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Electric dipole hyperfine structure of TlF

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The authors have calculated the electric dipole interaction energy of the ^{205}Tl nucleus in TlF assuming a nonzero electric dipole moment d_p on the proton. The result is used in the accompanying experimental paper to obtain a new value of $(-1.4 \pm 6) \times 10^{-21}$ e cm for d_p.

INTRODUCTION

Since the discovery that time reversal T is not an exact symmetry in the decay of long-lived K^0 particles,[1] there have been many unsuccessful efforts to observe T violation outside the kaon system. In particular, the possible existence of an electric dipole moment (edm) on elementary particles, which would imply simultaneous violations of parity P and T, has motivated experiments on neutrons,[2] electrons,[3] and protons.[4] The null results obtained in these experiments place useful constraints on the theory of T-violating interactions. In this work we are concerned with the effect of a nonzero proton edm on the energy levels of a thallium fluoride (^{205}TlF) molecule, chosen because it is extremely sensitive to any nuclear edm. The calculations which follow are complementary to an experiment reported in the accompanying paper and have been used to place a new upper limit on the magnitude of a possible proton edm.

A point nucleus in equilibrium with electrostatic forces alone can have no edm interaction energy. It was first noted by Schiff[5] that a nucleus may have a nonvanishing edm interaction by virtue of (i) its finite size and structure and (ii) its magnetic interactions which perturb the electrostatic equilibrium. These mechanisms will henceforth be called the volume effect and the magnetic effect. We will show that both mechanisms may be described by an effective term in the Hamiltonian of the form

$$H_{\text{eff}}^{V,M} = d^{V,M} \vec{\sigma}_N \cdot \hat{\lambda}. \tag{1}$$

where d^V or d^M characterizes the strength of the edm interaction, $\vec{\sigma}_N$ is the spin operator for the Tl nucleus, and $\hat{\lambda}$ is a unit vector along the internuclear axis. If such an interaction is to be observable experimentally, the molecule must be polarized in a large external electric field so that molecular rotation does not average $\vec{\sigma}_N \cdot \hat{\lambda}$ to zero.

In Secs. I–III we calculate the characteristic interaction energy d^V associated with the volume effect, while Sec. IV is devoted to a calculation of d^M. Related discussions of the effects of nuclear electric dipole moments in atoms have been given by Khriplovich[6] and Feinberg.[7]

I. EFFECTIVE ELECTRIC DIPOLE OPERATOR: VOLUME EFFECT

We will write the total wave function of the molecule as

$$\Psi = \psi_n(\vec{r}_n)\psi_e(\vec{r}_i)\psi_R(\vec{r}_N, \vec{I}) , \tag{2}$$

where $\psi_n(\vec{r}_n)$ describes the motion of individual Tl nucleons with respect to the centre of mass N of the Tl nucleus, and $\psi_e(\vec{r}_i)$ describes the motion of the F nucleus and the electrons with respect to N. $\psi_R(\vec{r}_N, \vec{I})$ describes the spin and motion of the Tl nucleus as a whole with respect to external coordinates (see Fig. 1). Throughout this section we will make the Born-Oppenheimer separation between the motion of individual nucleons with respect to N and other motions in the molecule. We will also separate the motion of the electrons about the internuclear axis from the motion of the molecule as a whole. Where convenient, we will use the abbreviated notation ψ_n, ψ_e, and ψ_R. Atomic units will be used throughout.

If we write the electric field at nucleon n due to charge q_i as $\vec{E}_{in}$, the average electrostatic force on the Tl nucleus is

$$\langle \vec{F}_N \rangle = \left\langle \Psi \middle| \sum_{i,n} q_n \vec{E}_{in} \middle| \Psi \right\rangle . \tag{3}$$

In first-order perturbation theory, the edm interaction energy of the Tl nucleus is

$$\langle H_{\text{edm}} \rangle = \left\langle \Psi \middle| \sum_{i,n} -\vec{d}_n \cdot \vec{E}_{in} \middle| \Psi \right\rangle . \tag{4}$$

On expanding $\vec{E}_{in}$ in spherical tensors[8] about the center of mass of the ^{205}Tl nucleus and making use of the nuclear spherical symmetry, it can be shown that

$$\langle \vec{F}_N \rangle = -\left\langle \Psi \middle| \sum_{i,n} q_n \frac{\vec{C}_i^1 q_i}{r_i^2} [1 - \Theta(r_i, r_n)] \middle| \Psi \right\rangle \tag{5}$$

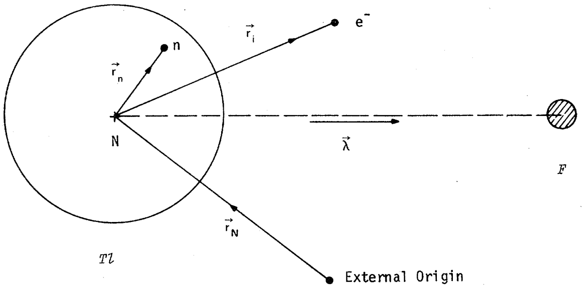

FIG. 1. Schematic diagram of the TlF molecule showing our notation.

and

$$\langle H_{\mathrm{edm}}\rangle = \left\langle \Psi \left| \sum_{i,n} \vec{\mathrm{d}}_n \cdot \frac{\vec{\mathrm{C}}_i^1 q_i}{r_i^2}\,[1-\Theta(r_i,r_n)] \right| \Psi \right\rangle , \tag{6}$$

where

$$\Theta(r_i,r_n) = \begin{cases} 1 \text{ for } r_i < r_n \\ 0 \text{ for } r_i > r_n \end{cases} .$$

