PHYSICAL REVIEW VOLUME 164, NUMBER 1 5 DECEMBER 1967

Quadrupole Shielding and Antishielding Factors for Atomic States*

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(Received 27 June 1967)

The atomic shielding (or antishielding) factor R for the quadrupole hyperfine structure has been evaluated for several excited atomic states. The values of R were determined by means of the perturbed wave functions $v_1'(nl \rightarrow l')$ as obtained by solving the inhomogeneous Schrödinger equation for each type of excitation of the core electrons by the nuclear quadrupole moment Q. For the case of copper, the calculations provide a quantitative explanation of the fact that the values of $Q(\mathrm{Cu}^{65})$ obtained from two different excited configurations ($3d^94s^2$ and $3d^{10}4p$) differ considerably from each other (by $\gtrsim 40\%$), when the correction factor $1/(1-R)$ is not applied. The calculated values of R, namely $R_{3d}=+0.178$ (shielding) and $R_{4p}=-0.175$ (antishielding), bring the two corrected values of Q into very good agreement. We thus obtain $Q(\mathrm{Cu}^{65}) = (-0.195\pm0.004)\times10^{-24}$ cm². Besides the work on Cu $3d$ and $4p$, the following calculations have also been carried out: (1) R_{5d} for the $5d$ states of Pr and Tm; (2) R_{2p} and R_{3p} for the $2p$ and $3p$ states of Li; (3) R_{2p} for the $2s2p$ ^3P excited state of beryllium.

I. INTRODUCTION

THE purpose of the present paper is to give the results of calculations of the quadrupole shielding (or antishielding) factor R for several atomic states.[1,2] The factor R represents the change in the hyperfine structure interval b for atomic states due to the quadrupole moment induced in the electron core by the nuclear quadrupole moment Q. Thus b can be written as follows:

$$b=b_0(1-R), \tag{1}$$

where b_0 (which is proportional to Q) is the value which b would have in the absence of the induced effects in the core. The calculated values of R are generally in the range from -0.3 to $+0.3$ where positive R corresponds to shielding [see Eq. (1)].

Values of R have been previously obtained in several papers.[1–3] Even before last year (1966), there had already been some good experimental evidence which supports the calculated values of R. This evidence concerns the following cases: (1) the $4f$ state of the rare earths, for which the theoretical value, $R\sim+0.2$, is in reasonable agreement with various experimental determinations[4]; (2) the $5d$ and/or $6p$ states of La^{139}, Lu^{175}, and Hg^{201}, for which Murakawa[5] showed that values of $R_{5d}\cong-0.4$ and $R_{6p}\cong-0.1$ are required to fit the experimental data; (3) the 5 $^2P_{3/2}$, 6 $^2P_{3/2}$, and 7 $^2P_{3/2}$ states of rubidium, for which zu Putlitz, Schenck, and Schüssler[6] have obtained evidence for the existence of an antishielding factor R_{np}, and its slow variation with the principal quantum number n.

It has been noticed recently that the quadrupole moment of Cu^{65}, $Q(\mathrm{Cu}^{65})$ as obtained without applying the correction factor $\mathfrak{C}=1/(1-R)$ [see Eq. (1)] differs considerably,[7,8] depending upon whether the hyperfine structure is measured in the atomic excited state with configuration $3d^94s^2$ ($^2D_{3/2}$ or $^2D_{5/2}$) or in the excited state $3d^{10}4p$ ($^2P_{3/2}$). According to two recent high-precision experiments,[7,8] Q [from $3d^94s^2$ ($^2D_{5/2}$)]$=(-0.161\pm0.003)\times10^{-24}$ cm², whereas Q [from $3d^{10}4p$ ($^2P_{3/2}$)]$=(-0.228\pm0.005)\times10^{-24}$ cm². It was pointed out by Fischer, Hühnermann, and Kollath[8] that the large difference between these two values (a factor of 1.42) may be due in large part to the fact that the correction factor $\mathfrak{C}_{nl}=1/(1-R_{nl})$ is appreciably different for the $3d$ electron hole and the $4p$ electron in the two excited states.

In the present work, we have carried out an accurate calculation of R for these two states of the copper atom (including the exchange terms of R). The result is that $(1-R_{4p})/(1-R_{3d})=1.429$, in very good agreement with the experimental ratio of the two uncorrected values of $Q(\mathrm{Cu}^{65})$. The comparison between theory and experiment for Cu thus provides a very good confirmation of the existence of the atomic shielding effect.

It may be noted, by way of contrast, that the induced effects for ions,[9] represented by the ionic antishielding

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* Work performed under the auspices of U. S. Atomic Energy Commission.

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factor γ_∞, are much larger ($\gamma_\infty \sim 10-100$), and for this reason it was much easier to verify them experimentally, as has been done in a number of experiments.[10]

In addition to the calculations for Cu, we have also obtained the theoretical values of R_{5d} for Pr and Tm (for comparison with the work of Murakawa[5]) and also of R_{2p} and R_{3p} for Li and R for Be $2s2p\ {}^3P$, in connection with atomic beam measurements of the hyperfine structure of lithium[11] and beryllium.[12]

II. CALCULATIONS OF R

A. Cu $3d^9 4s^2$ and $3d^{10}4p$

As has been previously discussed by the author,[1,2] the atomic shielding (or antishielding) factor R is obtained by the use of suitable functions $\gamma_{\text{ang}}(r)$ and $\gamma_{\text{rad}}(r)$ which are defined as follows. We introduce a function $\gamma(nl \to l'; r)$ of the distance r from the nucleus, by the equation

$$\gamma(nl \to l'; r) \equiv \frac{1}{Q}\left[\int_0^r Q_i(nl \to l')dr' + r^5 \times \int_r^\infty Q_i(nl \to l')r'^{-5}dr'\right], \quad (2)$$

where $Q_i(nl \to l')$ is the density of induced moment pertaining to the excitation $(nl \to l')$ of the nl shell of the core. $Q_i\ (nl \to l')$ is given by

$$Q_i(nl \to l') = c(nl \to l')Qu_0'(nl)v_1'(nl \to l')r^2, \quad (3)$$

where $c(nl \to l')$ is a coefficient arising from the integration over the angular variables and the summation over the magnetic substates of the shell nl; $u_0'(nl)$ is r times the unperturbed radial wave function, normalized according to

$$\int_0^\infty u_0'^2 dr = 1. \quad (4)$$

In Eq. (3), $v_1'(nl \to l')$ is the radial wave function pertaining to the excitation $(nl \to l')$; $v_1'(nl \to l')$ is determined by the following equation:

$$\left[-\frac{d^2}{dr^2} + \frac{l'(l'+1)}{r^2} + V_0 - E_0\right] v_1'(nl \to l') = u_0'(nl)\left[\frac{1}{r^3} - \left\langle\frac{1}{r^3}\right\rangle_{nl} \delta_{ll'}\right], \quad (5)$$

and by the orthogonality condition (for $l' = l$)

$$\int_0^\infty u_0'(nl)v_1'(nl \to l)dr = 0. \quad (6)$$

In Eq. (5), V_0 is the effective (unperturbed) potential pertaining to the state nl, and E_0 is the unperturbed energy eigenvalue. According to a method previously employed by the author,[1,2,13] $V_0 - E_0$ is obtained from the function $u_0'(nl)$ by means of the relation

$$V_0 - E_0 = \frac{1}{u_0'}\frac{d^2u_0'}{dr^2} - \frac{l(l+1)}{r^2}. \quad (7)$$

The coefficient $c(nl \to l')$ in Eq. (3) has the following values for the various excitation modes of the Cu atom[1,2]: 8/5 for $ns \to d$ and $nd \to s$; 48/25 for $np \to p$; 72/25 for $np \to f$; 16/7 for $nd \to d$; and 144/35 for $nd \to g$.

The direct interaction of the $(nl \to l')$ perturbed density with the valence electron is proportional to the integral $\Gamma_D(nl \to l'; n_el_e)$, which is defined as follows:

$$\Gamma_D(nl \to l'; n_el_e) \equiv \langle \gamma(nl \to l'; r)/r^3 \rangle_{n_el_e} = \int_0^\infty \gamma(nl \to l'; r)[w(n_el_e)]^2 r^{-3} dr, \quad (8)$$

where $w(n_el_e)$ is r times the radial part of the valence electron wave function (with quantum numbers n_el_e), normalized in the same manner as u_0' [Eq. (4)]. Thus,

$$\int_0^\infty [w(n_el_e)]^2 dr = 1. \quad (9)$$

In the following, for simplicity of notation, we will often refer to $w(n_el_e)$ simply as w.

