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## APPENDIX A

As explained in the text, Sec. II, the eigenvalue problem of the reduced Hamiltonian was programed and solved on the MIT IBM 709 Computer. The eigenvalues are obtained as power series expansions in $x=g_J\mu_0H_Z/ha$. The numerical values for the parameters $c$ and $\alpha$ that were defined in Sec. II are given here for each of the two isotopes. The range in $x$ for which the polynomials represent a least-squares fit to 1:10$^6$ is indicated for each isotope also.

Cl$^{35}$ $\alpha=0.223685\times10^{-3}$; $c=0.267612$

| $M_J$ | $M_I$ | Polynomial eigenvalue ($40\leq x\leq 46$) |
|---|---|---|
| $\frac{3}{2}$ | $\frac{3}{2}$ | $2.316903 \quad +1.50033553x$ |
| $\frac{3}{2}$ | $\frac{1}{2}$ | $0.86901164+1.4957920x+0.33443613\times10^{-4}x^2$ |
| $\frac{3}{2}$ | $-\frac{1}{2}$ | $-0.59367231+1.4945862x+0.41532171\times10^{-4}x^2$ |
| $\frac{3}{2}$ | $-\frac{3}{2}$ | $-2.0373559 \quad +1.4961546x+0.27660517\times10^{-4}x^2$ |
| $\frac{1}{2}$ | $\frac{3}{2}$ | $0.49712389 \quad +0.50465860x-0.33488876\times10^{-4}x^2$ |
| $\frac{1}{2}$ | $\frac{1}{2}$ | $0.29224395 \quad +0.50087606x-0.66565343\times10^{-5}x^2$ |
| $\frac{1}{2}$ | $-\frac{1}{2}$ | $-0.049036121+0.49689940x+0.22625953\times10^{-4}x^2$ |
| $\frac{1}{2}$ | $-\frac{3}{2}$ | $-0.59396607 \quad +0.49437571x+0.41384716\times10^{-4}x^2$ |
| $-\frac{1}{2}$ | $-\frac{3}{2}$ | $0.86907202-0.50465872x+0.33490513\times10^{-4}x^2$ |
| $-\frac{1}{2}$ | $-\frac{1}{2}$ | $0.29219691-0.49934555x-0.66783485\times10^{-5}x^2$ |
| $-\frac{1}{2}$ | $\frac{1}{2}$ | $-0.34427185-0.49605450x-0.30019072\times10^{-4}x^2$ |
| $-\frac{1}{2}$ | $\frac{3}{2}$ | $-1.0151464 \quad -0.49514143x-0.34712166\times10^{-4}x^2$ |
| $-\frac{3}{2}$ | $-\frac{3}{2}$ | $2.316903 \quad -1.50033553x$ |
| $-\frac{3}{2}$ | $-\frac{1}{2}$ | $0.49722175-1.4957938x-0.33424295\times10^{-4}x^2$ |
| $-\frac{3}{2}$ | $\frac{1}{2}$ | $-1.0153650 \quad -1.4953551x-0.34823223\times10^{-4}x^2$ |
| $-\frac{3}{2}$ | $\frac{3}{2}$ | $-2.3021966 \quad -1.4969776x-0.20519864\times10^{-4}x^2$ |

