

## Variational Approach to the Quadrupole Polarizability of Ions\*

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A variation method has been developed for treating the problem of polarization of electron shells of ions by external charges. The induced quadrupole moment has been calculated for a number of He-like ions and the two Ne-like ions  $\text{Al}^{+++}$  and  $\text{Na}^+$ . For the former a shielding effect occurs, while for the latter a net antishielding effect is obtained in agreement with Sternheimer's conclusions. It is possible to compare the results of Sternheimer's numerical solution of the first-order Schrödinger equation with the variation method used here in the case of  $\text{Na}^+$ . Agreement is reasonably good.

### INTRODUCTION

STERNHEIMER,<sup>1,2</sup> in a series of papers, has calculated various effects of polarization of atoms by extranuclear charges. In this paper, we are interested in the specific problem of determining the quadrupole moment induced in the electron shells of an atom by a completely external charge. Such a physical situation arises in a rather idealized model of an ionic crystal or an alkali halide molecule. Although the model is crude, these computations are a necessary preliminary to the interpretation of nuclear quadrupole coupling constants in alkali halide molecules and in ionic crystals.<sup>3,4</sup>

Consider the interaction energy of an external charge  $e$ , at a distance  $R$  from the nucleus in question with an electron at position  $r, \theta, \phi$  with respect to the nucleus and the radius vector  $\mathbf{R}$ . Expanding the energy in powers of  $r$ , we have

$$\frac{-e^2}{R_{\text{ext}}} = \frac{-e^2}{R} - \frac{e^2 r \cos\theta}{R^3} - \frac{e^2 r^2 (3 \cos^2\theta - 1)}{2R^3} - \dots$$

The first term cannot distort the electron distribution, the second term is responsible for the ordinary dipole polarization, and the third term produces a quadrupole polarization. Sternheimer has shown that the second-order effect of the dipole polarization of the electron shell makes a contribution to the field gradient at the nucleus which is negligible compared to the first-order contribution of the quadrupole term. Small higher order terms are neglected.

The effect of the term  $e^2 r^2 (3 \cos^2\theta - 1)/2R^3$  can be treated perturbation-wise in three mathematically different ways:

(a) Matrix mechanical perturbation theory can be used, as was done by Cohen.<sup>5</sup> This method suffers from the requirement that energies and wave functions of

excited states of the unperturbed atomic system must be known.

(b) One can find the exact solution of the inhomogeneous wave equation for the first-order perturbation of the wave function, as was done by Sternheimer and co-workers. This is the most accurate procedure in principle but in practice it is rather difficult to carry out. Numerical solution of the differential equation involves bothersome cumulative errors due to the finite intervals of integration.

(c) One can use a variation method as is done here. It is in principle less accurate than (b) but is much simpler to carry out and does not involve any cumulative error. Moreover, where analytical wave functions are available<sup>6,7</sup> the variational method has the additional advantage that it obviates numerical integration.

The variation method has been applied to some He-like and Ne-like ions and in the case of  $\text{Na}^+$ , where a value calculated by Sternheimer and Foley<sup>8</sup> is available, the results of the two methods are in reasonable agreement. In the next section the variation method is discussed.

### THE VARIATION METHOD

What we need to determine are those terms in the energy of the electrons which are proportional to  $Q/R^3$ , where  $Q$  is the nuclear quadrupole moment. There are two such terms. One is the interaction of the electronic quadrupole moment induced in the electron shells (by the aspherical nucleus) with the external field gradient. The other is the interaction of the nuclear quadrupole moment with the electric field gradient arising from the distortion of the electron shells by the external charge. It is only a matter of convenience which term is calculated because both terms are numerically equal (see Appendix). The variation method which we have used gives rise to divergent integrals if the first term is used for  $s$  functions. We therefore have confined the calculations to the second term.

The process of computation consists of the determination of (a) the induced charge density due to the

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<sup>1</sup> R. M. Sternheimer, *Phys. Rev.* **80**, 102 (1950); **84**, (1951); **86**, 316 (1953); **95**, 736 (1954).

<sup>2</sup> Foley, Sternheimer, and Tycko, *Phys. Rev.* **93**, 734 (1954).