The direct (i.e., nonexchange) contribution of R from the perturbation $(nl \to l')$ is given by

$$R_D(nl \to l'; n_el_e) = \frac{\Gamma_D(nl \to l'; n_el_e)}{\langle r^{-3} \rangle_{n_el_e}}, \quad (10)$$

where

$$\langle r^{-3} \rangle_{n_el_e} \equiv \int_0^\infty w^2 r^{-3} dr. \quad (11)$$

The exchange interaction of $(nl \to l')$ with the valence electron involves the following integral (for one or more values of L):

$$K(nl \to l'; n_el_e; L) \equiv \int_0^\infty u_0'(nl)w(n_el_e)g_L dr, \quad (12)$$

where g_L is given by

$$g_L(nl \to l'; n_el_e) = \frac{1}{r^{L+1}}\int_0^r v_1'(nl \to l')wr'^L dr' + r^L \int_r^\infty v_1'(nl \to l')wr'^{-L-1}dr'. \quad (13)$$

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TABLE I. Coefficients $c^{(L)}(lm;l'm')$ required to obtain the values of $C(nd\rightarrow g;3;p)$, $C(nd\rightarrow g;2;d)$ and $C(nd\rightarrow g;4;d)$. Note that $c^{(2)}(2m;4m)=c^{(2)}(4m;20)$.

Coefficient	Value
$c^{(2)}(20;40)$	$6/[7(5)^{1/2}]$
$c^{(2)}(21;41)$	$6^{1/2}/7$
$c^{(2)}(22;42)$	$3^{1/2}/7$
$c^{(3)}(40;10)$	$4(3)^{1/2}/21$
$c^{(3)}(41;10)$	$5^{1/2}/7$
$c^{(3)}(42;10)$	$2/7$
$c^{(4)}(40;20)$	$20(5)^{1/2}/231$
$c^{(4)}(41;20)$	$17(5)^{1/2}/231$
$c^{(4)}(42;20)$	$8(5)^{1/2}/231$

The interaction energy $\Gamma_E(nl\rightarrow l';\,n_el_e;L)$, which is analogous to Γ_D [cf. Eq. (8)], is given by

$$\Gamma_E(nl\rightarrow l';n_el_e;L)\\=-C(nl\rightarrow l';n_el_e;L)K(nl\rightarrow l';n_el_e;L),\quad(14)$$

where the coefficient $C(nl\rightarrow l';n_el_e;L)$ is given by Eq. (37) of Ref. 2, namely,

$$C(nl\rightarrow l';n_el_e;L)\\=\frac{4\sum_{m=-l}^{l}c^{(2)}(lm;l'm)c^{(L)}(lm;l_em_e)c^{(L)}(l'm;l_em_e)}{c^{(2)}(l_em_e;l_em_e)}.\quad(15)$$

Finally, the contribution to R due to the exchange term arising from $(nl\rightarrow l')$ is given by

$$R_E(nl\rightarrow l';n_el_e;L)=\frac{\Gamma_E(nl\rightarrow l';n_el_e;L)}{\langle r^{-3}\rangle_{n_el_e}},\quad(16)$$

in complete analogy to Eq. (10).

In Eq. (15), the coefficients $c^{(L)}(lm;l'm')$ are the same as those of Condon and Shortley,[14] namely,

$$c^{(L)}(lm;l'm')\\=[2/(2L+1)]^{1/2}\int_0^{\pi}\Theta_L^{m-m'}\Theta_l^{m}\Theta_{l'}^{m'}\sin\theta d\theta,\quad(17)$$

where Θ_l^m is the spherical harmonic normalized to 1.

The result of Eq. (15) is independent of the value of m_e, the magnetic quantum number of the valence electron. In practice, the expression is evaluated for the case $m_e=0$, and can then be checked by using $m_e=+1$.

In order to show how the relevant values of L are determined, we take as an example the perturbation $(np\rightarrow f)$ interacting with an external d electron (or a single hole in a filled $3d$ shell, as is the case for Cu). The density $v_1(np\rightarrow f)w(3d)$ can be written as a sum of three terms which behave as P_1, P_3, and P_5, respectively, where P_L is the Legendre polynomial. Similarly, the interacting density $u_0(np)w(3d)$ is a sum of two terms having P_1 and P_3 behavior. Hence the electrostatic (exchange) interaction will consist of two terms having $L_1=1$ and $L_2=3$. This follows from the expansion of $1/r_{12}$ in spherical harmonics [see Eqs. (25) and (26) of Ref. 2].

In order to evaluate the coefficients $C(nl\rightarrow l';n_el_e;L)$ of Eq. (15), we used the tables of Condon and Shortley[14] for the integrals $c^{(L)}(lm;l'm')$. These tables give all of the required coefficients for the case of Cu, except for those involved in the $3d\rightarrow g$ excitation of the $3d$ shell. For this latter case, nine additional coefficients are required (for $n_el_e=3d$ and $4p$). Their values are listed in Table I. In this connection, we note that

$$c^{(2)}(2m;4m)=c^{(2)}(4m;20).\quad(18)$$

For this reason, the coefficients $c^{(2)}(4m;20)$ were not listed separately in Table I.

Table II gives the resulting values of $C(nl\rightarrow l';n_el_e;L)$ for an atom with filled s, p, and d shells, and with an external p, d, or f electron (or electron hole). It may be noted that some of these results have been obtained previously in Refs. 1 and 2. We also mention that the table includes the results for $C(nf\rightarrow f;n_el_e;L)$ with $l_e=p$, d, or f. Note that

$$C(nl\rightarrow l';n_el_e;L)=C(nl'\rightarrow l;n_el_e;L).\quad(19)$$

Thus, the coefficients for $nd\rightarrow s$ and $nf\rightarrow p$ are not

TABLE II. The coefficients $C(nl\rightarrow l';n_el_e;L)$ pertaining to the exchange terms $\Gamma_E(nl\rightarrow l';n_el_e;L)$, where l_e is the azimuthal quantum number of the external (valence) electron. The value of L ($=L_1$, L_2, or L_3) is listed in parentheses after each coefficient. For $l_e=3$, there is an additional coefficient not given in the table, namely $C(nf\rightarrow f;n_ef;6)=+500/1287$, pertaining to $L_4=6$. Note that $C(nl\rightarrow l';n_el_e;L)=C(nl'\rightarrow l;n_el_e;L)$. Thus the coefficients for $nd\rightarrow s$ and $nf\rightarrow p$ are not listed separately. The table consists of three parts, corresponding to the case of an external p, d, or f electron.

$(nl\rightarrow l';l_e)$	$C(L_1)$	$C(L_2)$	$C(L_3)$
$(ns\rightarrow d:p)$	4/3(1)		
$(np\rightarrow p;p)$	4(0)	4/25(2)	
$(np\rightarrow f;p)$	36/25(2)		
$(nd\rightarrow d;p)$	4/3(1)	12/49(3)	
$(nd\rightarrow g;p)$	72/49(3)		
$(nf\rightarrow f;p)$	24/25(2)	8/27(4)	
$(ns\rightarrow d;d)$	4/5(2)		
$(np\rightarrow p;d)$	28/25(1)	36/175(3)	
$(np\rightarrow f;d)$	12/25(1)	144/175(3)	
$(nd\rightarrow d;d)$	4(0)	−12/49(2)	16/49(4)
$(nd\rightarrow g;d)$	144/245(2)	40/49(4)	
$(nf\rightarrow f;d)$	48/25(1)	−88/225(3)	40/99(5)
$(ns\rightarrow d;f)$	4/7(3)		
$(np\rightarrow p;f)$	108/175(2)	4/21(4)	
$(np\rightarrow f;f)$	72/175(2)	4/7(4)	
$(nd\rightarrow d;f)$	72/49(1)	−44/147(3)	500/1617(5)
$(nf\rightarrow f;f)$	4(0)	76/225(2)	−4/11(4)

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[14] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, London, 1935), p. 175.

listed separately. The values of L (denoted by L_1, L_2, L_3) are given in parentheses after each value of C.