Cl$^{37}$ $\alpha=0.186204\times10^{-3}$; $c=0.253361$

| $M_J$ | $M_I$ | Polynomial eigenvalue ($49\leq x\leq 55$) |
|---|---|---|
| $\frac{3}{2}$ | $\frac{3}{2}$ | $2.31334025+1.5002793x$ |
| $\frac{3}{2}$ | $\frac{1}{2}$ | $0.83834989+1.4971928x+0.18479538\times10^{-4}x^2$ |
| $\frac{3}{2}$ | $-\frac{1}{2}$ | $-0.63047548+1.4963201x+0.23256223\times10^{-4}x^2$ |
| $\frac{3}{2}$ | $-\frac{3}{2}$ | $-2.0673948 \quad +1.4973609x+0.15334545\times10^{-4}x^2$ |
| $\frac{1}{2}$ | $\frac{3}{2}$ | $0.53394851 \quad +0.50321876x-0.18855929\times10^{-4}x^2$ |
| $\frac{1}{2}$ | $\frac{1}{2}$ | $0.29675613 \quad +0.50051653x-0.30373363\times10^{-5}x^2$ |
| $\frac{1}{2}$ | $-\frac{1}{2}$ | $-0.074441892+0.49781736x+0.13163987\times10^{-4}x^2$ |
| $\frac{1}{2}$ | $-\frac{3}{2}$ | $-0.63109763 \quad +0.49615882x+0.23009683\times10^{-4}x^2$ |
| $-\frac{1}{2}$ | $-\frac{3}{2}$ | $0.8392752 \quad -0.50321445x+0.18815248\times10^{-4}x^2$ |
| $-\frac{1}{2}$ | $-\frac{1}{2}$ | $0.29665412-0.49966521x-0.30845920\times10^{-5}x^2$ |
| $-\frac{1}{2}$ | $\frac{1}{2}$ | $-0.31744481-0.49733898x-0.16627929\times10^{-4}x^2$ |
| $-\frac{1}{2}$ | $\frac{3}{2}$ | $-0.97912344-0.49657774x-0.20013306\times10^{-4}x^2$ |
| $-\frac{3}{2}$ | $-\frac{3}{2}$ | $2.31334025-1.5002793x$ |
| $-\frac{3}{2}$ | $-\frac{1}{2}$ | $0.53464419-1.4971804x-0.18597662\times10^{-4}x^2$ |
| $-\frac{3}{2}$ | $\frac{1}{2}$ | $-0.97958915-1.4967460x-0.20185368\times10^{-4}x^2$ |
| $-\frac{3}{2}$ | $\frac{3}{2}$ | $-2.2881504 \quad -1.4978089x-0.12160268\times10^{-4}x^2$ |

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# Second-Order Quadrupole Effect for the Nuclear Hexadecapole Coupling in Ions*

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In connection with the possible existence of a nuclear electric hexadecapole moment, and the resulting large induced hexadecapole moment for medium and heavy ions due to antishielding effects, expressions have been obtained for the additional induced hexadecapole moment, $H_{\text{ind}}{}^Q$, due to the perturbation of the ion by the field of the nuclear quadrupole moment $Q$ taken in second order. $H_{\text{ind}}{}^Q$ is proportional to $Q^2$. Numerical results for some of the terms of $H_{\text{ind}}{}^Q$ are presented for the Cu$^+$, Ag$^+$, and Hg$^{++}$ ions.

## I. INTRODUCTION

THE antishielding of ions for a possible nuclear electric hexadecapole moment $H$ has been discussed in two previous papers.[1,2] It has been shown that the relevant antishielding factor $\eta_\infty$, which gives the HDM (hexadecapole moment) induced in the ion core $H_{\text{ind}}=-\eta_\infty H$, will be very large for medium and heavy ions. Thus, it was found that for Cu$^+$, Ag$^+$, and Hg$^{++}$, $\eta_\infty$ has the values $\eta_\infty(\text{Cu}^+)=-1200$, $\eta_\infty(\text{Ag}^+)=-8050$, and $\eta_\infty(\text{Hg}^{++})=-63\,000$.

It has been recently pointed out by Foley[3] that the interaction of the nuclear quadrupole moment $Q$ taken in second order will also contribute to hexadecapole effects. For the present case of ions, we are interested

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[1] R. M. Sternheimer, Phys. Rev. Letters **6**, 190 (1961).

[2] R. M. Sternheimer, Phys. Rev. **123**, 870 (1961).

[3] H. M. Foley (private communication).

TABLE I. Values of $I_{l_1l_2}{}^{(L)m}$.