Integrating Eqs. (5) and (6) over r_n space, we obtain

$$\langle \vec{\mathrm{F}}_N \rangle = -Z \left\langle \psi_e\,\psi_R \left| \sum_i \frac{\vec{\mathrm{C}}_i^1 q_i}{r_i^2}\,[1-\rho_Z(r_i)] \right| \psi_e \psi_R \right\rangle , \tag{7}$$

$$\langle H_{\mathrm{edm}}\rangle = D \left\langle \psi_e \psi_R \left| \vec{\sigma}_N \cdot \sum_i \frac{\vec{\mathrm{C}}_i^1 q_i}{r_i^2}\,[1-\rho_D(r_i)] \right| \psi_e \psi_R \right\rangle , \tag{8}$$

where the following shorthand notation has been used:

$$\begin{aligned} &\left\langle \psi_n \left| \sum_n q_n \right| \psi_n \right\rangle = Z , \\ &\left\langle \psi_n \left| \sum_n q_n \Theta(r_i,r_n) \right| \psi_n \right\rangle = Z\rho_Z(r_i) , \end{aligned} \tag{9}$$

$$\begin{aligned} &\left\langle \psi_n \left| \sum_n \vec{\mathrm{d}}_n \right| \psi_n \right\rangle = D\vec{\sigma}_n , \\ &\left\langle \psi_n \left| \sum_n \vec{\mathrm{d}}_n \Theta(r_i,r_n) \right| \psi_n \right\rangle = D\vec{\sigma}_N \rho_D(r_i) . \end{aligned} \tag{10}$$

$\vec{\sigma}_N$ is a unit vector parallel to the nuclear spin $\vec{\mathrm{I}}$.

The contributions to $\langle \vec{\mathrm{F}}_N \rangle$ and $\langle H_{\mathrm{edm}} \rangle$ associated with the F nucleus are negligible because its wave function is vanishingly small close to the Tl nucleus. Henceforth, the sum over i will be considered to include only the electrons and q_i will be replaced by -1 a.u. The integral over r_i space vanishes except along the internuclear axis, the orientation of which is specified by the unit vector $\hat{\lambda}$, allowing us to write

$$\langle \vec{\mathrm{F}}_N \rangle = Z \langle \psi_R | \hat{\lambda} | \psi_R \rangle \left\langle \psi_e \left| \sum_i \frac{C_{0i}^1}{r_i^2}\,[1-\rho_Z(r_i)] \right| \psi_e \right\rangle , \tag{11}$$

$$\begin{aligned} \langle H_{\mathrm{edm}} \rangle &= -D \langle \psi_R | \hat{\lambda} \cdot \vec{\sigma}_N | \psi_R \rangle \\ &\quad \times \left\langle \psi_e \left| \sum_i \frac{C_{0i}^1}{r_i^2}\,[1-\rho_D(r_i)] \right| \psi_e \right\rangle . \end{aligned} \tag{12}$$

where C_{0i}^1 is the component of $\vec{\mathrm{C}}_i^1$ in the direction of $\hat{\lambda}$.

Ignoring the small magnetic forces on the F nucleus, we note that in equilibrium

$$\langle \vec{\mathrm{F}}_N \rangle = 0 . \tag{13}$$

It follows from Eqs. (11), (12), and (13) that

$$\begin{aligned} &\langle H_{\mathrm{edm}} \rangle \\ &\quad = -D \left\langle \psi_R \psi_e \left| \hat{\lambda} \cdot \vec{\sigma}_N \sum_i \frac{C_{0i}^1}{r_i^2}\,[\rho_Z(r_i) - \rho_D(r_i)] \right| \psi_R \psi_e \right\rangle . \end{aligned} \tag{14}$$

By writing $\rho_Z(r_i)$ and $\rho_D(r_i)$ explicitly, it is readily shown that

$$\langle H_{\mathrm{edm}} \rangle = -D \left\langle \psi_R \psi_n \left| \hat{\lambda} \cdot \sum_n \left(\frac{q_n}{Z} \vec{\sigma}_N - \frac{\vec{\mathrm{d}}_n}{D} \right) \left(\int_{r_i=0}^{r_n} \psi_e^* \sum_i \frac{C_{0i}^1}{r_i^2}\, \psi_e \, d^3\vec{\mathrm{r}}_i \right) \right| \psi_R \psi_n \right\rangle . \tag{15}$$

For the present nonrelativistic calculation, it is satisfactory to expand ψ_e in the following way:

$$\psi_e = \prod_i \psi_i(r_i) = \prod_i \sum_l a_l^i r_i^l Y_{m_l}^l(\theta_i, \phi_i) \tag{16}$$

for small r_i. The electronic integral in Eq. (15) is then given by $\sum_i a_0^i a_1^i r_n^2/\sqrt{3}$, neglecting small terms of order r_n^3 and higher. The nuclear integral may be simplified by noting that, on the shell model, only the unpaired $3s$ proton contributes to the total spin and dipole moment. Writing the edm of that proton as d_p, we find, from Eq. (15) that

$$\begin{aligned} \langle H_{\mathrm{edm}} \rangle &= -d_p \sum_i \frac{a_0^i a_1^i}{\sqrt{3}} \left\langle \psi_n \left| \sum_n \left(\frac{q_n}{Z} - \delta_{3s} \right) r_n^2 \right| \psi_n \right\rangle \\ &\quad \times \left\langle \psi_R \left| \hat{\lambda} \cdot \vec{\sigma}_N \right| \psi_R \right\rangle . \end{aligned} \tag{17}$$

On comparing Eqs. (1) and (17), we see that the characteristic interaction energy of the volume effect is

$$d^V = -d_p XR , \tag{18}$$

where

$$X = \sum_i X_i = \sum_i \frac{a_0^i a_1^i}{\sqrt{3}} , \tag{19}$$

TABLE I. Coefficients $a^i_{0,0}$ and $a^i_{1,1}$ obtained by RS and the corresponding values of X_i defined in Eq. (19). X_i^R is a relativistic value of X_i discussed in Sec. III.