<sup>3</sup> J. Van Kranendonk, *Physica* **20**, 781 (1954).

<sup>4</sup> F. Reif, *Phys. Rev.* **100**, 1597 (1955).

<sup>5</sup> M. H. Cohen, thesis, University of California (unpublished).

<sup>6</sup> P. O. Löwdin, *Phys. Rev.* **90**, 120 (1953).

<sup>7</sup> Green, Mulder, Lewis, and Woll, *Phys. Rev.* **93**, 757 (1954).

<sup>8</sup> R. M. Sternheimer and H. M. Foley, preceding paper [*Phys. Rev.* **102**, 731 (1956)].

external perturbation, and (b) the field gradient due to this charge density at the position of the nucleus. The variational method of course enters only in part (a). As mentioned before, the quadrupole part of the interaction energy of an external charge  $e$  with an electron in the given ion is given by

$$H_1 = -(3 \cos^2\theta - 1)r^2/R^3, \quad (1)$$

where atomic units are used throughout.

The zero-order Hamiltonian of the electron is given by

$$H_0 = -\nabla^2 + V_0; \quad (2)$$

and if  $u_0$  and  $u_1$  represent  $r$  times the zero-order wave function and its perturbation, respectively, then we have the equation

$$(H_0 - E_0)u_1 = -(H_1 - E_1)u_0. \quad (3)$$

$E_0$  and  $E_1$  represent the zero-order eigenvalue and its perturbation, respectively, for the electron under study. If we now consider an  $s$ -electron, then

$$u_0 = u_0'/\sqrt{2}, \quad (4)$$

where  $u_0'$  is the radial part of  $u_0$  and  $E_1 = 0$ . We therefore have

$$(H_0 - E_0)u_1 = -H_1u_0. \quad (5)$$

It is evident from (5) and (1) that  $u_1$  behaves like a  $d$ -function, (i.e., we have only an  $ns \rightarrow d$  excitation of the  $s$ -electrons). We therefore take it of the form

$$u_1 = \frac{3 \cos^2\theta - 1}{\sqrt{2}} u_{1s \rightarrow d}', \quad (6)$$

where  $u_{1s \rightarrow d}'$  is the radial part of  $u_{1s \rightarrow d}$ . We have essentially to calculate  $u_{1s \rightarrow d}'$ . But assuming for the present that  $u_{1s \rightarrow d}'$  has been calculated and remembering that we have two  $s$ -electrons the charge density due to the perturbation is given by

$$\Delta\rho = 4u_0u_{1s \rightarrow d}'/r^2. \quad (7)$$

The field gradient at the position of the nucleus due to this charge distribution is

$$\begin{aligned} \Delta q &= \int \frac{4u_0u_{1s \rightarrow d}'}{r^6} (3 \cos^2\theta - 1) d\tau \\ &= \int \int \frac{8u_0'u_{1s \rightarrow d}'}{4r^3} (3 \cos^2\theta - 1)^2 \sin\theta d\theta dr \\ &= \frac{16}{5} \int \frac{u_0'u_{1s \rightarrow d}'}{r^3} dr. \end{aligned} \quad (8)$$

Similarly, if the  $p$ -electron shall be the one under study, then for the  $p_z$  electron,

$$u_0 = u_0'(\sqrt{\frac{3}{2}}) \cos\theta, \quad (9)$$

and

$$E_1 = -\frac{4}{3}R^{-3}\langle r^2 \rangle, \quad (10)$$

where

$$\langle r^2 \rangle = \int u_0'^2 r^2 dr. \quad (11)$$

The right-hand side of (5) may now be written as

$$\begin{aligned} &\frac{2}{R^3}(\sqrt{\frac{3}{2}})[\frac{3}{2} \cos^3\theta - (9/10) \cos\theta]u_0' \\ &+ \frac{2}{R^3}(\sqrt{\frac{3}{2}}) \times (\frac{2}{5} \cos\theta)u_0' \end{aligned}$$

suggesting that  $u_1$  now consists of an  $f$ -part and a  $p$ -part. The former is the angular  $np \rightarrow f$  excitation and the latter the radial  $np \rightarrow p$  excitation. Following Sternheimer, we therefore take the perturbed wave function as

$$\begin{aligned} u_1 &= \frac{2}{R^3}(\sqrt{\frac{3}{2}})[\frac{3}{2} \cos^3\theta - (9/10) \cos\theta]u_{1p \rightarrow f}' \\ &+ (\sqrt{\frac{3}{2}})\frac{2}{R^3}(\frac{2}{5} \cos\theta)u_{1p \rightarrow p}'. \end{aligned} \quad (12)$$