We will now discuss specifically the case of Cu, with either a $3d$ electron hole ($3d^94s^2$), or a $4p$ electron outside closed shells ($3d^{10}4p$). Referring to Eq. (5), the perturbed wave functions $v_1'(2p\rightarrow p)$, $v_1'(3p\rightarrow p)$, and $v_1'(3d\rightarrow d)$, for which $l'=l$, have been previously obtained[15] in connection with the calculation of the ionic antishielding factor $\gamma_\infty(\mathrm{Cu}^+)$. For the "angular" modes of excitation, i.e., those with $l'=l\pm 2$, we have previously carried out calculations of $v_1'(3d\rightarrow s)$ and $v_1'(3d\rightarrow g)$.[16,17] The remaining angular modes, namely $v_1'(1s\rightarrow d)$, $v_1'(2s\rightarrow d)$, $v_1'(2p\rightarrow f)$, $v_1'(3s\rightarrow d)$, and $v_1'(3p\rightarrow f)$ were obtained in the present work. The solutions were found by inward integration of Eq. (5) on the CDC-6600 Computer, using a machine program written by Dr. R. F. Peierls.

As has been previously discussed in Refs. 1 and 2, for the case $l'=l+2$, the inward integration of Eq. (5) is carried out with several trial starting values $v_1'(r_1)$ at a large radius r_1. The correct value of $v_1'(r_1)$ is that for which the resulting solution $v_1'(r)$ is well-behaved at the nucleus ($r=0$). For the ($ns\rightarrow d$) perturbation, it is easily shown from Eq. (5) that v_1' has the following value at $r=0$: $v_1'(0)=a_1/6$, where a_1 is given by $[u_0'(ns)/r]_{r=0}$. In a similar fashion, for the ($np\rightarrow f$) perturbation, $v_1'=0$ at $r=0$, with the following slope:

$$\left(\frac{dv_1'}{dr}\right)_{r=0}=\frac{a_2}{12},\tag{20}$$

where $a_2\equiv[u_0'(np)/r^2]_{r=0}$. Thus $v_1'(np\rightarrow f)=(a_2/12)r$ near the nucleus.

In the computer program, the correct value at $r=0$ is specified within very narrow limits, and the computer is instructed to try a sequence of starting values $v_1'(r_1)$, and in each case to compare the resulting $v_1'(0)$ with the predetermined correct value [e.g., $a_1/6$ for $ns\rightarrow d$; or 0 for $np\rightarrow f$]. The procedure is self-correcting, in the sense that each successive trial value $v_1'(r_1)$ is based on a comparison of the previous $v_1'(0)$ with the desired value at the nucleus. The computer program stops the calculation when two functions $v_1'(r)$ have been found, for both of which $v_1'(0)$ differs from the desired $v_1'(0)$ by a very small amount. As an example, for $v_1'(3s\rightarrow d)$, two functions were computed for which $v_1'(0)=5.858$ and 5.899, the correct value being 5.875. The actual solution was then obtained by linear interpolation of these two final functions. In a similar manner, for $v_1'(2p\rightarrow f)$, where $v_1'=0.285$ at $r=0.005$ a_H [from Eq. (20)], two functions were found by the computer, with $v_1'(0.005)=0.2704$ and 0.2999. It may be noted that the values of $v_1'(nl\rightarrow l+2)$ away from the nucleus, and particularly in the region of the outermost maximum of $u_0'(nl)$, are determined to a very high accuracy by Eq. (5) (of the order of one part in 10^4 to 10^5), for the given values of V_0-E_0. The great stability of the solution is probably due to the presence of the centrifugal term $l'(l'+1)/r^2$ in Eq. (5).

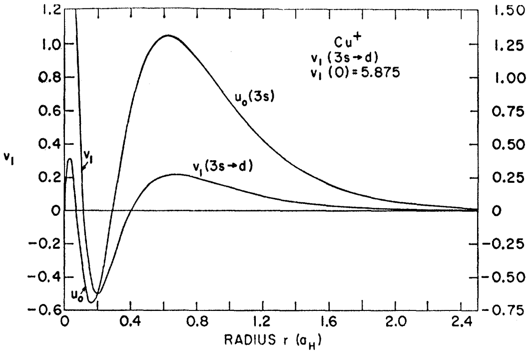

FIG. 1. The perturbed wave function $v_1(3s\rightarrow d)$ and the $3s$ function $u_0(3s)$ for Cu$^+$. The left-hand ordinate scale pertains to v_1; the right-hand scale pertains to u_0.

The unperturbed wave functions $u_0'(nl)$ used in the present work were the same as in our earlier calculations[1] for Cu, namely the Hartree-Fock wave functions determined by Hartree.[18] The five functions $v_1'(nl\rightarrow l+2)$ obtained here have been tabulated in a separate paper.[19] This paper also includes tables of $v_1'(3d\rightarrow s)$, $v_1'(3d\rightarrow g)$, and the radial modes $v_1'(nl\rightarrow l)$ which have been determined in earlier work.[15–17]

As an example of the results obtained, we show the following perturbed wave functions in Fig. 1 and 2: $v_1'(3s\rightarrow d)$, $v_1'(3d\rightarrow s)$ and $v_1'(3d\rightarrow g)$, together with $u_0'(3s)$ and $u_0'(3d)$. Figure 1 shows that $v_1'(3s\rightarrow d)$ has generally the same sign as the unperturbed $u_0'(3s)$. In a similar manner, $v_1'(3d\rightarrow g)$ and $u_0'(3d)$ have the same sign, as illustrated in Fig. 2. These two examples are special cases of a general property of the relative sign of $v_1'(nl\rightarrow l+2)$ and $u_0'(nl)$, as previously discussed in Refs. 1 and 2. This property also leads to the shielding of the nuclear moment Q by the modes ($nl\rightarrow l+2$).

As shown by Fig. 2, $v_1'(3d\rightarrow s)$ has opposite sign to that of $u_0'(3d)$ near the nucleus. This feature of the excitation modes ($nd\rightarrow s$) has been previously pointed out by the author in Sec. III of Ref. 17. It will be seen below that for a relatively penetrating electron such as $3d$, this feature leads to a small antishielding effect

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[15] R. M. Sternheimer and H. M. Foley, Phys. Rev. **102**, 731 (1956).

[16] R. M. Sternheimer, Phys. Rev. **127**, 812 (1962).

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

[19] Tables of the perturbed wave functions $v_1'(nl\rightarrow l')$ obtained in connection with the present calculations are given in a supplementary paper. This paper also contains tables of the valence wave functions calculated in the present work, namely $w(2p)$ and $w(3p)$ for Li, $w(4p)$ for Cu, and $w(5d)$ for Pr and Tm. The supplementary paper has been deposited as Document No. 9592 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting \$3.75 for photoprints, or \$2.00 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

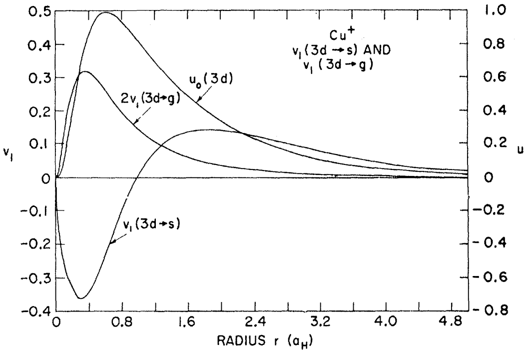

FIG. 2. The perturbed wave functions $v_1(3d \rightarrow s)$ and $v_1(3d \rightarrow g)$ and the $3d$ function $u_0(3d)$ for Cu$^+$. The left-hand ordinate scale pertains to the functions v_1; the right-hand scale pertains to u_0.

arising from $3d \rightarrow s$. On the other hand, for the more external $4p$ electron, the external region ($r \gtrsim 1a_H$), where $u_0(3d)v_1(3d \rightarrow s) > 0$, predominates and leads to a net shielding effect. The same also holds true for the contribution $\gamma_\infty(3d \rightarrow s)$ to the ionic factor γ_∞, which is shielding (positive), although rather small

$$[\gamma_\infty(3d \rightarrow s) = +0.524].$$

The total induced moment density $Q_{i,\mathrm{ang}}$ arising from the angular modes of excitation ($nl \rightarrow l \pm 2$) for the Cu$^+$ ion is shown in Fig. 3. The quantity which is plotted, namely $Q_{i,\mathrm{ang}}/Q$, is given by [cf. Eq. (3)]:

$$\frac{Q_{i,\mathrm{ang}}(r)}{Q} = \sum_{\substack{nl \\ l'=l\pm2}} c(nl \rightarrow l') u_0'(nl) v_1'(nl \rightarrow l') r^2, \quad (21)$$

where the sum goes over all occupied shells nl, and $l' = l+2$, except for $(3d \rightarrow s)$, where $l' = l-2$. The values of Eq. (21) are shown in Fig. 3 as Q_i(WF), to denote the fact that they were obtained from the wave functions $v_1'(nl \rightarrow l')$. The maxima of Q_i(WF) at $r \approx 0.1a_H$, $0.24a_H$, and $0.9a_H$ correspond to the electron shells with $n = 1$, 2, and 3, respectively. Furthermore, there is a barely noticeable inflection point at $r \sim 2.0a_H$, which is due to the shielding provided by $(3d \rightarrow s)$.