Molecular orbital i	Nominal atomic orbital Tl	F	$a^i_{0,0}$	$a^i_{1,1}$	X_i	X_i^R	X_i^R/X_i
2σ	$2s$		−539.176	+0.89	−277.1	-	-
3σ	$2p$		+0.047	+10 306.76	+279.7	-	-
4σ	$3s$		+291.415	−2.67	−449.2	−2663	5.93
5σ	$3p$		−0.139	−726.57	+459.6	+2898	6.31
8σ	$4s$		−160.727	+7.31	−678.3	−2317	3.42
9σ	$4p$		+0.406	+2 979.35	+698.4	+2380	3.41
11σ	$5s$		+68.373	−19.87	−784.4	−2467	3.15
13σ	$5p$		−1.229	−1 109.40	+787.2	+2472	3.14
14σ		$2s$	−1.286	+40.77	−30.3	−98	3.23
16σ		$2p$	+6.710	−68.64	−265.9	−838	3.15
17σ	$6s$		−9.641	−113.37	+631.0	+1964	3.11

$$R=\left\langle\psi_n\right|\sum_n\left(\frac{q_n}{Z}-\delta_{3s}\right)r_n^2\left|\psi_n\right\rangle=r_q^2-r_d^2\,. \tag{20}$$

See Eqs. (23) and (24) for the definitions of r_q and r_d.

II. CALCULATION OF d^V IN TlF

A. Evaluation of X

Richards and Scott[9] (henceforth referred to as RS) have calculated a restricted Hartree-Fock wave function for the $^1\Sigma$ electronic ground state of TlF in terms of a basic set of 33 Slater functions using the ALCHEMY program. The calculation assumes that each electron is in an orbital state of definite angular momentum $m_l\hbar$ about the internuclear axis, as we have done in Sec. I, and that the two electrons ($m_s=\pm\frac{1}{2}$) in each orbital have the same wave functions in coordinate space. The accuracy of this wave function is discussed in Sec. IV A. Within the approximations of Sec. I, we are concerned here with σ ($m_l=0$) orbitals, $\psi_i^\sigma(r_i)$, of which there are seventeen. These are expressed as linear combinations of the basis functions, thus

$$\psi_i^\sigma(r_i)=\sum_{n,l}a^i_{n,l}r_i^n e^{-\zeta(n,l)r_i}Y_0^l(\theta_i,\phi_i)\,, \tag{21}$$

where n is an integer $\geq l$. In four of the basis states r_i is measured with respect to the F nucleus. We find that these make a negligible contribution to the electronic integral in Eq. (15) and henceforth will be ignored. The contribution of the remaining Tl-centered orbitals is $\sum_i r_n^2 a^i_{0,0}a^i_{1,1}/\sqrt{3}$, when we neglect terms of order r_n^3 and higher. Table I shows the coefficients $a^i_{0,0}$ and $a^i_{1,1}$ obtained by RS and the corresponding values of X_i defined in Eq. (19).

It will be seen that the orbitals up to 13σ occur in pairs (corresponding to ns, np in the Tl atom) with opposite and almost equal values of X_i. This effect may be explained qualitatively in the following way. Since the ground-state configurations of Tl and F are $6s^2 6p$ and $2p^5$, respectively, one may crudely say that the $6p$ electron of Tl moves over to the F atom to form a closed p^6 shell, thereby binding the molecule. The result is a considerable distortion of the atoms and in particular a mixing of s and p functions. However, the distortion does not significantly raise the degeneracy between pairs of orbitals ns, np except for the pairs $6s$, $6p$ of Tl and $2s$, $2p$ of F which are directly involved with the migrating electron. Any p admixture into the ns orbital requires an equal and opposite s admixture into the np orbital in order to preserve their orthogonality. This is equivalent to saying that both orbitals are slightly shifted with respect to the Tl nucleus, on which they are nominally centered, with a corresponding change in the representation. Because the admixtures are equal and opposite, so are the X_i to which they give rise. The same argument is not applicable to the outer orbitals since the $6p$ electron of Tl is degenerate with neither the $6s$ or the $2s$ of F but has a thoroughly distorted orbit. It is these outer electrons which contribute to X for the most part. Summing over all the electrons (two per orbital), we find

$$X=741\text{ a.u.} \tag{22}$$

We repeated the calculation of X using wave functions for various internuclear separations. The results were:

Internuclear separation (a.u.)	X (a.u.)
4.13898	+721
3.93898 [equilibrium, Eq. (22)]	+741
3.73898	+716

This consistency is encouraging, but it gives no real indication of the error in our result. Schwenzer *et al.*[10] have examined the reliability of results obtained from minimal basis-set wave functions for heavy atoms. They conclude that the accuracy in comparable with that of similar calculations for light atoms. Thus we may expect that our result for X is a reasonable first approximation to the true value.