The same procedure as that used above for the  $s$ -electrons may now be used for calculating the field gradient. If we remember that we have two  $p_y$ - and two  $p_x$ -electrons besides the two  $p_z$ -electrons, it can be shown that the field gradient at the position of the nucleus due to the entire perturbed  $p$ -shell is

$$\Delta q = \frac{1008}{175} \int \frac{u_0'u_{1p \rightarrow f}'}{r^3} dr + \frac{96}{25} \int \frac{u_0'u_{1p \rightarrow p}'}{r^3} dr. \quad (13)$$

It must be remembered that by perturbation theory,  $u_1$  must in all cases be orthogonal to  $u_0$ . This is taken care of in the calculation of angular excitation like  $u_{1s \rightarrow d}$ , etc. by the angular part of the perturbed wave function and in the case of  $u_{1p \rightarrow p}$  by doctoring the radial part  $u_{1p \rightarrow p}$  as shown below.

We now outline the procedure for calculating  $u_1'$ . The first question is what is the form to be taken for the variation function? One is tempted to use the Hassé form<sup>9</sup>

$$u_1' = \alpha u_0' H_1(r), \quad (14)$$

where  $H_1(r) = r^2/R^3$ , the radial part of  $H_1$ . But Sternheimer has shown that in the case of hydrogenic wave functions, where exact solutions of Eq. (3) are possible, the solution for  $u_1'$  contains a polynomial in  $r$ . Further, we have also noticed in our variation calculations that a form like (14) does not give a good value of the perturbation energy, whereas the introduction of an addi-

<sup>9</sup> L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), p. 206.

tional term proportional to  $r$ , namely,

$$u_1' = (\alpha + \beta r) u_0' r^2 / R^3 \quad (15)$$

gives a much lower value of the perturbation energy.

We have therefore used both (15) and

$$u_1' = (\alpha + \beta r + \gamma r^2) u_0' r^2 / R^3 \quad (16)$$

for the variation function, minimizing the perturbation energy with respect to the parameters  $\alpha$ ,  $\beta$ , and  $\gamma$ . In the case of the radial excitation  $n\bar{p} \rightarrow \bar{p}$ , we have to subtract a term proportional to  $u_0'$  to retain the orthogonality of  $u_1'$  and  $u_0'$  referred to above. The variation function used for the radial excitation is therefore

$$u_1' = (u_0' / R^3) [(\alpha + \beta r + \gamma r^2) r^2 + \delta], \quad (17)$$

where

$$\delta = - \int u_0'^2 (\alpha + \beta r + \gamma r^2) r^2 dr = - [\alpha \langle r^2 \rangle + \beta \langle r^3 \rangle + \gamma \langle r^4 \rangle].$$

We thus have the net energy given by

$$E = \frac{\langle u_0 + u_1 | H_0 + H_1 | u_0 + u_1 \rangle}{\langle u_0 + u_1 | u_0 + u_1 \rangle} \\ \cong E_0 + E_1 + \langle u_1 | H_0 - E_0 | u_1 \rangle + 2 \langle u_0 | H_1 | u_1 \rangle, \quad (18)$$

remembering that  $u_1$  is orthogonal to  $u_0$  by virtue of the angular dependence of  $u_1$  in the case of angular excitation and of the adjusted orthogonality in the case of radial excitation. Evidently  $E_0$  and  $E_1$  do not involve the variation parameters  $\alpha$ ,  $\beta$  and  $\gamma$ . We are mainly interested in the last two terms, which we call  $\phi_2$  and  $\phi_1$ , respectively. Remembering that  $u_0$  obeys the Schrödinger equation,

$$H_0 u_0 = E_0 u_0,$$

we have from (2),

$$\left[ -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - E_0 + V_0 \right] u_0' = 0, \quad (19)$$