For comparison, we have also shown in Fig. 3 the Thomas-Fermi induced moment density,[20] denoted by Q_i(Th-F):

$$Q_i(\text{Th-F}) = \tfrac{3}{10} Q (\chi x)^{1/2} (x/r), \quad (22)$$

where χ and x are the Thomas-Fermi function and variable, respectively. We have: $x = (Z^{1/3}/0.8853)(r/a_H) = 3.470(r/a_H)$ for Cu.

It is seen that Q_i(Th-F) overestimates Q_i(WF) throughout the region of r. As has been previously discussed,[1,2] the use of (1/1.5) times the Thomas-Fermi density gives a reasonably good approximation to the angular part R_{ang} of R, as obtained from the actual wave function calculations. For this reason, we have also shown a plot of $(1/1.5)Q_i$(Th-F) in Fig. 3. This curve cuts rather evenly through the maxima and minima of Q_i(WF) which are due to the atomic shell structure, as was to be expected from the preceding arguments.

It may be noted that the contribution of $(nl \rightarrow l')$ to the ionic antishielding factor $\gamma_\infty(\mathrm{Cu}^+)$ is given by

$$\gamma_\infty(nl \rightarrow l') = c(nl \rightarrow l') \int_0^\infty u_0'(nl) v_1'(nl \rightarrow l') r^2 dr. \quad (23)$$

The values of $\gamma_\infty(nl \rightarrow l')$ (which are also listed in Ref. 19) are as follows: (1) for the radial modes: $\gamma_\infty(2p \rightarrow p) = -0.618$, $\gamma_\infty(3p \rightarrow p) = -7.995$, $\gamma_\infty(3d \rightarrow d) = -8.306$, which gives a total $\gamma_\infty(\mathrm{rad}) = -16.92$; (2) for the angular modes: $\gamma_\infty(1s \rightarrow d) = 0.02377$, $\gamma_\infty(2s \rightarrow d) = 0.05942$, $\gamma_\infty(2p \rightarrow f) = 0.08100$, $\gamma_\infty(3s \rightarrow d) = 0.1592$, $\gamma_\infty(3p \rightarrow f) = 0.2439$, $\gamma_\infty(3d \rightarrow s) = 0.5244$, $\gamma_\infty(3d \rightarrow g) = 0.3719$, so that the total $\gamma_\infty(\mathrm{ang}) = +1.464$. Finally, we obtain for the total γ_∞ of the Cu$^+$ ion:

$$\gamma_\infty(\mathrm{Cu}^+) = -16.92 + 1.46 = -15.46. \quad (24)$$

We will now discuss the calculation of $\Gamma_D(nl \rightarrow l'; n_el_e)$ and $\Gamma_E(nl \rightarrow l'; n_el_e; L)$ from the wave functions $v_1'(nl \rightarrow l')$, using Eqs. (2), (8) and (12)-(14). We note that the integrals involved in both Γ_D and Γ_E are special cases of the following general type of double integral:

$$I_L \equiv \int_0^\infty \left[\frac{1}{r^{L+1}} \int_0^r f_1 f_2 r'^L dr' + r^L \int_r^\infty f_1 f_2 r'^{-L-1} dr' \right] f_3 f_4 dr, \quad (25)$$

where f_1, f_2, f_3, f_4 are four arbitrary functions of the radius r.

We obtain the integral for Γ_D by taking: $f_1 = u_0'(nl)$, $f_2 = v_1'(nl \rightarrow l')$; $f_3 = f_4 = w(n_el_e)$, and $L = 2$. On the other hand, for Γ_E we must take: $f_1 = v_1'(nl \rightarrow l')$; $f_2 = w(n_el_e)$; $f_3 = u_0'(nl)$; $f_4 = w(n_el_e)$; and L has any of the values L_1, L_2, or L_3 listed in Table II.

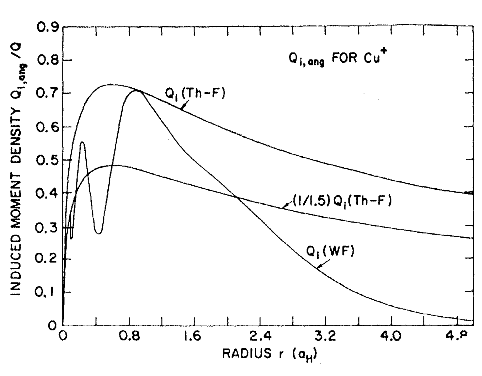

FIG. 3. The induced moment density $Q_{i,\mathrm{ang}}$ (in units of Q) pertaining to the angular modes of excitation ($l' = l \pm 2$) of the Cu$^+$ ion. The curve marked Q_i(WF) shows the result obtained from the calculated wave functions $v_1'(nl \rightarrow l')$ [Eq. (21)]. The curves marked Q_i(Th-F) and $(1/1.5)Q_i$(Th-F) were obtained from the Thomas-Fermi expression for $Q_{i,\mathrm{ang}}$ [Eq. (22)].

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[20] R. M. Sternheimer, Phys. Rev. 80, 102 (1950).

There are altogether 10 perturbed wave functions $v_1'(nl\rightarrow l')$ (7 with $l'=l\pm 2$; 3 with $l'=l$). Hence the total number of integrals involved in the terms $\Gamma_D(nl\rightarrow l';n_el_e)$ for both $n_el_e=3d$ and $4p$ is 20. In addition, it can be easily shown by means of Table II that the number of exchange terms $\Gamma_E(nl\rightarrow l';n_el_e;L)$ is 17 for $3d$ and 13 for $4p$, giving a total of 50 integrals (both direct and exchange).

In our previous calculations of R, in which only the direct terms were included (with some exceptions), it was not necessary to evaluate the separate terms $\Gamma_D(nl\rightarrow l';n_el_e)$. Instead, we had defined two functions $\gamma_{\mathrm{ang}}(r)$ and $\gamma_{\mathrm{rad}}(r)$, as follows:

$$\gamma_{\mathrm{ang}}(r)\equiv\frac{1}{Q}\left[\int_0^r Q_{i,\mathrm{ang}}dr'+r^5\int_r^\infty Q_{i,\mathrm{ang}}r'^{-5}dr'\right], \quad (26)$$

$$\gamma_{\mathrm{rad}}(r)\equiv\frac{1}{Q}\left[\int_0^r Q_{i,\mathrm{rad}}dr'+r^5\int_r^\infty Q_{i,\mathrm{rad}}r'^{-5}dr'\right], \quad (27)$$

where $Q_{i,\mathrm{ang}}(r)$ is given by Eq. (21), and similarly

$$\frac{Q_{i,\mathrm{rad}}(r)}{Q}=\sum_{nl}c(nl\rightarrow l)u_0'(nl)v_1'(nl\rightarrow l)r^2, \quad (28)$$

where the sum extends over the filled p and d shells of the ion. The total correction factor R (excluding exchange terms) is now given by

$$R=R_{\mathrm{ang}}+R_{\mathrm{rad}}, \quad (29)$$

where

$$R_{\mathrm{ang}}=\frac{\Gamma_{\mathrm{ang}}}{\langle r^{-3}\rangle_{n_el_e}}, \quad (30)$$

$$R_{\mathrm{rad}}=\frac{\Gamma_{\mathrm{rad}}}{\langle r^{-3}\rangle_{n_el_e}}, \quad (31)$$

with

$$\Gamma_{\mathrm{ang}}\equiv\int_0^\infty \gamma_{\mathrm{ang}}(r)w^2r^{-3}dr, \quad (32)$$

$$\Gamma_{\mathrm{rad}}\equiv\int_0^\infty \gamma_{\mathrm{rad}}(r)w^2r^{-3}dr. \quad (33)$$

Equations (26)–(33) show that if one is considering the direct interaction alone, it is not necessary to evaluate the individual terms $\Gamma_D(nl\rightarrow l';n_el_e)$ in order to obtain the total R. The reason is, of course, that the direct interaction involves only the total induced density: $Q_{i,\mathrm{ang}}+Q_{i,\mathrm{rad}}$.