| Quantity | $m=0$ | $m=1$ | $m=2$ | $m=3$ | $m=4$ |
|---|---|---|---|---|---|
| $I_{11}{}^{(2)m}$ | $+2/5$ | $-1/5$ | | | |
| $I_{22}{}^{(2)m}$ | $+2/7$ | $+1/7$ | $-2/7$ | | |
| $I_{33}{}^{(2)m}$ | $+4/15$ | $+1/5$ | $0$ | $-1/3$ | |
| $I_{44}{}^{(2)m}$ | $+20/77$ | $+17/77$ | $+8/77$ | $-1/11$ | $-4/11$ |
| $I_{22}{}^{(4)m}$ | $+2/7$ | $-4/21$ | $+1/21$ | | |
| $I_{33}{}^{(4)m}$ | $+2/11$ | $+1/33$ | $-7/33$ | $+1/11$ | |
| $I_{44}{}^{(4)m}$ | $+162/1001$ | $+81/1001$ | $-9/91$ | $-27/143$ | $+18/143$ |
| $I_{02}{}^{(2)m}$ | $+1/(5)^{\frac{1}{2}}$ | | | | |
| $I_{04}{}^{(4)m}$ | $+1/3$ | | | | |
| $I_{13}{}^{(2)m}$ | $+3(21)^{\frac{1}{2}}/35$ | $+(6/35)(7/2)^{\frac{1}{2}}$ | | | |
| $I_{13}{}^{(4)m}$ | $+(4/63)(21)^{\frac{1}{2}}$ | $-(2/21)(7/2)^{\frac{1}{2}}$ | | | |
| $I_{24}{}^{(2)m}$ | $+6/7(5)^{\frac{1}{2}}$ | $+(2/7)(3/2)^{\frac{1}{2}}$ | $+(1/7)(3)^{\frac{1}{2}}$ | | |
| $I_{24}{}^{(4)m}$ | $+20(5)^{\frac{1}{2}}/231$ | $+(10/231)(3/2)^{\frac{1}{2}}$ | $-10(3)^{\frac{1}{2}}/231$ | | |

in the induced HDM, $H_{\text{ind}}{}^{Q}$, which is due to the second-order effect in $Q$.

In the present paper, we will obtain the expression for $H_{\text{ind}}{}^{Q}$ for any given type of second-order excitation of the ion core. Numerical results for the Ag$^+$ ion will also be presented. We note that second-order quadrupole effects have been previously considered in connection with the quadrupole hfs by Foley, Sternheimer, and Tycko.[4]

## II. CALCULATION OF $H_{\text{ind}}{}^{Q}$

The equation for the first-order perturbation of the wave function due to the nuclear $Q$ is:

$$(H_0-E_0)u_1=(-H_1+E_1)u_0, \qquad (1)$$

where $H_0$ and $E_0$ are the unperturbed Hamiltonian and energy eigenvalue, respectively; $H_1$ is the potential due to the nuclear $Q$:

$$H_1=-(QP_2{}^0/r^3)\text{ Ry}, \qquad (2)$$

where $r$ is in units $a_{\text{H}}$ and $Q$ is in units $a_{\text{H}}{}^2$. $E_1$ is the first-order perturbation of the energy; $u_0$ is $r$ times the unperturbed wave function; and $u_1$ is $r$ times the first-order perturbation considered. The radial part of $u_0$ will be denoted by $u_0'$. Thus, we have

$$u_0=u_0'\Theta_l{}^m, \qquad (3)$$

where $\Theta_l{}^m$ is the angular part of the wave function (spherical harmonic) normalized to 1:

$$\int_0^\pi |\Theta_l{}^m|^2 \sin\theta d\theta=1.$$

For simplicity, in order to derive the result for $u_1$, we will assume that $E_1=0$ for the excitation considered. (The final results for $H_{\text{ind}}{}^{Q}$ will include the possibility of $E_1\neq 0$.) Then the right-hand side of Eq. (1) becomes

$$-H_1u_0=(QP_2{}^0/r^3)u_0'\Theta_l{}^m. \qquad (4)$$

We assume that we are considering the excitation of $nl$ to a particular $l$ state, to be denoted by $l_1$. (Thus, $l_1=l$ or $l_1=l\pm 2$.) The $l_1$ part of Eq. (4) is given by

$$(-H_1u_0)_{l_1}=(Qu_0'/r^3)I_{ll_1}{}^{(2)m}\Theta_{l_1}{}^m, \qquad (5)$$

where, in general, the integral $I_{l_1l_2}{}^{(L)m}$ is defined by

$$I_{l_1l_2}{}^{(L)m}\equiv\int_0^\pi P_L{}^0\Theta_{l_1}{}^m\Theta_{l_2}{}^m \sin\theta d\theta. \qquad (6)$$

Obviously, we have

$$I_{l_1l_2}{}^{(L)m}=I_{l_2l_1}{}^{(L)m}; \quad \text{and} \quad I_{l_1l_2}{}^{(L)m}=I_{l_1l_2}{}^{(L),-m}. \qquad (7)$$

Values of $I_{l_1l_2}{}^{(L)m}$ are given in Table I.