$l$  referring to the unperturbed state of the electron shell considered. We therefore have

$$(V_0 - E_0) = \frac{1}{u_0'} \left( \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} \right). \quad (20)$$

Another relation that is useful is

$$\int u_0' r^n \frac{\partial u_0'}{\partial r} dr = -\frac{n}{2} \int u_0'^2 r^n dr = -\frac{n}{2} \langle r^n \rangle. \quad (21)$$

Using these expressions, we obtain for  $\phi_1$  and  $\phi_2$  the expressions given below. We also give the values of  $\gamma_\infty$ , defined as the ratio of  $\Delta q$  and  $q = 2/R^3$  produced by the external charge.

$ns \rightarrow d$ .—

$$\phi_1 = -\frac{16}{5R^6} [\alpha \langle r^4 \rangle + \beta \langle r^5 \rangle + \gamma \langle r^6 \rangle],$$

$$\phi_2 = \frac{8}{5R^6} [10\alpha^2 \langle r^2 \rangle + 15\beta^2 \langle r^4 \rangle + 22\gamma^2 \langle r^6 \rangle \\ + 24\alpha\beta \langle r^3 \rangle + 36\beta\gamma \langle r^5 \rangle + 28\gamma\alpha \langle r^4 \rangle],$$

$$\gamma_\infty = (8/5) [\alpha \langle r^{-1} \rangle + \beta + \gamma \langle r \rangle].$$

$np \rightarrow f$ .—

$$\phi_1 = -\frac{1008}{175R^6} [\alpha \langle r^4 \rangle + \beta \langle r^5 \rangle + \gamma \langle r^6 \rangle],$$

$$\phi_2 = \frac{504}{175R^6} [14\alpha^2 \langle r^2 \rangle + 19\beta^2 \langle r^4 \rangle + 26\gamma^2 \langle r^6 \rangle \\ + 32\alpha\beta \langle r^3 \rangle + 44\beta\gamma \langle r^5 \rangle + 36\alpha\gamma \langle r^4 \rangle],$$

$$\gamma_\infty = (504/175) [\alpha \langle r^{-1} \rangle + \beta + \gamma \langle r \rangle].$$

$np \rightarrow p$ .—

$$\phi_1 = -\frac{96}{25R^6} [\alpha (\langle r^4 \rangle - \langle r^2 \rangle \langle r^2 \rangle) + \beta (\langle r^5 \rangle \\ - \langle r^3 \rangle \langle r^2 \rangle) + \gamma (\langle r^6 \rangle - \langle r^4 \rangle \langle r^2 \rangle)],$$

$$\phi_2 = \frac{48}{25R^6} [4\alpha^2 \langle r^2 \rangle + 9\beta^2 \langle r^4 \rangle + 16\gamma^2 \langle r^6 \rangle \\ + 12\alpha\beta \langle r^3 \rangle + 16\alpha\gamma \langle r^4 \rangle + 24\beta\gamma \langle r^5 \rangle],$$

$$\gamma_\infty = (48/25) [\alpha \langle r^{-1} \rangle + \beta + \gamma \langle r \rangle - \delta \langle r^{-3} \rangle].$$

Minimizing  $\phi_1 + \phi_2$  with respect to  $\alpha$ ,  $\beta$ , and  $\gamma$  separately, we get a set of 3 linear equations in  $\alpha$ ,  $\beta$ , and  $\gamma$  involving the expectation values of  $r^n$  over the zero-order functions. These can be calculated numerically from tabulated Hartree or Hartree-Fock functions, or analytically for those atoms for which analytical expressions for the ground-state wave functions have been obtained.<sup>6,7</sup> Two checks on the correctness of the calculations are available. First, by the nature of the minimization procedure adopted, it may be shown that with the values of  $\alpha$ ,  $\beta$ , and  $\gamma$  obtained.

$$\phi_1 = -2\phi_2.$$

Secondly, with the addition of an extra parameter the energy must be lowered, and the test of the convergence of the variation calculation is that the change in  $\phi_1 + \phi_2$  and in  $\gamma_\infty$  caused by the addition of the last variation parameter should be very small. This is evident from Tables I, II, and III.