However, the preceding procedure will obviously not work for the exchange terms $\Gamma_E(nl\rightarrow l';n_el_e;L)$, each one of which has to be evaluated separately. The calculation of the double integral I_L [Eq. (25)] was programmed for the CDC-6600 computer by Dr. R. F. Peierls. The computer program was basically straightforward. The integrations were carried out using Simpson's rule. However, it should be noted that if the values of f_1 and f_2 [Eq. (25)] are specified on a grid: $0, r_1', r_2', r_3', \cdots r_{N-1}', r_N'$ (i.e., the set of r values corresponding to the tables of Ref. 19), then the integrals over r' will be obtained only at the points $r=r_2, r_4, \cdots r_{N-2}, r_N$ (assuming that N is even). Therefore, in order not to lose accuracy in performing the second integration (over r), it is necessary to carry out an interpolation procedure so as to obtain the values of the first integral at $r_1, r_3, r_5, \cdots r_{N-1}$. For this reason, two features were incorporated into the program: (1) An interpolation was carried out to obtain the values of the first integral at r_1, r_3, etc., so that the grid for the two integrations was always the same. In addition, the number of points for both integrations could be increased. As an example, it was possible to use twice the number of points on the first integration over f_1f_2, by interpolation on f_1f_2, i.e., at $\frac{1}{2}r_1'$, $\frac{1}{2}(r_1'+r_2')$, $\frac{1}{2}(r_2'+r_3')$, $\cdots$. Then the interpolation was repeated on the integral over f_1f_2, which was thus also obtained for $r=\frac{1}{2}r_1$, $\frac{1}{2}(r_1+r_2)$, $\frac{1}{2}(r_2+r_3)$, and subsequently Simpson's rule was used for this finer mesh to obtain I_L. (2) As concerns the method of interpolation, both quadratic and cubic interpolation were employed.

TABLE III. Values of $\Gamma(nl\rightarrow l';3d)$ (in units a_H^{-3}) for the angular modes of excitation of the copper atom in the state $3d^94s^2$ ($l'=l\pm 2$).

Excitation	Direct	Exchange	Total
$\Gamma(1s\rightarrow d;3d)$	0.1743	−0.0057	0.1686
$\Gamma(2s\rightarrow d;3d)$	0.2731	−0.0766	0.1965
$\Gamma(2p\rightarrow f;3d)$	0.4193	−0.0910	0.3283
$\Gamma(3s\rightarrow d;3d)$	0.1304	−0.0501	0.0803
$\Gamma(3p\rightarrow f;3d)$	0.2039	−0.0739	0.1300
$\Gamma(3d\rightarrow s;3d)$	−0.0953	+0.0476	−0.0477
$\Gamma(3d\rightarrow g;3d)$	0.2181	−0.0576	0.1605
Sum	1.3238	−0.3073	1.0165
$R_{\mathrm{ang}}(3d)$	0.1760	−0.0409	0.1351

In practice, an integral (for a given type of interpolation) required about 4 sec of CDC-6600 computer time. For each type of integral I_L (i.e., given functions f_i and value of L), two integrations were carried out: (1) $I_{L,1}$ obtained with the same number of points as the original wave function set of r values, and using quadratic interpolation; (2) $I_{L,2}$ calculated with twice the number of mesh points and using cubic interpolation. The two results $I_{L,1}$ and $I_{L,2}$ for each integral I_L differ generally by less than 1% (and usually by a few parts in 10^3), which confirms the accuracy of the integration program.

In Table III (pertaining to the angular modes only), we have listed the resulting values of $\Gamma_E(nl\rightarrow l';3d)$ defined as follows:

$$\Gamma_E(nl\rightarrow l';3d)\equiv\sum_{L_i}\Gamma_E(nl\rightarrow l';3d;L_i), \quad (34)$$

where the sum goes over the L_i values listed in Table II.

TABLE IV. Values of $\Gamma(nl\rightarrow l';\,4p)$ (in units a_H^{-3}) for the angular modes of excitation of the copper atom in the state $3d^{10}4p$ ($l'=l\pm 2$).

Excitation	Direct	Exchange	Total
$\Gamma(1s\rightarrow d;\,4p)$	0.01493	−0.01019	0.00474
$\Gamma(2s\rightarrow d;\,4p)$	0.00575	−0.00046	0.00529
$\Gamma(2p\rightarrow f;\,4p)$	0.01034	−0.00210	0.00824
$\Gamma(3s\rightarrow d;\,4p)$	0.00599	−0.00080	0.00519
$\Gamma(3p\rightarrow f;\,4p)$	0.00942	−0.00114	0.00828
$\Gamma(3d\rightarrow s;\,4p)$	0.00836	−0.00708	0.00128
$\Gamma(3d\rightarrow g;\,4p)$	0.01208	−0.00112	0.01096
Sum	0.06687	−0.02289	0.04398
$R_{\text{ang}}(4p)$	0.0524	−0.0179	0.0345

As an example, we have

$$\Gamma_E(np\rightarrow f;\,3d)=\Gamma_E(np\rightarrow f;\,3d;\,1)+\Gamma_E(np\rightarrow f;\,3p;\,3)\,, \quad (35)$$

where the coefficients C of the two terms on the right-hand side have the values 12/25 and 144/175, respectively.

The last column of Table III gives the corresponding values of the total $\Gamma(nl\rightarrow l';\,3d)$ defined by

$$\Gamma(nl\rightarrow l';\,3d)\equiv\Gamma_D(nl\rightarrow l';\,3d)+\Gamma_E(nl\rightarrow l';\,3d)\,. \quad (36)$$

The bottom row of the table lists the direct and exchange terms of $R_{\text{ang}}(3d)$. These results were obtained by dividing the entries of the preceding row (marked "Sum") by $\langle r^{-3}\rangle_{3d}=7.52a_H^{-3}$. This value of $\langle r^{-3}\rangle_{3d}$ was calculated from the Hartree-Fock $3d$ wave function.[18]

Table III shows that except for $3d\rightarrow s$, all of the direct terms are shielding, whereas the exchange terms provide an antishielding, which, however, is quite weak (less than $\frac{1}{4}$ of the dominant shielding term). For $3d\rightarrow s$, the signs of the two effects are reversed. The reason for the negative value of $\Gamma_D(3d\rightarrow s;\,3d)$ has been discussed above in connection with the negative sign of $v_1'(3d\rightarrow s)$ near the nucleus (see Fig. 2).

The value of the total direct term $R_{\text{ang}}(3d;\text{ direct})=+0.176$ can be compared with the value

$$R_{\text{ang}}=2.02/7.52=0.269$$

which was previously deduced[21] by using the Thomas-Fermi expression[20] for $Q_{i,\text{ang}}$ [Eq. (22)]. The factor by which the two results differ is 0.269/0.176=1.53, and this confirms our previous discussion,[1,2] according to which the statistical model overestimates R_{ang} by a factor of ~1.5 (see Fig. 3).

For the $4p$ electron in the excited $3d^{10}4p$ state, we used a modification of the Hartree-Fock wave function obtained by Synek.[22] The modification consisted in using a slightly more internal wave function which would reproduce the experimental value of $\langle r^{-3}\rangle_{4p}=1.276a_H^{-3}$, as deduced by Elbel[23] from the measured fine structure. The determination of $w(4p)$ is discussed in Ref. 19, which also includes a table of values of $w(4p)$.