B. Evaluation of R for the Tl^{205} nucleus

Using semiempirical methods, Green *et al.*[11] have calculated values of $\langle r_n^2\rangle$ for nuclei up to $A=250$. Using their results, we find that

$$r_q^2=\frac{1}{Z}\left\langle\psi_n\left|\sum_n q_n r_n^2\right|\psi_n\right\rangle=33\ \mathrm{F}^2\,, \tag{23}$$

$$r_d^2=\langle\psi_n|r_{3s}^2|\psi_n\rangle=28\ \mathrm{F}^2\,. \tag{24}$$

Here R, defined in Eq. (20) is found to be

$$R=1.8\times 10^{-9}\ \mathrm{a.u.} \tag{25}$$

Because of the large cancellation between the first and second terms in R, the accuracy of Eq. (25) is questionable. At present, however, these appear to be the most reliable numbers available. The value for R in Eq. (25) agrees with that quoted by Khriplovich,[6] $\delta r^2/r_0^2=0.12$, obtained by V. B. Telitsyn using a Saxon-Woods potential.

C. Conclusion

Collecting together Eqs. (18), (22), and (25), we see that the characteristic edm energy of the volume effect is

$$|d^V|=d_p XR=1.3\times 10^{-6}d_p\ \mathrm{a.u.} \tag{26}$$

As we will show in Sec. III, it is necessary to make a large relativistic correction to Eq. (26).

III. RELATIVISTIC CORRECTION TO d^V

A. Relativistic expression for X

In the Tl atom, where $Z\alpha\simeq 0.6$, relativistic effects cannot be ignored because we are concerned with precisely the region where they are largest, namely, near the nucleus. Moreover, the radial integral in Eq. (15) is rather sensitive in the relativistic case to the exact form of the electron wave function inside the Tl nucleon. Following the procedure of Sec. I, we expand the electron wave function, but this time use relativistic functions [compare with Eq. (16)].

$$|\psi_e\rangle=\prod_i|\psi_i(r_i)\rangle$$

$$=\prod_i\sum_\kappa\frac{1}{r_i}\left|\begin{matrix}R_\kappa^i(r_i)\chi_\kappa^\mu(\theta_i,\phi_i)\\ iQ_\kappa^i(r_i)\chi_\kappa^\mu(\theta_i,\phi_i)\end{matrix}\right\rangle\,, \tag{27}$$

where

$$\chi_\kappa^\mu(\theta_i,\phi_i)$$

$$=\sum_{m_l,m_s}\langle l,m_l;\tfrac{1}{2},m_s|j\mu\rangle Y_{m_l}^l(\theta_i,\phi_i)\chi_{m_s}\,, \tag{28}$$

χ_{m_s} is a single-electron spin function, and $\kappa=l(l+1)-(j+\frac{1}{2})^2$.

The functions $R_\kappa(r)$ and $Q_\kappa(r)$ must satisfy the radial Dirac equation for a central field. At the small radii of interest, this may be written in atomic units as

$$\frac{d}{dr}\begin{pmatrix}R_\kappa(r)\\ Q_\kappa(r)\end{pmatrix}=\begin{pmatrix}-\kappa/r & 2/\alpha-\alpha V(r)\\ \alpha V(r) & \kappa/r\end{pmatrix}\begin{pmatrix}R_\kappa(r)\\ Q_\kappa(r)\end{pmatrix}. \tag{29}$$

where we have neglected the eigenvalue of the electron compared with the electrostatic potential $V(r)$. Expanding $V(r)$ in a power series,

$$V(r)=V(0)+V_1 r+\cdots\,, \tag{30}$$

one can readily show that the radial functions have the following forms for sufficiently small r:

If $\kappa>0$,

$$R_\kappa(r)=\frac{2/\alpha-\alpha V(0)}{1+2\kappa}b_\kappa r^{1+\kappa}+\text{higher-order terms}, \tag{31}$$

$$Q_\kappa(r)=b_\kappa r^\kappa+\text{higher-order terms}. \tag{32}$$

If $\kappa<0$,

$$R_\kappa(r)=b_\kappa r^{-\kappa}+\text{higher-order terms}, \tag{33}$$

$$Q_\kappa(r)=\frac{\alpha V(0)}{1-2\kappa}b_\kappa r^{1-\kappa}+\text{ higher-order terms}. \tag{34}$$

We have considered the higher-order terms and find that their contribution to the electronic integral in Eq. (15) is negligibly small, henceforth they will be ignored. Table II summarizes the appropriate forms of the radial functions inside the Tl nucleus. With the help of Table II, it will be seen that the electronic integral consists of the following terms to lowest order in r_n:

$$\sum_i\int_0^{4\pi}\int_0^{r_n}\Big((R_{-1}\chi_{-1}^\mu)^*\frac{C_0^1}{r^2}(R_{+1}\chi_{+1}^\mu)$$

$$+(R_{-1}\chi_{-1}^\mu)^*\frac{C_0^1}{r^2}(R_{-2}\chi_{-2}^\mu)$$

$$+(Q_{-1}\chi_{+1}^\mu)^*\frac{C_0^1}{r^2}(Q_{+1}\chi_{-1}^\mu)$$

$$+\text{complex conjugates}\Big)\,d\Omega\,dr\,, \tag{35}$$

where the notation has been simplified in an obvious way for convenience. Evaluating Eq. (35), we obtain

TABLE II. Appropriate forms of the radial functions inside the Tl nucleus.

