used as the measure of relative cross section. The collision chamber pressure was maintained below 10^{-4} Torr to insure that multiple collisions were not occurring and to insure that the primary proton beam was not significantly attenuated. The primary proton-beam current was monitored by a Faraday cup beyond the collision chamber. Variations in this current during the beam scans were automatically compensated for by a newly developed servo system, which drove the proportional counter scanning mechanism at a speed proportional to the beam current arriving in the Faraday cup. The addition of this servo system was the only change made in the apparatus described in Ref. 5.

Careful tests were performed to ascertain that the negative ions emergent from the collision chamber were not produced by single-electron capture on a small fraction of H atoms present in the beam entering the collision chamber.

The negative ions were found to emerge from the collision chamber in a beam less than $\frac{1}{2}°$ wide, indicating that the collision chamber exit solid angle and the length of the detector slit were both adequate to transmit all of the fast H^- ions produced. The negative ions were deflected by the electrostatic deflection plates through an angle equal and opposite to the angle of positive ion deflection, and the pulse-height distribution produced by the negative ions was exactly the same as that produced by the primary protons.

The experimental results are shown in Fig. 1. The collision-chamber calibration factor was chosen so as to normalize the $\sigma_{1,0}$ curve to the value 8.2×10^{-16} cm^2 at 10 keV. With the same factor applied to all cross section values, the $\sigma_{1,0}$ curve was found to fit within a few percent the mean of several sets of absolute data taken from a recent review article.[6] The $\sigma_{1,-1}$ curve agrees well with the latest Fogel results[4] near the maximum, but departs seriously from these results on either side of the maximum. The discrepancy is far outside an estimated $\pm10\%$ uncertainty of the present data.

[6] S. K. Allison and M. Garcia Munoz, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962), p. 751.

PHYSICAL REVIEW VOLUME 132, NUMBER 4 15 NOVEMBER 1963

Quadrupole Antishielding Factors of Ions*

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(Received 2 July 1963)

Values of the quadrupole antishielding factor γ_∞ have been calculated for the F^-, Br^-, Rb^+, Pr^{3+}, and Tm^{3+} ions, using the method of direct solution of the inhomogeneous Schroedinger equation for the perturbed wave functions.

A SUMMARY of calculated values of the quadrupole antishielding factor[1-3] γ_∞ has been given in a recent paper.[4] The purpose of the present note is to give the results of additional calculations of γ_∞ for the following ions: F^-, Br^-, Rb^+, Pr^{3+}, and Tm^{3+}. The method of calculation is the same as in our earlier work.[3,4] For F^-, Br^-, and Rb^+, Hartree-Fock wave functions were used. For the two rare-earth ions, Pr^{3+} and Tm^{3+}, only Hartree functions are available for the calculations.

The method of calculation will be briefly outlined. The contribution $\gamma_\infty(nl\rightarrow l)$ to γ_∞ due to a given radial mode of excitation $(nl\rightarrow l)$ is given by

$$\gamma_\infty(nl\rightarrow l)=C_{ll}^{(2)}\int_0^\infty u_0'u_1'r^2dr, \tag{1}$$

where u_0' is r times the unperturbed radial wave function, normalized to 1; u_1' is r times the perturbation of the wave function, and is determined by the equation

$$\left[-\frac{d^2}{dr^2}+\frac{l(l+1)}{r^2}+V_0-E_0\right]u_1'=u_0'\left(\frac{1}{r^3}-\left\langle\frac{1}{r^3}\right\rangle_{nl}\right), \tag{2}$$

together with the orthogonality condition

$$\int_0^\infty u_0'u_1'dr=0. \tag{3}$$

In Eq. (1), the coefficient $C_{ll}^{(2)}$ represents the effect of the integration over the angular variables and the summation over the magnetic substates. We have $C_{11}^{(2)}=48/25$ for $np\rightarrow p$, and $C_{22}^{(2)}=16/7$ for $nd\rightarrow d$, for completed p and d shells, respectively. In Eq. (2), $\langle1/r^3\rangle_{nl}$ is the average value of $1/r^3$ for the wave function u_0'. In solving Eq. (2), the expression V_0-E_0 on the left hand side is directly obtained from the unperturbed function u_0', as follows