## RESULTS AND CONCLUSIONS

The results of our calculation for He-like ions are presented in Table I. The convention regarding signs is that for shielding,  $\gamma_\infty$  is positive and for antishielding, it is negative. Taking into account the negative charge of the electron shells, the net field gradient due to an

TABLE I.  $1s \rightarrow d$  excitation in  $H^-$ , He,  $Li^+$ ,  $Be^{++}$ ,  $B^{+++}$ .

Ion	Values of variation parameters			Second-order energy $\times 5R^6/8$ (a.u.)	$\gamma_\infty$
	$\alpha$	$\beta$	$\gamma$		
$H^-$	0.3356028	0.49683608	-0.005616722	-1008.6694	1.141
	0.5702009	0.41674636	0	-1008.0022	1.293
	3.031221	0	0	-839.80796	3.326
He	0.0783238	0.12947099	-0.0015542998	-1.4297073	0.416
	0.085412538	0.12224131	0	-1.4296427	0.426
	0.32475818	0	0	-1.2463932	0.877
$Li^+$	0.03240597	0.073545278	-0.00073421712	-0.070975891	0.256
	0.033628103	0.071487868	0	-0.070975202	0.259
	0.11837002	0	0	-0.062528348	0.508
$Be^{++}$	0.017590145	0.051036421	-0.00056753525	-0.0095332268	0.185
	0.018071372	0.049903267	0	-0.009525101	0.186
	0.06039845	0	0	-0.0084561937	0.356
$B^{+++}$	0.01100305	0.039098578	-0.00042760391	-0.0021396438	0.145
	0.011222852	0.03843474	0	-0.0021396368	0.146
	0.036631084	0	0	-0.0019039642	0.275

TABLE II. Radial and angular excitations in  $Na^+$ .<sup>a</sup>

Excitation	Values of variation parameters				Second-order energy $\times f(R)$ , a.u.	$\gamma_\infty$
	$\alpha$	$\beta$	$\gamma$	$\delta$		
$2p \rightarrow p$	0.07195285	0.11777345	-0.004223458	0.17376296	-0.2791560	-5.226
	0.08872469	0.10037521	0	0.1761006	-0.2790966	-5.275
	0.078248157	0	0	0.22793299	-0.25510510	-6.541
$2p \rightarrow f$	0.010658300	0.086732194	0.0006978874	0	-0.26517411	0.304
	0.008857789	0.089170979	0	0	-0.26517073	0.300
	0.13814045	0	0	0	-0.21774832	0.674
$2s \rightarrow d$	0.09257035	0.022473668	0.0140761	0	-0.19654567	0.326
	0.060295345	0.067978521	0	0	-0.19593480	0.286
	0.1536525	0	0	0	-0.18109207	0.452
$1s \rightarrow d$	0.002209646	0.015820508	0.0041921636	0	-0.0000168196	0.064
	0.001767677	0.01878369	0	0	-0.0000168140	0.060
	0.007275995	0	0	0	-0.0000145665	0.124
Net $\gamma_\infty$						-4.532

<sup>a</sup>  $f(R) = (25/48)R^6$ , for  $2p \rightarrow p$   
 $= (25/72)R^6$ , for  $2p \rightarrow f$   
 $= 5/8R^6$ , for  $1s \rightarrow d$  and  $2s \rightarrow d$ .