Angular state	κ	$R_\kappa(r)$	$Q_\kappa(r)$
$S_{1/2}$	-1	$b_{-1}r$	$\frac{1}{3}\alpha V(0)b_{-1}r^2$
$P_{1/2}$	$+1$	$[2-\alpha^2V(0)/3\alpha]b_{+1}r^2$	$b_{+1}r$
$P_{3/2}$	-2	$b_{-2}r^2$	$\frac{1}{5}\alpha V(0)b_{-2}r^3$

$$r_n^2\sum_i[(\sqrt{2}/3)b^i_{-1}b^i_{-2}-(4\mu/9\alpha)b^i_{-1}b^i_{+1}]=r_n^2X^R\,, \qquad (36)$$

where X^R is the relativistic equivalent of X. The angular integrals have been evaluated with the phase convention of Edmonds.[12] Conveniently, the lowest-order radial dependence is r_n^2, and the remaining analysis therefore proceeds as in Sec. I. Thus, the appropriate relativistic correction factor for d^V is X^R/X.

B. Evaluation of X^R in TlF

So far we have been concerned with the wave function inside the Tl nucleus which has been expressed in terms of normalization constants b^i_κ. If we knew the wave function immediately outside the nucleus, these constants could be determined at once by the condition that the wave function be continuous. However, the nonrelativistic molecular wave function of RS is clearly invalid close to the nucleus, and such a matching cannot be carried out. The problem is overcome by extending our relativistic wave function into a region sufficiently far from the nucleus for the RS wave function to be reliable. The two are then matched to determine the b^i_κ.

1. Extending the relativistic functions

Outside the Tl nucleus, it is no longer satisfactory to use the approximate radial functions given in Table II. We have obtained suitable radial functions over the range $r_i \le 0.2$ a.u. by numerical integration of Eq. (29), with a realistic electrostatic potential $V(r)$ (see Fig. 2). In this region the potential is that of atomic Tl to a good approximation. In the absence of any suitable data on the Tl potential, we made use of a relativistic self-consistent field calculation[13] for Hg. The potential given by Cohen was scaled by a factor $\frac{81}{80}$ to obtain an approximate Tl potential outside the nucleus of sufficient accuracy for our purposes. The potential inside the nucleus was inferred from calculations by Green *et al.*[11] of the charge distribution in various nuclei. Thus we are able to extend all the

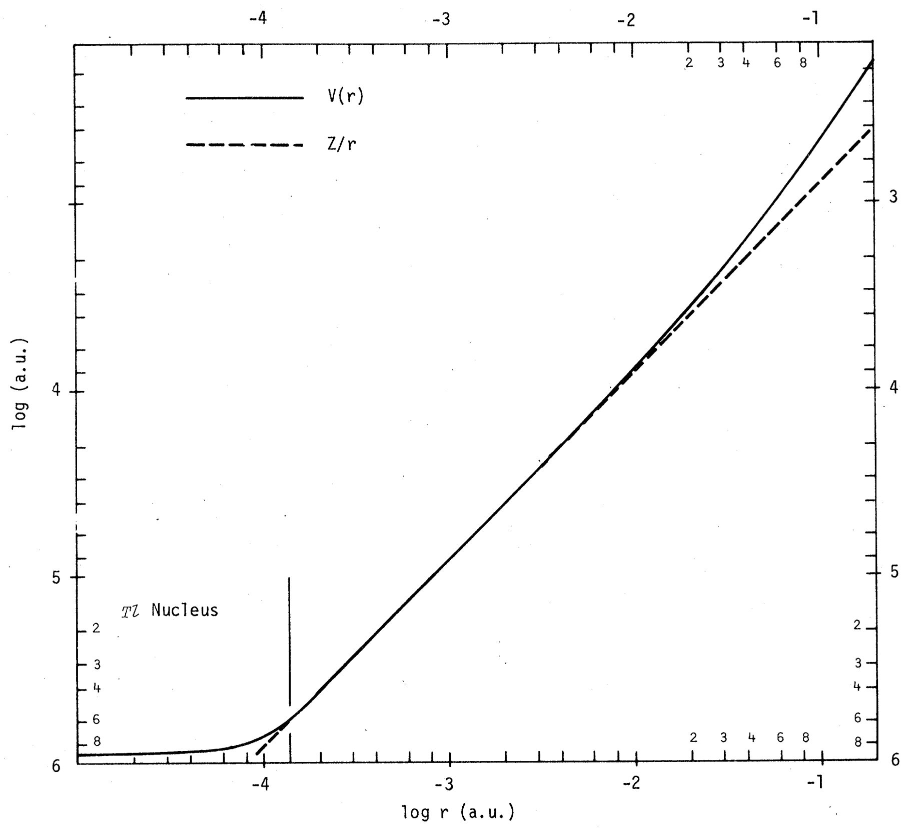

FIG. 2. Approximate atomic Tl potential $V(r)$ used in Eq. (29).

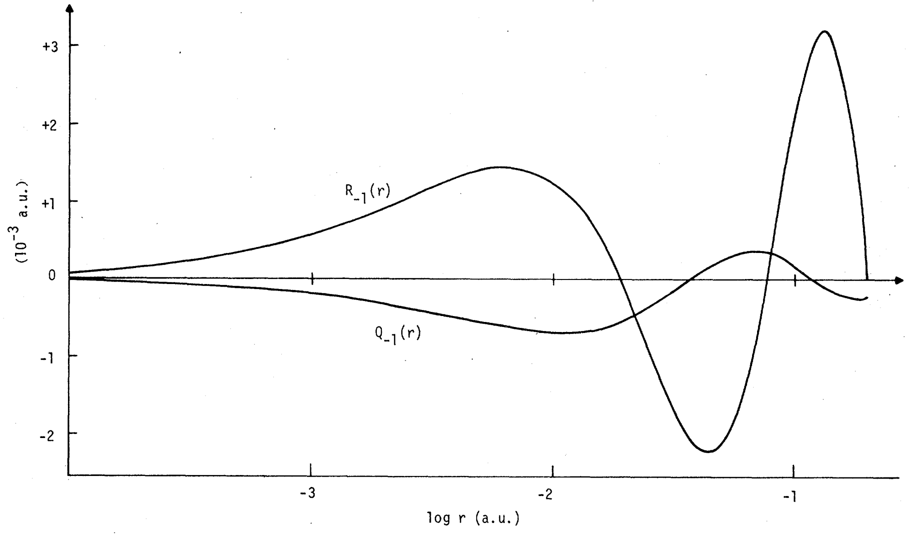

FIG. 3. Radial functions of $S_{1/2}$ electrons in Tl found by integrating Eq. (29). The normalization is $b_{-1}=1$.