Table IV (which is completely similar to Table III) pertains to the interaction of the angular modes $nl\rightarrow l\pm 2$ with a valence electron in the $4p$ state. In analogy to Eq. (34), the total exchange term $\Gamma_E(nl\rightarrow l';\,4p)$ is given by

$$\Gamma_E(nl\rightarrow l';\,4p)=\sum_{L_i}\Gamma_E(nl\rightarrow l';\,4p;\,L_i)\,. \quad (37)$$

The contributions to $R_{\text{ang}}(4p)$ given in the bottom row of the table were obtained by dividing the sum of the Γ terms (Γ_D, Γ_E, or Γ) by $\langle r^{-3}\rangle_{4p}=1.276a_H^{-3}$.

It is seen that all of the terms Γ_D are positive (shielding), whereas the exchange terms Γ_E are antishielding. The net contribution of the angular terms, $R_{\text{ang}}(4p)$ is still shielding ($=0.0345$), although it is much smaller than the corresponding $R_{\text{ang}}(3d)$ ($=0.1351$).

In Table V, we have listed the results for the terms due to the radial modes, for both $3d$ and $4p$. For the $3d$ case, the sum of the direct terms Γ_D is $-0.108a_H^{-3}$, in good agreement with our previous result[21] ($-0.12a_H^{-3}$), as was expected. The total direct term R_{rad} ($3d$; direct) is very small, as a result of the near-cancellation of the contributions from $2p\rightarrow p$, $3p\rightarrow p$, and $3d\rightarrow d$. This result was previously noted in Ref. 21 (see p. 161). The sum of the exchange terms $\Gamma_E(nl\rightarrow l;\,3d)$ provides a small shielding, which is numerically larger than the direct term, resulting in a net shielding $R_{\text{rad}}(3d)=0.0426$.

Thus the total R factor for the $3d^94s^2$ state becomes

$$R(3d)=R_{\text{ang}}(3d)+R_{\text{rad}}(3d)=0.1351+0.0426=0.1777\,, \quad (38)$$

which amounts to an appreciable net shielding.

Referring now to the second part of Table V, which pertains to $4p$, we find that the direct terms result in an appreciable antishielding, mainly on account of the external character of the $4p$ wave function. The exchange terms reduce this effect somewhat, but the resultant total $R_{\text{rad}}(4p)=-0.2097$ is still definitely antishielding. The antishielding which has been obtained from the direct radial terms for $4p$ is similar both in origin and in magnitude to the antishielding which has been previously calculated for the np excited states of the alkali atoms.[1]

Finally, from Tables IV and V, we obtain for the total R factor of $3d^{10}4p$:

$$R(4p)=R_{\text{ang}}(4p)+R_{\text{rad}}(4p)=0.0345-0.2097=-0.1752\,. \quad (39)$$

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[21] R. M. Sternheimer, Phys. Rev. **105**, 158 (1957). See Table I on p. 159.

[22] M. Synek, Phys. Rev. **131**, 1572 (1963).

[23] M. Elbel, quoted by W. Fischer, H. Hühnermann. and K. J. Kollath, Z. Physik **200**, 158 (1967).

As was discussed in the Introduction, the ratio of the two uncorrected values of Q is

$$\frac{Q(3d^{10}4p)}{Q(3d^94s^2)}=\frac{-0.228\pm0.005}{-0.161\pm0.003}=1.416\pm0.04. \tag{40}$$

The theoretical value of this ratio is

$$\frac{1-R(4p)}{1-R(3d)}=\frac{1.175}{0.822}=1.429, \tag{41}$$

in very good agreement with the experimental result [Eq. (40)].

Another way of showing the agreement is to calculate the corrected values of Q from the hfs of both states. We thus obtain from $3d^94s^2$:

$$Q=-\frac{0.161\pm0.003}{0.822}=-0.196\pm0.004\text{ b}, \tag{42}$$

and from $3d^{10}4p$,

$$Q=-\frac{0.228\pm0.005}{1.175}=-0.194\pm0.004\text{ b}, \tag{43}$$

The good agreement which has been obtained gives support to the assumption that the difference between the two uncorrected values of $Q(\mathrm{Cu}^{65})$ is indeed due to the shielding and antishielding effects produced by the Cu^+ core. We thus obtain: $Q(\mathrm{Cu}^{65})=-0.195\pm0.004$ b and $Q(\mathrm{Cu}^{63})=-0.211\pm0.004$ b.

It may be noted that the influence of the exchange terms on the final result, Eq. (41), is quite small. Thus, from Tables III–V, one finds for the values of R without exchange (i.e., including only the direct terms): $R_D(3d)=0.1616$, $R_D(4p)=-0.2266$, which give

$$\frac{1-R_D(4p)}{1-R_D(3d)}=\frac{1.227}{0.838}=1.464. \tag{44}$$

This value is quite close to our previous result (1.429), from which it can be concluded that the effect of the exchange terms is rather unimportant in the present case.

B. Pr 5*d* and Tm 5*d*

For praseodymium and thulium, we have previously obtained[2] the shielding factor R for the $4f$ electrons in the ground state. The results of this calculation are given in Table VII of Ref. 2. They indicate a small shielding $R\sim0.13$, in reasonable agreement with various experimental determinations using the Mössbauer effect.[4]

As discussed above, Murakawa[5] has shown that for the $5d$ states of La^{139} and Lu^{175}, the spectroscopic hfs data require the presence of a rather strong antishielding, namely $R_{5d}\cong-0.4$. Since lanthanum ($Z=57$) and lutetium ($Z=71$) are at the two ends of the rare-earth region, it seemed of interest to calculate R_{5d} for the neighboring elements: Pr ($Z=59$) and Tm ($Z=69$), in order to see whether agreement with a value of the order of -0.4 could be obtained.

Table V. Values of $\Gamma(nl\rightarrow l;\,3d)$ and $\Gamma(nl\rightarrow l;\,4p)$ (in units a_H^{-3}) for the radial modes of excitation of the copper atom ($l'=l$).

Excitation	Direct	Exchange	Total
$\Gamma(2p\rightarrow p;\,3d)$	-1.973	$+1.532$	-0.441
$\Gamma(3p\rightarrow p;\,3d)$	$+1.177$	-1.114	$+0.063$
$\Gamma(3d\rightarrow d;\,3d)$	$+0.688$	$+0.011$	$+0.699$
Sum	-0.108	$+0.429$	$+0.321$
$R_{\mathrm{rad}}(3d)$	-0.0144	$+0.0570$	$+0.0426$
$\Gamma(2p\rightarrow p;\,4p)$	-0.0297	-0.0002	-0.0299
$\Gamma(3p\rightarrow p;\,4p)$	-0.1871	$+0.0004$	-0.1867
$\Gamma(3d\rightarrow d;\,4p)$	-0.1392	$+0.0882$	-0.0510
Sum	-0.3560	$+0.0884$	-0.2676
$R_{\mathrm{rad}}(4p)$	-0.2790	$+0.0693$	-0.2097

The determination of R_{5d} for Pr and Tm did not entail an excessive amount of calculation, because the perturbed wave functions for the radial modes $v_1'(nl\rightarrow l)$ had been previously obtained,[2,9] in connection with the calculation of γ_∞ and of R_{4f}. In the same manner as in Ref. 2, we used the Thomas-Fermi density divided by 1.5 for $Q_{i,\mathrm{ang}}$ [see Eq. (22) and Fig. 3].

The radial wave functions for the $5d$ state were obtained by means of the tables of Herman and Skillman,[24] whose calculations are based on the Hartree-Fock-Slater method.[25] The actual determination of the $5d$ functions is discussed in Ref. 19, which also gives a table of their numerical values. The resulting values of $\langle r^{-3}\rangle_{5d}$ are $3.354a_H^{-3}$ for Pr and $4.403a_H^{-3}$ for Tm. A comparison of these results with the corresponding values of $\langle r^{-3}\rangle_{4f}$ ($=5.369a_H^{-3}$ for Pr and $12.86a_H^{-3}$ for Tm) shows that the $5d$ wave function is considerably more external than the $4f$ function, as was expected. This difference is responsible for the fact that for $5d$, the radial term Γ_{rad} [see Eq. (33)] predominates, giving a net antishielding, in contrast to $4f$, where $\Gamma_{\mathrm{ang}}>|\Gamma_{\mathrm{rad}}|$, which results in an over-all shielding effect.

