(l+1)]^{1/2} g \sum_{i \neq j} (\vec{\mathbf{w}}_i^{(01)} \vec{\mathbf{w}}_j^{(11)})^{(10)1} \right], \\ \vec{\mathbf{P}}^{(01)1} &= \tfrac{2}{3} \mu_0 [6l(l+1)(2l+1)]^{1/2} \left[-\frac{1}{4} \left(\frac{2}{3l(l+1)(2l+1)} \right)^{1/2} f \vec{\mathbf{W}}^{(01)1} \right. \\ &\qquad \left. + \left(\frac{1}{2(2l+3)(2l-1)} \right)^{1/2} g \sum_{i \neq j} (\vec{\mathbf{w}}_i^{(12)} \vec{\mathbf{w}}_j^{(11)})^{(01)1} \right], \\ \vec{\mathbf{P}}^{(12)1} &= 2\mu_0 \left(\frac{l(l+1)(2l+1)}{(2l+3)(2l-1)} \right)^{1/2} \left(-\frac{8l^2+8l+3}{12[6l(l+1)(2l+1)]^{1/2}} f \vec{\mathbf{W}}^{(12)1} \right. \\ &\qquad \left. + \tfrac{1}{3} [10(2l+3)(2l-1)]^{1/2} g \sum_{i \neq j} (\vec{\mathbf{w}}_i^{(01)} \vec{\mathbf{w}}_j^{(11)})^{(12)1} + 3^{1/2} \tfrac{1}{2} g \sum_{i \neq j} (\vec{\mathbf{w}}_i^{(12)} \vec{\mathbf{w}}_j^{(11)})^{(12)1} \right). \end{aligned} \tag{25}$$

It is interesting to note that only two radial parameters, f and g, describe perturbations for both the magnetic-dipole and electric-quadrupole interactions. Explicitly, these quantities are given by

$$f=2\left(\frac{3}{2(l+1)}\right)^{1/2}\sum_{l_c,l_e}\left[\frac{D(l_e,l_c)}{\Delta E(l_c,l_e)}[A(l_c\,l;ll_e)+A(ll_c;l_e\,l)]+\frac{D(l,l_e)}{\Delta E(l,l_e)}A(ll_e;ll)+\frac{D(l,l_c)}{\Delta E(l_c,l)}A(l_c\,l;ll)\right.$$
$$\left.-\frac{N}{2(2l+1)}\left(\frac{D(l,l_e)}{\Delta E(l,l_e)}[A(l_e\,l;ll)+A(ll_e;ll)]-\frac{D(l_c,l)}{\Delta E(l_c,l)}[A(l_c\;\,l;ll)+A(ll_c;ll)]\right)\right],$$
$$g=\frac{2^{1/2}}{[3(2l+1)]^{1/2}}\sum_{l_e,l_c}\left(\frac{D(l,l_e)}{\Delta E(l,l_e)}A(l_e\,l;ll)-\frac{D(l_c,l)}{\Delta E(l_c,l)}A(l_c\,l;ll)\right), \tag{26}$$

where l_e stands for the quantum numbers $n_e\,l_e$, and refers to an empty shell; l_c stands for the numbers $n_c\,l_c$, and refers to a closed shell; and $D(l_i,l_j)=\int R_{l_i}R_{l_j}(1/r^3)dr$.

VI. DISCUSSION

Sandars and Beck[5] showed that relativistic effects could be taken into account in a nonrelativistic hyperfine-structure Hamiltonian if $\mathcal{H}_{\rm hfs}$ of Eq. (1) is replaced, assuming still the electron configuration (closed shells) l^N, by