In view of Eq. (5), the $(nl\rightarrow l_1)$ part of $u_1$ is given by

$$u_1(nl\rightarrow l_1)=QI_{ll_1}{}^{(2)m}u_1'(nl\rightarrow l_1)\Theta_{l_1}{}^m, \qquad (8)$$

where the radial function $u_1'(nl\rightarrow l_1)$ is determined by the equation

$$M_{l_1}u_1'(nl\rightarrow l_1)=u_0'(1/r^3-\langle 1/r^3\rangle_{nl}\delta_{ll_1}), \qquad (9)$$

$M_{l_1}$ being defined by

$$M_{l_1}\equiv -d^2/dr^2+l_1(l_1+1)/r^2+V_0-E_0. \qquad (10)$$

In Eq. (9) the term $\propto \langle 1/r^3\rangle_{nl}$ corresponds to the term $E_1u_0$ in Eq. (1).

A part of the second-order quadrupole effect for $H_{\text{ind}}{}^{Q}$ arises from the terms $u_1{}^2$ in the electron density. For a given $m$ state, the sum of the corresponding electron densities (times $r^2$) $\rho_{11}{}^m$ for the two spin directions is given by

$$\rho_{11}{}^m=2u_1'^2Q^2(I_{ll_1}{}^{(2)m})^2(\Theta_{l_1}{}^m)^2. \qquad (11)$$

According to the definition of the HDM as given in Eq. (2) of reference 1, the induced HDM pertaining to $\rho_{11}{}^m$ is given by

$$H_{11}{}^m=8\int_0^\infty\int_0^\pi \rho_{11}{}^mP_4{}^0r^4dr\sin\theta d\theta. \qquad (12)$$

Upon inserting Eq. (11) into (12), and summing

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[4] H. M. Foley, R. M. Sternheimer, and D. Tycko, Phys. Rev. **93**, 734 (1954).

over all possible magnetic quantum numbers $m$, one obtains for the total induced HDM due to $\rho_{11}{}^m$

$$H_{11}=16Q^2K_{11}\sum_{m=-l}^{l}(I_{ll_1}{}^{(2)m})^2 I_{l_1l_1}{}^{(4)m}, \tag{13}$$

where $K_{11}$ is the radial integral

$$K_{11}\equiv\int_0^\infty u_1'^2 r^4 dr. \tag{14}$$

The second-order perturbation of the wave function $u_2$ is determined by the equation

$$(H_0-E_0)u_2=(-H_1+E_1)u_1+E_2u_0, \tag{15}$$

where $E_2$ is the second-order perturbation of the energy, and is given by

$$E_2=\int_0^\infty\int_0^\pi H_1u_0u_1 dr\,\sin\theta d\theta. \tag{16}$$

For simplicity, in deriving the result for the induced HDM due to $u_2$, we will assume that $E_1=E_2=0$ for the excitation considered. (The final expression obtained will include the possibility that $E_1$ or $E_2\neq 0$.) With the present assumption, the right-hand side of Eq. (15) becomes

$$-H_1u_1=Q^2(P_2{}^0/r^3)u_1'I_{ll_1}{}^{(2)m}\Theta_{l_1}{}^m. \tag{17}$$

We now consider the part of $u_2$ with azimuthal quantum number $l_2$. (Thus, $l_2=l_1$ or $l_2=l_1\pm 2$.) The $l_2$ part of Eq. (17) is given

$$(-H_1u_1)_{l_2}=Q^2(u_1'/r^3)I_{ll_1}{}^{(2)m}I_{l_1l_2}{}^{(2)m}\Theta_{l_2}{}^m. \tag{18}$$