The calculations were carried out by means of Eqs. (26)–(33), in which $Q_{i,\mathrm{ang}}=(1/1.5)Q_i(\text{Th-F})$ [Eq. (22)] and $Q_{i,\mathrm{rad}}$ was evaluated using the perturbed wave functions $v_1'(nl\rightarrow l)$.

The results are presented in Table VI. As mentioned above, Γ_{rad} predominates over Γ_{ang}, and gives an antishielding factor $R_{\mathrm{rad}}\sim-0.4$ in both cases, which is in good agreement with the experimental determination of Murakawa.[5] It should be pointed out, however, that the calculated values of both R_{5d} and R_{4f} (Ref. 2) do not include the effect of the exchange terms. Therefore, the agreement with experiment is meaningful only if

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[24] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall Inc., Englewood Cliffs, New Jersey, 1963).

[25] J. C. Slater, Phys. Rev. **81**, 385 (1951).

TABLE VI. Values of quantities involved in the calculation of the atomic antishielding factor R_{5d} for the Pr $5d$ and Tm $5d$ excited states. The values of Γ and $\langle r^{-3}\rangle$ are in units a_H^{-3}.

State	Pr $5d$	Tm $5d$
Γ_{ang}	$+0.354$	$+0.428$
Γ_{rad}	-1.643	-2.377
Γ_{total}	-1.289	-1.949
$\langle r^{-3}\rangle_{5d}$	3.354	4.403
R_{ang}	$+0.106$	$+0.097$
R_{rad}	-0.490	-0.540
R_{5d}(total)	-0.384	-0.443
$1/(1-R_{5d})$	0.723	0.693

the exchange terms are relatively small compared to the direct Coulomb terms, as is the case for Cu $3d$ and $4p$.

C. Li $2p$ and $3p$

In connection with atomic beam measurements on the excited $2p$ and $3p$ states of the lithium atom,[11] we have obtained the values of R for these states. In carrying out the calculations, it is essential to use wave functions which approximate as closely as possible to the experimental values of the energy (ionization potential) and of $\langle r^{-3}\rangle_{np}$ $(n=2$ or $3)$. For this reason, we have calculated the valence wave functions $w(2p)$ and $w(3p)$ by integrating the Schrödinger equation in the effective potential obtained by Seitz.[26] This potential was determined from the condition that it should reproduce the experimental spectroscopic eigenvalues of the lithium atom. The resulting functions $w(2p)$ and $w(3p)$ are tabulated in Ref. 19. The calculated values of $\langle r^{-3}\rangle_{np}$ are very close to the values deduced by Marcus and Novick[11] from the experimental fine structure and magnetic hyperfine structure. Thus for $2p$, $\langle r^{-3}\rangle_{\text{calc}}=0.06494a_H^{-3}$, as compared to $\langle r^{-3}\rangle_{\text{exp}}=0.06451a_H^{-3}$. Similarly for $3p$, the calculated and experimental values are $0.01983a_H^{-3}$ and $0.01909a_H^{-3}$, respectively.

For the $1s$ electrons, we used the same wave function as was employed by James,[27] namely

$$u_0'(1s)=2Z_0^{3/2}r\exp(-Z_0r)\,, \tag{45}$$

with $Z_0=2.69$. For such a hydrogenic wave function, $v_1'(1s\rightarrow d)$ is given by

$$v_1'(1s\rightarrow d)=\frac{Z_0^{3/2}}{3}[1+(Z_0/3)r]\exp(-Z_0r)\,. \tag{46}$$

The direct interaction term of R can be obtained from Eqs. (2), (3), (8), and (10), with $c(ns\rightarrow d)=8/5$. We thus find

$$R_D(np)=\frac{8}{5}\frac{K_a(1s\rightarrow d)}{\langle r^{-3}\rangle_{np}}\,, \tag{47}$$

$$K_a(1s\rightarrow d)\equiv\int_0^\infty w^2(np)g_a dr\,, \tag{48}$$

$$g_a(r)\equiv\frac{1}{r^3}\int_0^r u_0'(1s)v_1'(1s\rightarrow d)r'^2dr' +r^2\int_r^\infty u_0'(1s)v_1'(1s\rightarrow d)r'^{-3}dr'\,. \tag{49}$$

In a similar manner, the exchange term $R_E(np)$ is obtained from Eqs. (12)–(16), with $L=1$ and $C=\frac{4}{3}$.

$$R_E(np)=-(4/3)\frac{K_b(1s\rightarrow d)}{\langle r^{-3}\rangle_{np}}\,, \tag{50}$$

with

$$K_b(1s\rightarrow d)\equiv\int_0^\infty u_0'(1s)w(np)g_b dr\,, \tag{51}$$

$$g_b(r)\equiv\frac{1}{r^2}\int_0^r v_1'(1s\rightarrow d)w(np)r'dr' +r\int_r^\infty v_1'(1s\rightarrow d)w(np)r'^{-2}dr'\,. \tag{52}$$

The resulting values of R_D, R_E, and the total R $(=R_D+R_E)$ are presented in Table VII. This table also includes the values of the correction factor $1/(1-R)$, as well as $\langle r^{-3}\rangle_{np}$ (calc) and $\langle r^{-3}\rangle_{np}$ (exp). It is seen that both for Li $2p$ and $3p$, the shielding due to the direct term R_D predominates over the smaller (negative) exchange term R_E, thus leading to a net shielding effect. The correction factors $\mathfrak{C}=1/(1-R)$ are practically the same for the two excited p states, and the values of Q(Li) should be increased by about 10% to take into account the shielding effect.

If we denote the two terms on the right-hand side of Eq. (49) by $g_{a,\text{int}}$ and $g_{a,\text{ext}}$, respectively, we can write

$$K_a(1s\rightarrow d)=K_{a,\text{int}}+K_{a,\text{ext}}\,, \tag{53}$$

where

$$K_{a,\text{int}}\equiv\int_0^\infty w^2(np)g_{a,\text{int}}dr\,, \tag{54}$$

$$K_{a,\text{ext}}\equiv\int_0^\infty w^2(np)g_{a,\text{ext}}dr\,. \tag{55}$$

Each of the two terms $K_{a,\text{int}}$ and $K_{a,\text{ext}}$ makes a contribution to $R_D(np)$ [see Eq. (47)].

For $2p$, these two terms of R_D are 0.1682 and 0.0137, respectively, which shows that the integral, i.e., $g_{a,\text{int}}$ for which the $1s\rightarrow d$ density $u_0'v_1'$ lies inside the $2p$ electron makes the predominant contribution to R_D. This was, of course, to be expected since the $1s$ wave function is localized close to the nucleus (maximum of

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[26] F. Seitz, Phys. Rev. **47**, 400 (1935); W. Kohn and N. Rostoker, *ibid.* **94**, 1111 (1954).

[27] H. James, J. Chem. Phys. **2**, 794 (1934).

u_0' at $r=1/Z_0=0.37a_H$), whereas the $2p$ function is quite external (maximum at $r=3.8a_H$).

D. Be $2s2p\ ^3P$

In connection with atomic beam measurements on the excited ^3P state of beryllium (with configuration $1s^22s2p$) by Blachman and Lurio,[12] we have obtained the value of R for the $2s2p$ configuration, using the Hartree-Fock wave functions obtained by Hartree.[28] In the same manner as for Li and Cu, we have included both the direct and the exchange terms.

The equations used to obtain $R_D(2p)$ and $R_E(2p)$ are completely similar to those used for lithium [Eqs. (47)–(52)], with one exception, namely that for $2s\to d$, the coefficient of $K_a(2s\to d)/\langle r^{-3}\rangle_{2p}$ [see Eq. (47)] is 4/5 instead of 8/5, since there is only a single $2s$ electron for the state considered.

The perturbed wave functions $v_1'(1s\to d)$ and $v_1'(2s\to d)$ were obtained from the following equation, which is a special case of Eq. (5):

$$\left[-\frac{d^2}{dr^2}+\frac{6}{r^2}+V_0-E_0\right]v_1'(ns\to d)=\frac{u_0'(ns)}{r^3}, \qquad (56)$$

in which V_0-E_0 is obtained from $u_0'(ns)$ by means of Eq. (7) (with $l=0$). Equation (56) was integrated numerically on the CDC-6600 computer, using the machine program described above (in Sec. IIA). Tables of the wave functions $v_1'(ns\to d)$ are given in Ref. 19.