TABLE III. Radial and angular excitations in  $Al^{+++}$ .<sup>a</sup>

Excitation	Values of variation parameters				Second-order energy $\times f(R)$ , a.u.	$\gamma_\infty$
	$\alpha$	$\beta$	$\gamma$	$\delta$		
$2p \rightarrow p$	0.04814817	0.0628385	-0.0002513122	0.047107345	-0.034315502	-3.129
	0.04865026	0.06211016	0	0.047145364	-0.034315174	-3.131
	0.13358910	0	0	0.059824626	-0.031967674	-3.711
$2p \rightarrow f$	0.010082868	0.057530872	0.00010218562	0	-0.036034641	0.230
	0.0099506844	0.057781853	0	0	-0.036034628	0.230
	0.07015586	0	0	0	-0.030857797	0.447
$2s \rightarrow d$	0.070807514	0.004215303	0.14042451	0	-0.046054312	0.278
	0.051937413	0.038631541	0	0	-0.045944795	0.250
	0.09382259	0	0	0	-0.04420743	0.611
$1s \rightarrow d$	0.0014044418	-0.02158402	0.092175695	0	-0.0000071858283	0.031
	-0.00068355194	0.028013462	0	0	-0.00000712325	0.031
	0.00182859	0	0	0	-0.0000012834662	0.037
Net $\gamma_\infty$						-2.590

<sup>a</sup>  $f(R)$  is defined in Table II.

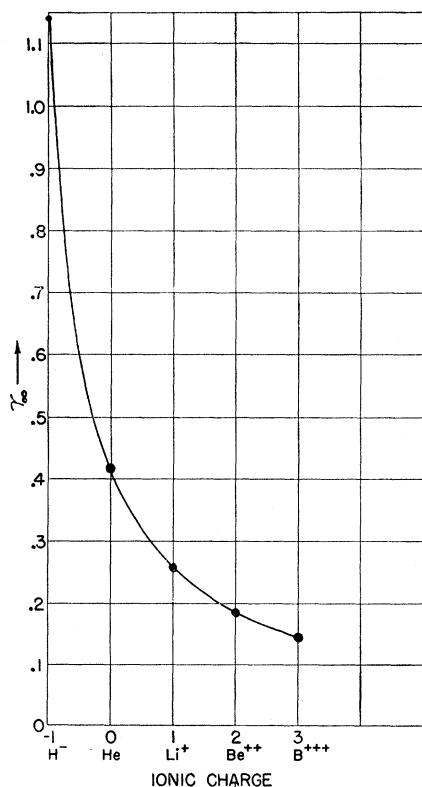


FIG. 1. Plot of  $\gamma_\infty$  versus ionic charge for He-like ions.

external charge at the position of the nucleus is a factor  $(1-\gamma_\infty)$  times the field gradient due to the charge alone.

The variation of  $\gamma_\infty$  with ionic charge for He-like ions is shown in Fig. 1. The nature of the variation is as expected, the more positive ions being less deformable. The results of the calculations for Na<sup>+</sup> and Al<sup>+++</sup> ions are given in Tables II and III. In particular for Na<sup>+</sup>, the total value of  $\gamma_\infty$  is  $-4.5$  which is to be compared with Sternheimer and Foley's value<sup>8</sup> of  $-4.1$ . The quadrupole polarizabilities<sup>10</sup> can be simply obtained from our second-order perturbation energies.

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#### APPENDIX

We prove here the equivalence of polarization calculations in which the source of the perturbation is the quadrupole moment of the nucleus or the external charge.

The interaction energy of the quadrupole moment of the nucleus with the electron,  $\bar{H}_1 = -r^2 P_2(\theta)Q$ , produces

<sup>10</sup> R. M. Sternheimer, Phys. Rev. **96**, 951 (1954).

a first-order change  $\bar{u}_1 = \bar{u}_1^* Q$  in the electron wave function.<sup>11</sup> Also the interaction of the field gradient (due to the external charge) with the electron,

$$H_1 = [-r^2 P_2(\theta)]/R^3$$

produces a first-order charge in the electronic wave function,  $u_1 = u_1^*/R^3$ . To first order in the small parameters  $Q$  and  $1/R^3$ , the wave function is

$$u = u_0 + u_1^*/R^3 + Q\bar{u}_1^*. \quad (A1)$$

The Schrödinger equation is

$$(H_0 + H_1 + \bar{H}_1)u = (E_0 + E_1 + \bar{E}_1)u, \quad (A2)$$

where  $E_0$ ,  $E_1$ , and  $\bar{E}_1$  are the expectation values over  $u_0$  of  $H_0$ ,  $H_1$ , and  $\bar{H}_1$  respectively. Separating the terms of first order in  $Q$  and in  $1/R^3$ , we have