functions shown in Table II as far as $r=0.2$ a.u. Figure 3 shows our result for $R_{-1}(r)$ and $Q_{-1}(r)$ with the normalization $b_{-1}=1$. The accuracy of our extended radial functions is discussed at the end of Sec. III B.

2. *Matching the wave functions*

We will now describe how the extended relativistic functions are matched to the RS functions by a method due to Sandars and Beck.[13] We expand the RS wave function of the *i*th electron in the following way:

$$r_i\psi_i(r_i)=R_s^i(r_i)Y_0^0(\theta_i,\phi_i)\chi_{m_s}+R_p^i(r_i)Y_0^1(\theta_i,\phi_i)\chi_{m_s}+\cdots. \tag{37}$$

Carrying out an angular recoupling with the phase convention of Edmonds[12] and simplifying the notation, we obtain

$$r_i\psi_i=R_s^i\chi_{-1}^{\mu}-(2\mu/\sqrt{3})R_p^i\chi_{+1}^{\mu}+(\tfrac{2}{3})^{1/2}R_p^i\chi_{-2}^{\mu}+\cdots. \tag{38}$$

Figure 4 shows $R_s^{17\sigma}$. The proper normalization of $R_{-1}^{17\sigma}$ is found by choosing $b_{-1}^{17\sigma}$ so that the two antinodes at $r=0.13$ a.u. have equal amplitude as shown in Fig. 4. The region $r\simeq 0.13$ a.u. is a suitable one for matching the wave functions because it is sufficiently close to the nucleus for the potential to be essentially that of atomic Tl, but distant enough for the electron to be treated nonrelativistically. It is clear from Fig. 4 that $R_{-1}^{17\sigma}$ cannot be joined smoothly onto $R_s^{17\sigma}$ because the two are slightly shifted from each other, but the method of matching antinodes is an adequate one for present purposes. The functions R_{+1}^i and R_{-2}^i

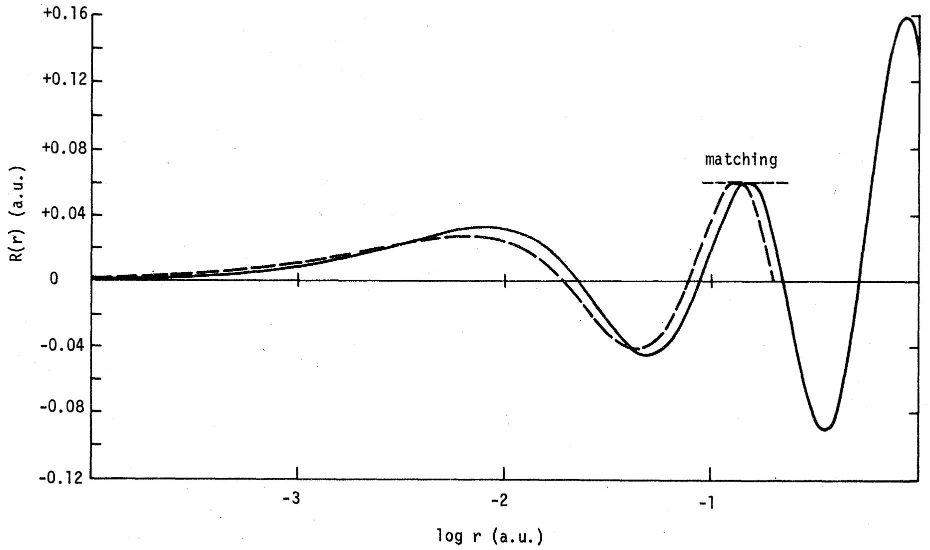

FIG. 4. The matching of $R_{-1}(r)$ (dashed line) to $R_s^{17\sigma}$ (continuous line) of the RS molecular wave function.

are found to have antinodes at 0.12 and 0.13 a.u., respectively. These were matched in the same way to $-(2\mu/\sqrt{3})R_p^i$ and $+(2/3)^{1/2}R_p^i$.

Having found the normalization coefficients b_κ^i of interest, we substitute them into Eqs. (36), yielding the values of X_i^R shown in Table I. A problem arises in matching the inner orbitals; the relativistic functions R_κ^i differ only in normalization because the eigenvalue was neglected in Eq. (29). It follows that the matching process breaks down for the inner orbitals which have principal antinodes close to or inside the matching radius. A convenient way to check the eigenvalue dependence of the RS wave functions inside 0.13 a.u. is to consider the ratio X_i^R/X_i. If the radial functions of different orbitals differ only in normalization (are independent of eigenvalue), then X_i^R/X_i is constant. Table I shows that this is indeed the case for the outer orbitals. The 8σ and 9σ orbitals show a slight eigenvalue dependence because the principal antinodes are adjacent to the matching antinodes. The matching of 4σ and 5σ functions at their principal antinodes is clearly wrong. It seems reasonable to assume that the correct ratio X_i^R/X_i for the inner orbitals is approximately the same as that for the outer orbitals, namely, 3.15. Since electrons in the orbitals up to 5σ contribute less than 3% to X, this approximation is not expected to introduce an error greater than 3% in our value of X^R. We conclude that the relativistic correction factor for d^V is:

$$X^R/X = 3.15\,. \tag{39}$$

Equation (39) is considerably more reliable than our value of d^V because it is simply the result of comparing the shape of relativistic and nonrelativistic radial functions in a region where the potential is atomic. As we have already noted, there is an error of ±3% or less due to the difficulty of matching inner orbitals. An additional uncertainty is due to the approximate potential (Fig. 2) used in Eq. (29). By making reasonable variations in that potential, we estimate the additional error to be less than ±3%. Thus the relativistic correction factor given in Eq. (39) is expected to be correct within 10%.