The results of the calculations of R_D, R_E, and R (total) are presented in Table VIII. The second and third columns list separately the contributions of $1s\to d$ and $2s\to d$, respectively; the last column gives the resulting total values for R_D, R_E, and R. The final value of R is $+0.040$, and hence the correction factor $\mathcal{C}=1/(1-R)=1.042$.

It is seen from Table VIII that for Be, the total exchange term (-0.1214) almost cancels the direct term (0.1613), which leads to a very small amount of net shielding. The reason is that there is a great deal of overlap between the $2s$ and $2p$ wave functions, and as a result the exchange term pertaining to $v_1'(2s\to d)$ is relatively large, and actually exceeds the direct (shielding) term by a factor of ~ 2 (see Table VIII). However, for $1s\to d$, the situation is reversed [$R_D>|R_E|$], and upon taking the sum of the two contributions ($1s$ and $2s$), one finds the small net shielding factor $R=+0.040$. It should be noted that the exchange terms of R are theoretically somewhat uncertain,[1] and therefore one can conclude only that for Be $2s2p$, the value of R is small, of the order of 0.05, and probably shielding. It is possible that a more reliable calculation of R for beryllium could be carried out by using the unrestricted Hartree-Fock method.[29]

TABLE VII. Values of terms of the shielding factor R for the $2p$ and $3p$ excited states of lithium. The values of $\langle r^{-3}\rangle_{np}$ are in units a_H^{-3}.

State	Li $2p$	Li $3p$
R_D	0.1819	0.1734
R_E	-0.0663	-0.0744
R (total)	0.1156	0.0990
$1/(1-R)$	1.131	1.110
$\langle r^{-3}\rangle_{np}$(calc)	0.06494	0.01983
$\langle r^{-3}\rangle_{np}$(exp)	0.06451	0.01909

TABLE VIII. Values of terms of the shielding factor R for the $1s^22s2p\ ^3P$ state of beryllium. The value of $\gamma_\infty(1s^22s^2)$ pertains to the atom in the ground state.

Excitation	$1s\to d$	$2s\to d$	Total
R_D	0.1296	0.0317	0.1613
R_E	-0.0579	-0.0635	-0.1214
R (total)	0.0717	-0.0318	0.0399
$1/(1-R)$	$\cdots$	$\cdots$	1.042
$\gamma_\infty(1s^22s^2)$	0.1883	0.8062	0.9945

In the same manner as in Eqs. (53)–(55), we can write $R_D(ns\to d)$ as a sum of two parts: $R_{D,\mathrm{int}}$ and $R_{D,\mathrm{ext}}$, which arise from the integrals $K_{a,\mathrm{int}}$ and $K_{a,\mathrm{ext}}$, respectively. As expected, for $1s\to d$, the internal contribution predominates ($R_{D,\mathrm{int}}=0.1169$, $R_{D,\mathrm{ext}}=0.0127$), whereas for $2s\to d$, the two contributions are of the same order of magnitude ($R_{D,\mathrm{int}}=0.0171$, $R_{D,\mathrm{ext}}=0.0146$), because of the large amount of overlap of $u_0'(2s)$ and $u_0'(2p)$.

III. SUMMARY

In the present paper, we have given the results of calculations of the quadrupole shielding (or antishielding) factor R for several excited atomic states. The calculations of R for Cu $3d^94s^2$ and $3d^{10}4p$ and their agreement with the experimental data[7,8] provide a very good confirmation of the existence and method of calculation of the atomic shielding and antishielding effects. The test of the theoretical values of R is especially accurate for Cu, since the experimental uncorrected values of Q are known with an uncertainty of only 2%, whereas the size of the total induced effect is larger than 40%.

A further point of agreement concerns the fact that the values of R_{5d} for Pr and Tm were found to be antishielding ($R_{5d}\sim -0.4$) and of the same order of magnitude as the values required by the experimental determinations of Murakawa[5] for the neighboring ele-

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ments, lanthanum and lutetium. This result for R_{5d} is in contrast to the shielding effect for the $4f$ ground state ($R_{4f}\sim+0.2$) which was previously obtained in Ref. 2, and which is also in agreement with the experimental determinations[4] for the $4f$ electrons.

Finally, the results for Li $2p$ and $3p$, and for Be $2p$ indicate a small shielding effect ($R\sim0.1$), and place an upper limit on the correction factors $\mathcal{C}=1/(1-R)$ to be applied to the values of Q derived from the hyperfine structure of these states.

ACKNOWLEDGMENTS

I wish to thank Dr. R. F. Peierls for programming the inward integration of Eq. (5) and the double integral of Eq. (25) for the CDC-6600 computer. Without these programs, the present calculations for Be and Cu would not have been possible in the limited time available. I am also indebted to Dr. H. Bucka, Dr. A. Lurio, Dr. S. Marcus, and Dr. R. Novick for helpful discussions, and to Dr. H. Hühnermann for correspondence.

PHYSICAL REVIEW VOLUME 164, NUMBER 1 5 DECEMBER 1967

Optical Emission Produced by Proton and Hydrogen-Atom Impact on Nitrogen*

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(Received 30 June 1967)

Optical emissions produced in collisions of protons and hydrogen atoms incident on nitrogen molecules were studied in the spectral region from 1200 to 6000 Å. Relative emission cross sections were measured in the energy range from 10 to 130 keV. The prominent features of the nitrogen spectrum below 2000 Å were the Lyman-α line and atomic nitrogen lines. The Lyman-Birge-Hopfield system appeared also, but it was weak. At the longer wavelengths, the N_2^+ first negative and the N_2 second positive systems dominated the spectrum. Relative emission cross sections for the production of the first negative bands in collisions of hydrogen atoms with nitrogen molecules were nearly constant as a function of energy, and at an energy of 40 keV the cross section was one-half as large as the cross section for proton collisions. The cross section for the second positive band due to hydrogen-atom impact was about 3×10^{-18} cm^2 at 25 keV, whereas for proton impact the cross section was about 2×10^{-19} cm^2 at its maximum value. The cross sections for the atomic nitrogen lines produced in hydrogen-atom impact were approximately 75% of the cross sections for the same lines produced in proton impact. Hydrogen-atom collisions had higher cross sections throughout the energy range for the production of Lyman-α emission.

INTRODUCTION

ONE method for studying collisions between two systems is to measure the photon energy which is emitted in optical transitions resulting from the collision. For particular cases, a measurement of the photon emission provides a direct means of obtaining cross sections for exciting atomic and molecular states. A comparison of these experimentally obtained excitation cross sections with theoretical predictions can assist in understanding collision mechanisms.

Atmospheric research indicates that fast protons are entering the atmosphere and contribute to the production of auroras.[1] Because of the charge-exchange process whereby protons pick up electrons from atmospheric gases, there would also be fast hydrogen atoms present. It is evident from the work of Allison and others[2] that the equilibrium fraction of hydrogen atoms produced in charge exchange is significant for projectile energies of a few keV to 100 keV. It is of interest, therefore, to determine the effectiveness of the hydrogen atoms in exciting the atmospheric gases and also their contribution to the auroras. The knowledge of hydrogen-atom excitation cross sections is also important in studying the history of a proton entering the atmosphere.

For these reasons optical emissions produced in collisions of protons and hydrogen atoms with nitrogen molecules have been studied. Spectral scans of the light emitted in the collisions of protons with nitrogen gas in the spectral region from 1200 to 6000 Å indicated which transitions of the molecules, of the atoms and ions originating from molecular dissociation, and of the incident particle produced sufficient light intensities for emission cross-section measurements. The results of the scans led to relative emission cross-section measurements for the production of the N_2^+ first negative band system ($B^2\Sigma_u^+$-$X^2\Sigma_g^+$), the N_2 second positive band system ($C^3\Pi_u$-$B^3\Pi_g$), atomic and ionic nitrogen lines, and the Lyman α line. The emission cross sections

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* Supported in part by the National Aeronautics and Space Administration under the Sustaining University Program, Grant No. NsG-430.

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