$$(H_0 - E_0)u_1 = (E_1 - H_1)u_0, \quad (A3)$$

$$(H_0 - E_0)\bar{u}_1 = (\bar{E}_1 - \bar{H}_1)u_0. \quad (A4)$$

Now the total perturbed energy of the electron is evidently

$$E = \frac{\langle u_0 + u_1 + \bar{u}_1 | H_0 + H_1 + \bar{H}_1 | u_0 + u_1 + \bar{u}_1 \rangle}{\langle u_0 + u_1 + \bar{u}_1 | u_0 + u_1 + \bar{u}_1 \rangle}. \quad (A5)$$

Hence, to terms of second order in the two small parameters,

$$\begin{aligned} E = E_0 &+ \frac{1}{R^3} \langle u_0 | P_2 r^2 | u_0 \rangle + Q \langle u_0 | P_2 r^{-3} | u_0 \rangle \\ &+ \frac{1}{R^6} [\langle u_1^* | H_0 - E_0 | u_1^* \rangle - 2 \langle u_1^* | P_2 r^2 | u_0 \rangle] \\ &+ Q^2 [\langle \bar{u}_1^* | H_0 - E_0 | \bar{u}_1^* \rangle - 2 \langle \bar{u}_1^* | P_2 r^{-3} | u_0 \rangle] \\ &+ \frac{Q}{R^3} [\langle u_1^* | H_0 - E_0 | \bar{u}_1^* \rangle - 2 \langle u_0 | P_2 r^2 | \bar{u}_1^* \rangle] \\ &+ \langle u_1^* | H_0 - E_0 | \bar{u}_1^* \rangle - 2 \langle u_0 | P_2 r^{-3} | u_1^* \rangle. \end{aligned} \quad (A6)$$

This expression can be simplified, by using the Schrödinger equations (A3) and (A4), to

$$\begin{aligned} E = E_0 + E_1 + \bar{E}_1 &- \frac{1}{R^6} \langle u_1^* | P_2 r^2 | u_0 \rangle - Q^2 \langle \bar{u}_1^* | P_2 r^{-3} | u_0 \rangle \\ &- \frac{Q}{R^3} [\langle u_0 | P_2 r^2 | u_1^* \rangle + \langle u_0 | P_2 r^{-3} | u_1^* \rangle]. \end{aligned} \quad (A7)$$

The last two terms are both interaction energies of the nuclear  $Q$  with the electronic shells. The next to the last term is the interaction of the induced electronic quadrupole moment with the external field gradient and the last term is the interaction of the nuclear  $Q$

<sup>11</sup> The asterisk in this appendix does not mean complex conjugate.

with the field gradient induced in the electronic shells by the external charge. Both terms are equal if  $u_1$  and  $\bar{u}_1$  satisfy the Schrödinger equations (A3) and (A4).

If now  $u_1$  and  $\bar{u}_1$  are not exact solutions, the energy (A6) exceeds the true energy but it is to be minimized. It is not, however, the total energy which is minimized and not even the term in  $Q/R^3$ , but the term in  $1/R^6$ , which is essentially the quadrupole polarizability of the ion. This procedure can be defended by noticing that

minimizing the  $1/R^6$  energy should ultimately lead to a trial function  $u_1$  which is negligibly different from the true solution  $u_1$  of (A3). If  $u_1$  satisfies (A3), then for any integrable function  $\bar{u}_1$  orthogonal to  $u_0$ ,

$$\langle u_1^* | H_0 - E_0 | \bar{u}_1^* \rangle = \langle u_0 | P_2 r^2 | \bar{u}_1^* \rangle.$$

The term proportional to  $Q/R^3$  in (A6) then can be written entirely in terms of the true  $u_1$  and is therefore obtained correctly.