$$\mathcal{H}'_{\rm hfs}=\mathcal{H}'_D+\mathcal{H}'_Q,$$

where

$$\mathcal{H}'_D=\frac{2\mu_Q\mu_I}{I}\left\{\sum_{i=1}^{N}\left[\frac{[2(2l+1)]^{1/2}}{3}\langle\delta(r)/r^2\rangle_{10}\vec{\mathbf{w}}_i^{(10)1}+\frac{[6l(l+1)(2l+1)]^{1/2}}{3}\langle1/r^3\rangle_{01}\vec{\mathbf{w}}_i^{(01)1}\right.\right.$$
$$\left.\left.+\left(\frac{l(l+1)(2l+1)}{(2l+3)(2l-1)}\right)^{1/2}\langle1/r^3\rangle_{12}\vec{\mathbf{w}}_i^{(12)1}\right]\cdot\vec{\mathbf{I}}^{(1)}\right\},$$
$$\mathcal{H}'_Q=e\left\{\sum_{i=1}^{N}\left[\left(\frac{l(l+1)(2l+1)}{6}\right)^{1/2}\langle1/r^3\rangle_{11}\vec{\mathbf{w}}_i^{(11)2}+\left(\frac{2l(l+1)(2l+1)}{5(2l-1)(2l+3)}\right)^{1/2}\langle1/r^3\rangle_{02}\vec{\mathbf{w}}_i^{(02)}\right.\right.$$
$$\left.\left.-\left(\frac{l(l+1)(2l+1)(l+2)(l-1)}{56(2l-1)(2l+3)}\right)^{1/2}\langle1/r^3\rangle_{13}\vec{\mathbf{w}}_i^{(13)2}\right]\cdot\vec{\mathbf{F}}^{(2)}\right\}. \tag{27}$$

In these equations, $\langle\delta(r)/r^2\rangle_{10}$, $\langle1/r^3\rangle_{11}$, and $\langle1/r^3\rangle_{13}$ represent radial integrals which vanish in the nonrelativistic limit (we assume that $l>0$). In addition, $\langle1/r^3\rangle_{01}$, $\langle1/r^3\rangle_{12}$, and $\langle1/r^3\rangle_{02}$ represent radial integrals which do not necessarily have the same value, although in the nonrelativistic limit they will become equal.

The effects of the leading term in the CP-C interaction[1,12] can also be studied using the effective-operator approach. The results, although complicated, show that CP-C can be absorbed into the Hamiltonian $\mathcal{H}'_{\rm hfs}$ if we allow scaling of some of the radial parameters. In particular, we must change the values of each of the parameters $\langle\delta(r)/r^2\rangle_{10}$, $\langle1/r^3\rangle_{01}$, $\langle1/r^3\rangle_{12}$, and $\langle1/r^3\rangle_{02}$ by amounts which will be constant for matrix elements taken between states of an LS term. We recall, however, that CP-C does not change the values of the relativistic integrals $\langle1/r^3\rangle_{11}$ and $\langle1/r^3\rangle_{13}$.

Using the results of the previous sections, we can easily see the manner in which $\mathcal{H}'_{\rm hfs}$ is changed by the new operators. As an example, we consider the electric quadrupole interaction, where the results are very clear-cut. From the results of Sec. V, we see that the one-body part of, for example, $\vec{\mathbf{P}}^{(11)2}$ can be absorbed directly into $\mathcal{H}'_{\rm hfs}$ if we replace $\langle1/r^3\rangle_{11}$ by

$$\langle1/r^3\rangle_{11}+\frac{1}{5[l(l+1)(2l+1)]^{1/2}}f\,.$$

The two-body part of $\vec{\mathbf{P}}^{(11)2}$ can also be absorbed directly into an effective $\mathcal{H}'_{\rm hfs}$, valid for use within the states SLJ of an LS multiplet, if we further add to $\langle1/r^3\rangle_{11}$ the quantity

$$3\left(\frac{2}{5l(l+1)(2l+1)}\right)^{1/2}\frac{g}{\langle SL\|W^{(11)}\|SL\rangle}$$
$$\times\langle SL\|\tfrac{1}{2}\sum_{i\neq j}(w_i^{(02)}w_j^{(11)})^{(11)}\|SL\rangle,$$

which will be constant within the LS multiplet. Similar conclusions obviously follow for $\vec{\mathbf{P}}^{(13)2}$: the effects of $\vec{\mathbf{P}}^{(13)2}$ can be absorbed into $\mathcal{H}'_{\rm hfs}$ by replacing $\langle1/r^3\rangle_{13}$ by

$$\langle 1/r^3\rangle_{13}+\frac{1}{5}\left(\frac{56}{l(l+1)(2l+1)}\right)^{1/2} f$$
$$-\left(\frac{7[56(2l+3)(2l-1)]}{5l(l+1)(2l+1)(l+2)(l-1)}\right)^{1/2}$$
$$\times \frac{g}{\langle SL\|W^{(13)}\|SL\rangle}$$
$$\times \langle SL\|\tfrac{1}{2}\sum_{i\neq j}(w_i^{(02)}w_j^{(11)})^{(13)}\|SL\rangle,$$