Thus the $l_2$ part of $u_2$ can be written as follows:

$$u_2(nl\rightarrow l_1\rightarrow l_2)=Q^2I_{ll_1}{}^{(2)m}I_{l_1l_2}{}^{(2)m}u_2'(nl\rightarrow l_1\rightarrow l_2)\Theta_{l_2}{}^m, \tag{19}$$

where the radial function $u_2'(nl\rightarrow l_1\rightarrow l_2)$ is determined by the equation

$$M_{l_2}u_2'(nl\rightarrow l_1\rightarrow l_2)=u_1'(nl\rightarrow l_1)(1/r^3-\langle 1/r^3\rangle_{nl}\delta_{l_1l_2})-\lambda_{l_1}u_0'\delta_{ll_2}; \tag{20}$$

$\lambda_{l_1}$ is proportional to $E_2$ and is given by

$$\lambda_{l_1}\equiv\int_0^\infty u_0'(nl)u_1'(nl\rightarrow l_1)r^{-3}dr. \tag{21}$$

TABLE II. Values of the angular factor $A$ for Eqs. (13) and (25).

| Term | $A$ |
|---|---|
| $(s, s\rightarrow d\rightarrow g)$ | 64/35 |
| $(s\rightarrow d)^2$ | 32/35 |
| $(p, p\rightarrow p\rightarrow f)$ | 384/175 |
| $(p, p\rightarrow f\rightarrow f)$ | 128/525 |
| $(p\rightarrow f)^2$ | 96/175 |
| $(d, d\rightarrow s\rightarrow d)$ | 64/35 |
| $(d, d\rightarrow d\rightarrow d)$ | 256/343 |
| $(d\rightarrow d)^2$ | 128/343 |
| $(d, d\rightarrow d\rightarrow g)$ | 640/539 |
| $(d, d\rightarrow g\rightarrow d)$ | 64/1715 |
| $(d, d\rightarrow g\rightarrow g)$ | 8320/41503 |
| $(d\rightarrow g)^2$ | 864/1715 |

For $l_2=l$, the presence of the $\lambda_{l_1}$ term ensures that the right-hand side of Eq. (20) is orthogonal to $u_0'$. In this case, $u_0'$ is a solution of the homogeneous equation, and the normalization condition shows that one must add a suitable multiple of $u_0'$ to $u_2'$, such that the resulting $u_2'$ shall satisfy the condition

$$\int_0^\infty\{[u_1'(nl\rightarrow l_1)]^2+2u_0'u_2'(nl\rightarrow l_1\rightarrow l)\}dr=0 \tag{22}$$

[cf. Eqs. (70) and (71) of reference 4].

In this connection, it may be noted[4,5] that for $l_1=l$, there is a similar requirement for Eq. (9), namely, that the solution $u_1'$ must be made orthogonal to $u_0'$ by adding a suitable multiple of $u_0'$.

The contribution of $u_2$ to the induced HDM arises from the overlap of $u_2$ with the unperturbed function $u_0$. For a given $m$ state, the overlap density (times $r^2$) for both spin directions is given by

$$\rho_{02}{}^m=4u_0u_2=4u_0'u_2'Q^2I_{ll_1}{}^{(2)m}I_{l_1l_2}{}^{(2)m}\Theta_l{}^m\Theta_{l_2}{}^m. \tag{23}$$

The resulting contribution to the induced HDM is given by

$$H_{02}{}^m=8\int_0^\infty\int_0^\pi \rho_{02}{}^m P_4{}^0 r^4 dr\,\sin\theta d\theta. \tag{24}$$

Upon inserting (23) into (24), and summing over all $m$ values, one obtains for the total induced HDM for the excitation considered $(nl\rightarrow l_1\rightarrow l_2)$:

$$H_{02}=32Q^2K_{02}\sum_{m=-l}^{l}I_{ll_1}{}^{(2)m}I_{l_1l_2}{}^{(2)m}I_{ll_2}{}^{(4)m}, \tag{25}$$

where $K_{02}$ is the radial integral:

$$K_{02}\equiv\int_0^\infty u_0'u_2'r^4dr. \tag{26}$$

In Table II, we have given the values of the factor multiplying $Q^2K_{11}$ in Eq. (13) and $Q^2K_{02}$ in Eq. (25) for all of the excitations involving $s$, $p$, and $d$ electrons (except $d\rightarrow g\rightarrow i$). This factor is referred to as the angular factor $A$. The notation for the types of terms is obvious: Thus, $(s\rightarrow d)^2$ refers to the term of type $H_{11}$ pertaining to $[u_1'(ns\rightarrow d)]^2$, whereas $(s, s\rightarrow d\rightarrow g)$ denotes the term $H_{02}$ pertaining to the overlap of $u_0'(ns)$ with $u_2'(ns\rightarrow d\rightarrow g)$.