## Paramagnetic Resonance Hyperfine Structure of $\text{Co}^{56\dagger}$

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The microwave paramagnetic resonance hyperfine structure of 72-day  $\text{Co}^{56}$  has been observed in a magnetically dilute single crystal of cobalt potassium sulfate at 20°K. From the number of hfs components and their spacing relative to  $\text{Co}^{59}$ , the spin  $I(\text{Co}^{56})=4$  and the magnetic moment  $|\mu(\text{Co}^{56})|=3.855\pm 0.007$  nm are directly determined. These results are discussed in relation to those of nuclear alignment experiments and the nuclear shell model.

### I. INTRODUCTION

IN a recent paper,<sup>1</sup> referred to as I, the direct measurement of the spin and magnetic moment of  $\text{Co}^{60}$  by microwave paramagnetic resonance was described. The present paper presents the results of a similar measurement of the spin and magnetic moment of 72-day  $\text{Co}^{56}$ . These values, as those of  $\text{Co}^{60}$ , are of particular interest in connection with previous investigations of these nuclei by nuclear alignment and  $\beta$ ,  $\gamma$  spectroscopy. The paramagnetic resonance of divalent cobalt ions in a Tutton salt single crystal is observed at 20°K in a conventional paramagnetic resonance spectrometer. As described in I, from the number of hyperfine components and their spacing relative to that of  $\text{Co}^{59}$  we can determine respectively the spin and magnetic moment. For details on the crystallography of the Tutton salts, the Hamiltonian determining the line spacings, and the experimental apparatus we refer to I.

### II. EXPERIMENTAL PROCEDURE

The radiocobalt was produced by the  $\text{Fe}^{56}(p,n)\text{Co}^{56}$  reaction with 12-Mev protons from the 60-in. Crocker cyclotron using an iron-plated water-cooled copper target. Two bombardments were made, the first using iron plated from a bath of reagent grade purity. Preliminary examination of the cobalt paramagnetic resonance hfs from this sample indicated that stable  $\text{Co}^{59}$  was more abundant than  $\text{Co}^{56}$  by a factor 200, undoubtedly because of a cobalt impurity in the iron.

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<sup>1</sup> Dobrowolski, Jones, and Jeffries, Phys. Rev. **101**, 1001 (1956).

Since the intense  $\text{Co}^{59}$  hfs lines obscured some of the  $\text{Co}^{56}$  hfs lines, a second bombardment was made using iron plated from a bath obtained by ether extraction to remove the trace impurity of cobalt. The radiocobalt was extracted from this bombarded target by a procedure similar to that of Maxwell *et al.*,<sup>2</sup> and was added in the form of  $\text{CoSO}_4$  to a heavy-water solution of  $\text{ZnK}_2(\text{SO}_4)_2$ . A single crystal of the Tutton salt  $(\text{Co}, \text{Zn})\text{K}_2(\text{SO}_4)_2 \cdot 6\text{D}_2\text{O}$  was grown, weighing about 70 mg and containing about 4 mC of  $\text{Co}^{56}$ . The activity was identified as that of  $\text{Co}^{56}$  by observing its  $\gamma$ -ray spectrum with a recording scintillation spectrometer. This crystal was mounted in the cavity of the paramagnetic resonance spectrometer with  $z_1$ , the symmetry axis of the crystalline electric field, oriented parallel to the external magnetic field  $H$ , and the susceptibility axis  $K_2$  perpendicular to the field  $H$ . The observed spectrum at 20°K is shown in Fig. 1. The eight hfs lines labeled 1, 2,  $\dots$ , 8 have the  $g$  factor and spacing of  $\text{Co}^{59}$  and are due to a residual trace impurity of cobalt in the iron target. The nine lines labeled 1', 2',  $\dots$ , 9' have the same  $g$  factor and are thus also due to cobalt; in fact they are the hfs lines of  $\text{Co}^{56}$ , the only other cobalt isotope present in the sample. For the paramagnetic resonance transitions observed there are  $2I+1$  hfs components for a nuclear spin  $I$ ; thus we conclude

$$I(\text{Co}^{56})=4. \quad (1)$$

This interpretation is verified by rotating the crystal about the  $K_2$  axis: the two sets of hfs lines move to-

<sup>2</sup> Maxwell, Gile, Garrison, and Hamilton, J. Chem. Phys. **17**, 1340 (1949).