IV. MAGNETIC EFFECT

A. Effective electric dipole operator

In this section we treat the Tl nucleus as a point particle having charge Z, spin $\frac{1}{2}\hbar$, magnetic moment $\mu_N\vec{\sigma}_N$ and edm $d_p\vec{\sigma}_N$. Using a result given by Salpeter,[14] we write the Dirac Hamiltonian of the Tl nucleus as

$$H = \beta Mc^2 + \vec{\alpha}_N\cdot c\vec{p}_N + Z\phi_N - d_p\beta(\vec{\sigma}_N\cdot\vec{E}_N + i\vec{\alpha}_N\cdot\vec{B}_N)\,, \tag{40}$$

where $\vec{E}_N$ and $\vec{B}_N$ are the electric and magnetic fields at the nucleus and the remaining notation is standard. By means of the Foldy-Wouthuysen transformation, it can be shown that the nonrelativistic limit of Eq. (40), correct to order v_N/c, is

$$\begin{aligned} H = {} & \beta\left(Mc^2 + \frac{p_N^2}{2M}\right) + Z\phi_N \\ & + d_p\left(\frac{i}{2Mc}[\vec{\sigma}_N\cdot\vec{p}_N, \vec{\sigma}_N\cdot\vec{B}_N] - \beta\vec{\sigma}_N\cdot\vec{E}_N\right). \end{aligned} \tag{41}$$

where terms involving d_p^2 have been neglected.

Assuming the center of mass of the molecule to be at rest, we may conveniently replace the operator $\vec{p}_N$ by $\sum_i -\vec{p}_i$, where the sum over i includes the electrons and the F nucleus. Equation (41) then gives the following operator for the edm interaction energy due to the magnetic effect:

$$H_{\text{edm}} = -d_p\left(\frac{i}{2Mc}\sum_i(\vec{\sigma}_N\cdot\vec{p}_i, \vec{\sigma}_N\cdot\vec{B}_{iN}) + \beta\vec{\sigma}_N\cdot\vec{E}_N\right), \tag{42}$$

where $\sum_i\vec{B}_{iN} = \vec{B}_N$. Schiff (1963) has derived an operator equivalent to $\beta d_p\vec{\sigma}_N\cdot\vec{E}_N$. Substituting that operator into Eq. (42), we find that

$$H_{\text{edm}} = -id_p\left(\frac{\mu_N}{Z} + \frac{1}{2Mc}\right)\sum_i(\vec{\sigma}_N\cdot\vec{p}_i, \vec{\sigma}_N\cdot\vec{B}_{iN})\,. \tag{43}$$

The commutator in Eq. (43) may be written as

$$i\vec{\sigma}_N\cdot\sum_i(\vec{p}_i\times\vec{B}_{iN} - \vec{B}_{iN}\times\vec{p}_i)$$

plus terms independent of $\vec{\sigma}_N$ which will be ignored because they are not observable in nuclear-resonance experiments such as the one described in the accompanying experimental paper. We will also ignore the F nucleus in future summations over i because it contributes negligibly to H_{edm}. With the appropriate operator for $\vec{B}_{iN}$, Eq. (43) becomes

$$\begin{aligned} H_{\text{edm}} = {} & d_p\left(\frac{\mu_N}{Z} + \frac{1}{2Mc}\right)\vec{\sigma}_N \\ & \times\sum_i\left(\vec{p}\times\frac{(\vec{r}\times\vec{\alpha})}{r^3} - \frac{(\vec{r}\times\vec{\alpha})}{r^3}\times\vec{p}\right)_i\,. \end{aligned} \tag{44}$$

After some tedious manipulation, one can show that the electronic operator is equivalent to $2\sum_i(\vec{\alpha}\times\vec{l}/r^3)_i$, where $\vec{l} = \vec{r}\times\vec{p}$. Using that fact and the spherical tensor identity $\vec{\alpha}\times\vec{l} = -i\sqrt{2}\{\vec{\alpha}\vec{l}\}^1$, we write equation (44) as

$$H_{\text{edm}} = -2\sqrt{2}\,id_p\left(\frac{\mu_N}{Z} + \frac{1}{2Mc}\right)\vec{\sigma}_N\cdot\sum_i\left(\frac{\{\vec{\alpha}\vec{l}\}^1}{r^3}\right)_1\,. \tag{45}$$

B. Evaluation of d^M

For simplicity we write the electronic operator in Eq. (45) as Y. If we expand the electronic wave function $|\psi_e\rangle$ as shown in Eq. (27), the expectation value of Y may be written, with obvious simplifi-