where, again, the second correction term is constant only within the states of an LS multiplet. We see from these results that the one-body part of $\vec{P}^{(kk)2}$ changes $\langle 1/r^3\rangle_{13}$ by an amount roughly eight times as large as the corresponding change in $\langle 1/r^3\rangle_{11}$; no comparisons are possible for the two-body contributions without an explicit for the state $|SL\rangle$. There is, of course, no contribution from this effect to $\langle 1/r^3\rangle_{02}$. The perturbation involving $\mathcal{H}_{BP}$ will provide only two-body effective operators, and will affect all three of the radial parameters appearing in $\mathcal{H}'_{hfs}$. Again, the changes brought about by the effective operators will be constant within the levels of a term; again, because of the two-body nature of the effective operators, the relative magnitudes of the changes cannot be predicted without explicit knowledge of the states. As mentioned above, however, one expects these effects to be small.

We can now see the "hierarchy" of changes brought about by the various terms in the electric-quadrupole interaction. The first-order relativistic effect produces a nonvanishing $\langle 1/r^3\rangle_{11}$ and $\langle 1/r^3\rangle_{13}$, and changes $\langle 1/r^3\rangle_{02}$ from the nonrelativistic value $\langle 1/r^3\rangle$. The CP-C term further changes $\langle 1/r^3\rangle_{02}$, but does not affect $\langle 1/r^3\rangle_{11}$ or $\langle 1/r^3\rangle_{13}$. Finally, the spin-orbit correction to CP-C changes $\langle 1/r^3\rangle_{11}$ and $\langle 1/r^3\rangle_{13}$, but causes no further change in $\langle 1/r^3\rangle_{02}$.

The results are somewhat more complicated when we consider the magnetic-dipole interaction. We can, of course, continue to describe the results in terms of changes in the radial parameters. Regarding first the effective operators of Sec. V, we see that all three of the radial parameters of the dipole interaction are changed by the second-order spin-orbit term. These changes are so trivially obtained from the results of Sec. V that it should not be necessary to describe them explicitly. Again, the change will be described by a term-independent and a term-dependent contribution to the radial parameters. We note that the term-independent change in $\langle\delta(r)/r^2\rangle_{10}$ is $-2l(l+1)$ times the term-independent change in $\langle 1/r^3\rangle_{01}$ and $-6l(l+1)/(8l^2+8l+3)\cong-\frac{3}{4}$ times the term-independent change in $\langle 1/r^3\rangle_{12}$; and correspondingly, the term-independent change in $\langle 1/r^3\rangle_{12}$ is $\frac{1}{3}(8l^2+8l+3)$ times the term-independent change in $\langle 1/r^3\rangle_{01}$. Thus, we see that $\langle 1/r^3\rangle_{12}$ and $\langle\delta(r)/r^2\rangle_{10}$ are affected much more strongly than is $\langle 1/r^3\rangle_{01}$ by the term-independent part of this second-order perturbation. Again, no conclusions are possible concerning the term-dependent perturbations without knowledge of the specific term involved. The statements concerning the effect on the electric-quadrupole interaction of the perturbation term involving $\mathcal{H}_{BP}$ hold also for the effect of this term on the magnetic-dipole term.

We can also compare magnitudes of the term-independent effect in the quadrupole interaction with those in the dipole interaction. The results of Sec. V show that the term-independent changes in $\langle 1/r^3\rangle_{01}$ and $\langle 1/r^3\rangle_{11}$ are roughly equal in magnitude but opposite in sign, and small compared to the changes in the other parameters (smaller by approximately a factor of 10); all of the other term-independent changes are of roughly the same magnitude for d electrons, with the dipole corrections becoming much more important for f electrons.

There remain the first-order terms of Δ_D to consider. These terms are of particular interest because, being first-order terms, they can easily be evaluated. Thus, addition of this part of Δ_D to hyperfine-structure calculations is both possible and practical. We can, of course, indicate the general effects of these operators, once again in terms of changes in the radial parameters of Eq. (27); the first-order terms which contain the operator s will affect the radial parameters $\langle 1/r^3\rangle_{12}$ and $\langle\delta(r)/r^2\rangle_{10}$, and the term which does not contain s will contribute only to the radial parameter $\langle 1/r^3\rangle_{01}$.

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*On leave of absence from the Johns Hopkins University, Baltimore, Md. Work supported in part by the National Science Foundation.

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