Concerning the values of the integrals $I_{l_1l_2}{}^{(L)m}$, we can make the following comments:

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[5] R. M. Sternheimer, Phys. Rev. **84**, 244 (1951); **86**, 316 (1952); **95**, 736 (1954); and **105**, 158 (1957).

(1) For $l_1 = l_2$, one has the relation

$$\sum_{m=-l}^{l} I_{ll}{}^{(L)m} = 0 \quad \text{for} \quad L \neq 0. \tag{27}$$

(2) The angular factors $C_{ll_1}{}^{(2)}$ for the quadrupole antishielding factor[4,5] $\gamma_\infty(nl \to l_1)$ are given by

$$C_{ll_1}{}^{(2)} = 8 \sum_{m=-l}^{l} (I_{ll_1}{}^{(2)m})^2 \tag{28}$$

(e.g., $C_{ll}{}^{(2)} = 48/25$ for $l=1$, 16/7 for $l=2$, 224/75 for $l=3$).

(3) Similarly, the angular factors for the hexadecapole antishielding factor $\eta_\infty(nl \to l_1)$ are given by

$$C_{ll_1}{}^{(4)} = 8 \sum_{m=-l}^{l} (I_{ll_1}{}^{(4)m})^2 \tag{29}$$

[cf. Eq. (8) of reference 1].

(4) The angular coefficients $C$ for the second-order quadrupole effect for the quadrupole hfs, as given in Eqs. (58) and (61) of reference 4, can be obtained from the following expressions, which are similar to Eqs. (13) and (25):

$$\text{For } (nl \to l_1)^2\text{:} \quad C = 8 \sum_{m=-l}^{l} (I_{ll_1}{}^{(2)m})^2 I_{l_1 l_1}{}^{(2)m}; \tag{30}$$

for $(nl, nl \to l_1 \to l_2)$:

$$C = 16 \sum_{m=-l}^{l} I_{ll_1}{}^{(2)m} I_{l_1 l_2}{}^{(2)m} I_{ll_2}{}^{(2)m}. \tag{31}$$

## III. RESULTS

TABLE III. Values of $\gamma_\infty(nd \to l_1)$ and $J(nd \to l_1)$ for the $Cu^+$, $V^{++}$, $Ag^+$, and $Hg^{++}$ ions. (The values of $\langle r^{-3} \rangle_{nd}$ and $\langle r^{-5} \rangle_{nd}$ are in units $a_H{}^{-3}$ and $a_H{}^{-5}$, respectively.)

| Perturbation | $\langle r^{-3} \rangle_{nd}$ | $\langle r^{-5} \rangle_{nd}$ | $\gamma_\infty(nd \to l_1)$ | $J(nd \to l_1)$ |
|---|---|---|---|---|
| $Cu^+$ $3d \to d$ | 7.53 | 219.0 | $-$ 8.29 | 24.10 |
| $Cu^+$ $3d \to g$ | 7.53 | 219.0 | + 0.369 | 2.091 |
| $V^{++}$ $3d \to d$ | 2.763 | 41.46 | ··· | 5.41 |
| $V^{++}$ $3d \to g$ | 2.763 | 41.46 | ··· | 0.5565 |
| $Ag^+$ $4d \to d$ | 8.11 | 932.2 | $-$13.14 | 39.48 |
| $Ag^+$ $4d \to g$ | 8.11 | 932.2 | + 0.464 | 4.773 |
| $Hg^{++}$ $5d \to d$ | 13.07 | 5577.4 | $-$27.6 | ~130 |

TABLE IV. Values of $K_{11}(nd \to d)$ and $\rho_{\text{ion}}[(nd \to d)^2]$.

| Perturbation | $K_{11}(nd \to d)$ | $\lvert\eta_\infty\rvert$ | $\rho_{\text{ion}}/(Q^2/H)$ |
|---|---|---|---|
| $Cu^+$ $3d \to d$ | 275.1 | 1200 | 0.0856 |
| $Ag^+$ $4d \to d$ | 480.7 | 8050 | 0.0223 |
| $Hg^{++}$ $5d \to d$ | 1631 | 63000 | 0.00966 |