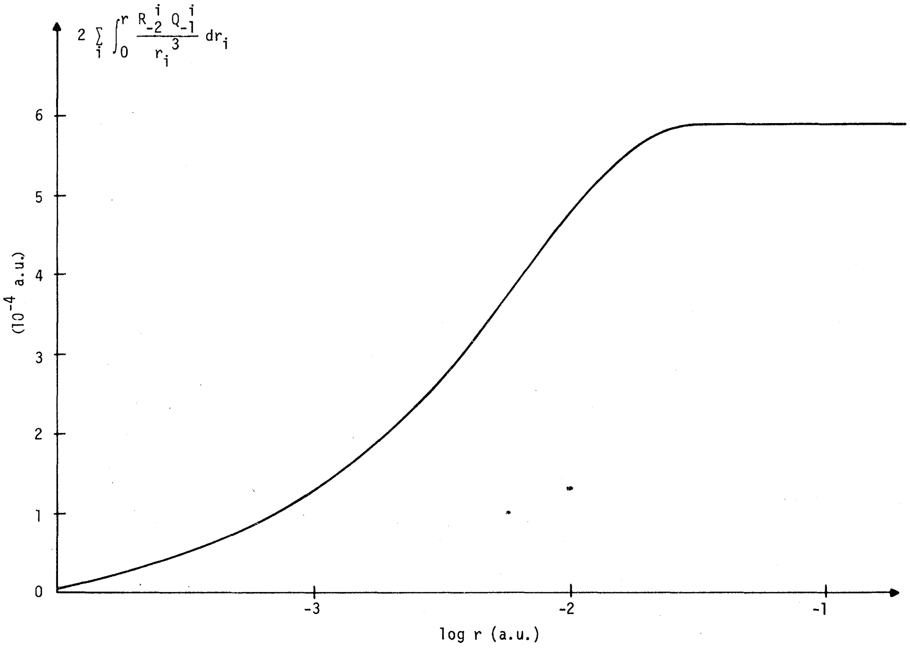

FIG. 5. Graph showing $2\sum_i \int_0^r [R_{-2}^i Q_{-1}^i / r_i^3]\,dr_i$ as a function of r. It is clear that the upper limit of integration in Eq. (48) need not be extended beyond 0.1 a.u.

cation of the notation,

$$\langle\psi_e|Y|\psi_e\rangle = \vec{\lambda}\sum_i \sum_{\kappa,\kappa'} \int_0^{4\pi}\int_0^{\infty}\left[(R_\kappa\chi_\kappa^\mu)^*\frac{\{\vec{\sigma}\vec{1}\}_0^1}{r^3}(iQ_{\kappa'}\chi_{-\kappa'}^\mu) + (iQ_\kappa\chi_{-\kappa}^\mu)^*\frac{\{\vec{\alpha}\vec{1}\}_0^1}{r^3}(R_{\kappa'}\chi_{\kappa'}^\mu)\right]d\Omega\,dr\,, \quad (46)$$

where $\{\vec{\alpha}\vec{1}\}_0^1$ is the component of $\{\vec{\alpha}\vec{1}\}^1$ along $\hat{\lambda}$. It is readily shown that the angular part of the first integral is

$$(-1)^{j-\mu}\begin{pmatrix} j & 1 & j' \\ -\mu & 0 & \mu \end{pmatrix}[3(2j+1)(2j'+1)]^{1/2} \times \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ l & \bar{l}' & 1 \\ j & j' & 1 \end{Bmatrix} \langle\tfrac{1}{2}\|\vec{\sigma}\|\tfrac{1}{2}\rangle\langle l\|\vec{1}\|\bar{l}'\rangle\,, \quad (47)$$

where $\bar{l}'$ is the orbital angular momentum associated with the small component $Q_{\kappa'}\chi_{-\kappa'}^\mu$. Unless $\bar{l}'=l$, the reduced matrix element vanishes, and when $\bar{l}'=l$, the 9-j symbol vanishes unless $j=j'$. An exactly similar argument applies to the angular part of the second integral in Eq. (46). Of the functions having $l=0, 1$, only $R_{-2}\chi_{-2}^\mu$ and $Q_{-1}\chi_{+1}^\mu$ satisfy these angular conditions, leaving just two terms in the sum over κ, κ' [Eq. (46)]. Evaluating the angular integrals with the help of Eq. (47), we find

$$\langle\psi_e|Y|\psi_e\rangle = 2i\hat{\lambda}\sum_i \int_0^\infty \frac{R_{-2}^i Q_{-1}^i}{r_i^3}\,dr_i\,. \quad (48)$$

Here we have reinstated the labels i which were omitted in Eq. (46). We have investigated the contribution to $\langle Y\rangle$ from functions having $l \geq 2$ and find it to be negligible. The integral in Eq. (48) was evaluated numerically as far out as $r=0.1$ a.u. with the extended radial functions developed in Sec. III B. The result of that integration is shown in Fig. 5. It will be seen that there is a negligible contribution to the integral outside 0.1 a.u. We find that

$$\langle\psi_e|Y|\psi_e\rangle = 5.91 i\hat{\lambda}\text{ a.u.} \quad (49)$$

When we substitute this result into Eq. (45) with the numerical values of the other constants and compare with Eq. (1), we find that

$$d^M = 6.79\times 10^{-7} d_p\text{ a.u.} \quad (50)$$

The comments at the end of Sec. II A concerning the reliability of X are equally applicable to our value of d^M. However, d^M is more certain than d^V because no nuclear structure calculations are involved.

V. CONCLUSION

We have calculated operators of the form given in Eq. (1) representing the electric dipole hyperfine interaction in TlF. Our results are

$$d^V = 4.1\times 10^{-6} d_p\text{ a.u.} \quad (51)$$

including the relativistic correction, and

$$d^M = 6.8\times 10^{-7} d_p\text{ a.u.} \quad (52)$$

These results are used in the following experimental paper to obtain a new value for d_p.

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