In connection with related calculations on the second-order quadrupole effect for the nuclear hexadecapole coupling for atomic states, we have obtained various perturbed wave functions for the outer ($d$) electrons of the $Cu^+$, $V^{++}$, $Ag^+$, and $Hg^{++}$ ions. These wave functions describe the $nd \to d$ and $nd \to g$ perturbations of the outermost $d$ electrons, as a result of the potential due to the nuclear quadrupole moment $Q$. Thus, $u_1'(nd \to d)$ and $u_1'(nd \to g)$ are the appropriate solutions of Eq. (9) with $l = l_1 = 2$ for $nd \to d$, and $l=2$, $l_1 = 4$ for $nd \to g$. The procedure of the calculation of $u_1'$ has been described previously.[5,6] For $Cu^+$, $V^{++}$, and $Ag^+$, the Hartree-Fock ($3d$ or $4d$) wave functions[7,8] were used for the unperturbed functions $u_0'$. For $Hg^{++}$, only Hartree functions[9] were available, so that the Hartree $5d$ function (without exchange) was used. In Table III, we have given the results of these calculations. For each unperturbed wave function, the values of $\langle r^{-3} \rangle_{nd}$ and $\langle r^{-5} \rangle_{nd}$ are listed in the first two columns of the table. In the next column, we have given the quadrupole shielding or antishielding factor $\gamma_\infty$ for all perturbations, except for $V^{++}$, where $\gamma_\infty(3d \to l_1)$ is not given, since the $3d$ function for this ion[8] (with configuration $3s^2 3p^6 3d 4s^2$) pertains to a single valence electron, rather than a completed $d$ shell, as in the other cases. We have also given the values of the integral $J(nl \to l_1)$ for each perturbation, where $J(nl \to l_1)$ is defined by

$$J(nl \to l_1) \equiv \int_0^\infty u_0'(nl) u_1'(nl \to l_1) r^{-3} dr. \tag{32}$$

The integrals $J(nd \to d)$ and $J(nd \to g)$ enter into the calculation of the second-order quadrupole energy ($\propto Q^2$) for atomic states.

In connection with the present work which is concerned with the evaluation of the second-order induced HDM for ions, $H_{\text{ind}}{}^Q$, the above-mentioned calculations of $u_1'(nd \to d)$ are relevant, since they permit the evaluation of the terms proportional to $K_{11}(nd \to d)$, i.e., the terms which are due to the density $[u_1'(nd \to d)]^2$. In view of Eq. (14), $K_{11}(nd \to d)$ is given by

$$K_{11}(nd \to d) = \int_0^\infty [u_1'(nd \to d)]^2 r^4 dr. \tag{33}$$

As is seen from Table II, the angular factor associated with $(nd \to d)^2$ is: $A = 128/343 = 0.373$, so that the ratio $\rho_{\text{ion}}[(nd \to d)^2]$ of $H_{\text{ind}}{}^Q$ to $H_{\text{ind}}$ due to a nuclear $H$ is given by:

$$\rho_{\text{ion}}[(nd \to d)^2] = 0.373 K_{11}(nd \to d) Q^2 / \lvert\eta_\infty\rvert H. \tag{34}$$

Table IV lists the values of $K_{11}(3d \to d)$ for $Cu^+$, $K_{11}(4d \to d)$ for $Ag^+$, and $K_{11}(5d \to d)$ for $Hg^{++}$; the

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[6] R. M. Sternheimer, Document No. 6044, ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C.

[7] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A157**, 490 (1936).

[8] B. H. Worsley, Proc. Roy. Soc. (London) **A247**, 390 (1958).

[9] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A149**, 210 (1935).

corresponding values[2] of $|\eta_\infty|$ and the resulting ratios $\rho_{\text{ion}}[(nd\to d)^2]/(Q^2/H)$. It is seen that $\rho_{\text{ion}}[(nd\to d)^2]$ is in all cases less than $0.1(Q^2/H)$ and decreases with increasing $Z$ (for the ions whose outermost shell is a filled $d$ shell).

In connection with the other perturbations [aside from $(nd\to d)^2$], we have obtained results for $(4d, 4d\to d\to d)$ and $(4d\to g)^2$ for Ag$^+$. The equation for the perturbation $u_2'(4d\to d\to d)$ was integrated numerically:

$$[-d^2/dr^2+6/r^2+V_0-E_0]u_2' = u_1'(4d\to d)[1/r^3-\langle 1/r^3\rangle_{4d}]-\lambda_d u_0'(4d), \qquad (35)$$

where $\langle 1/r^3\rangle_{4d}=8.11\ a_{\text{H}}^{-3}$, and

$$\lambda_d=\int_0^\infty u_0'u_1'r^{-3}dr=39.48. \qquad (36)$$

We have

$$\int_0^\infty u_1'^2dr=9.746, \qquad (37)$$

so that, according to Eq. (22), we must have

$$\int_0^\infty u_0'u_2'dr=-\tfrac{1}{2}(9.746)=-4.873. \qquad (38)$$

This is achieved by adding a suitable multiple of $u_0'$ to the function $u_2'$ obtained by numerical integration.

The resulting value of $K_{02}$ is

$$K_{02}=\int_0^\infty u_0'(4d)u_2'(4d\to d\to d)r^4dr=8.10, \qquad (39)$$

which is very small compared to $K_{11}(4d\to d)=480.7$ (see Table IV). Thus the term in $\rho_{\text{ion}}$ due to $4d\to d\to d$ is given by

$$\rho_{\text{ion}}(4d\to d\to d) = (256/343)K_{02}Q^2/|\eta_\infty|H=7.51\times10^{-4}(Q^2/H), \qquad (40)$$

which is quite negligible compared to $\rho_{\text{ion}}[(4d\to d)^2]$ $[=0.0223(Q^2/H)]$.

We have also evaluated the $(4d\to g)^2$ term for Ag$^+$. The contribution of this term is completely negligible. Thus, $K_{11}(4d\to g)=0.01820$. The angular factor is: $A=864/1715=0.504$ (see Table II). Hence the correction to $\rho_{\text{ion}}$ is

$$\rho_{\text{ion}}[(4d\to g)^2]=1.14\times10^{-6}(Q^2/H). \qquad (41)$$

We have also obtained an estimate of the integral $K_{02}(4d\to s\to d)$ for Ag$^+$ pertaining to the overlap of $u_0'(4d)$ with the second-order perturbation

$$u_2'(4d\to s\to d)$$

as calculated from Eq. (20). The resulting value of $\rho_{\text{ion}}(4d\to s\to d)$ is $+0.026(Q^2/H)$. Thus, for Ag$^+$, the total effect due to $(4d\to d)^2$, $(4d, 4d\to d\to d)$, and $(4d, 4d\to s\to d)$ is given by

$$\sum \rho_{\text{ion}}=(0.022+0.001+0.026)(Q^2/H) =0.049(Q^2/H). \qquad (42)$$

In the absence of calculations of the other types of perturbations of the outermost ($n=4$) shell, as listed in Table II, we cannot draw any definite conclusions about the value of the complete $\rho_{\text{ion}}$ for Ag$^+$. However, there are reasons to believe that among the terms due to the $d$ electrons, those due to $nd\to g$ are considerably smaller than those due to $nd\to d$ and $nd\to s$. This result is borne out by the smallness of $\rho_{\text{ion}}[(4d\to g)^2]$ for Ag$^+$, and also by the relative smallness of $\gamma_\infty(nd\to g)$ as compared to $\gamma_\infty(nd\to d)$, and of $J(nd\to g)$ in comparison with $J(nd\to d)$ for all of the cases considered in Table III. If this assumption is correct, and if excitations which involve $d\to g$ at any stage (e.g., $4d\to d\to g$) are unimportant, then the total ratio $\rho_{\text{ion}}$ due to the $4d$ electrons of Ag$^+$ would be essentially given by Eq. (42), i.e., of order $0.05(Q^2/H)$. On the basis of previous results for $\gamma_\infty$ and $\eta_\infty$, it is expected that the inner shells ($n=1,2,3$) do not contribute appreciably to $H_{\text{ind}}{}^Q$. However, it should be pointed out that no calculations have been carried out for the perturbations of the $4s$ and $4p$ electrons of the Ag$^+$ ion.

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