$$V_0-E_0=\frac{1}{u_0'}\frac{d^2u_0'}{dr^2}-\frac{l(l+1)}{r^2}. \tag{4}$$

* Work performed under the auspices of the U. S. Atomic Energy Commission.
[1] R. M. Sternheimer, Phys. Rev. **84**, 244 (1951).
[2] H. M. Foley, R. M. Sternheimer, and D. Tycko, Phys. Rev. **93**, 734 (1954).
[3] R. M. Sternheimer and H. M. Foley, Phys. Rev. **102**, 731 (1956).
[4] R. M. Sternheimer, Phys. Rev. **130**, 1423 (1963).

For each case, two types of integration were carried out for Eq. (2): (1) Several inward integrations starting from a large radius r_1 were performed by means of an IBM 7090 computer. These solutions differ only by a multiple of the unperturbed function u_0', as can be seen from Eq. (2). The use of several functions u_1' with different starting values $u_1'(r_1)$ serves as a check on the calculations. (2) An outward numerical integration starting at $r=0$ with a power series (up to $r\sim 0.02a_H$) was also carried out. The two solutions are joined at an intermediate radius r_2, of order 0.1–$0.2a_H$. We note that the value of r_1 at which the inward integrations are started depends, of course, on the specific case considered; thus, r_1 must be well outside the location of the outermost (principal) maximum of the unperturbed wave function. In the present work, the values of r_1 range from $2.0a_H$ for Rb^+ $3p\rightarrow p$ to $9a_H$ for F^- $2p\rightarrow p$ and Br^- $4p\rightarrow p$.

For F^-, the $2p$ Hartree-Fock wave function obtained by Froese[5] was used. For Br^- and Rb^+, the Hartree-Fock $3p$, $3d$, and $4p$ functions obtained by Watson and Freeman[6] were employed. For Pr^{3+} and Tm^{3+}, we used the Hartree wave functions calculated by Ridley.[7]

The results of the calculations of $\gamma_\infty(nl\rightarrow l)$ and the total γ_∞ are shown in Table I. It should be noted that

TABLE I. Values of γ_∞ for several ions.

Ion	F^-	Br^-	Rb^+	Pr^{3+}	Tm^{3+}
$\gamma_\infty(2p\rightarrow p)$	−23.30	−0.49	−0.45		
$\gamma_\infty(3p\rightarrow p)$		−4.51	−3.93		
$\gamma_\infty(3d\rightarrow d)$		−1.63	−1.23		
$\gamma_\infty(4p\rightarrow p)$		−118.7	−43.8	−8.81	−6.79
$\gamma_\infty(5p\rightarrow p)$				−69.7	−67.2
γ_∞(ang)	+0.77	+2.3	+2.2		
γ_∞	−22.53	−123.0	−47.2	$\sim$−78.5	$\sim$−74.0

numerical calculations of $\gamma_\infty(nl\rightarrow l)$ were carried out for the following cases[8]: $2p\rightarrow p$ for F^-; $3p\rightarrow p$, $3d\rightarrow d$, and $4p\rightarrow p$ for Br^- and Rb^+; $4p\rightarrow p$ and $5p\rightarrow p$ for Pr^{3+} and Tm^{3+}. For Rb^+ and Br^-, the value of $\gamma_\infty(2p\rightarrow p)$ is expected to be insensitive to the small differences between the Hartree and the Hartree-Fock wave function for the $2p$ shell. In addition, the $\gamma_\infty(2p\rightarrow p)$ term makes only a very small contribution to the total γ_∞. Accordingly, $\gamma_\infty(2p\rightarrow p)$ for Rb^+ was obtained from our previous calculation using Hartree wave functions (see Table I of Ref. 3). The value of $\gamma_\infty(2p\rightarrow p)$ for Br^- was obtained in a similar fashion by interpolation of the previous results[3] for Cu^+ and Rb^+. The present results for Rb^+ $3p$, $3d$, and $4p$ enable us to calculate the factor by which the use of Hartree-Fock wave functions (including exchange) reduces the values of $|\gamma_\infty(nl\rightarrow l)|$, as compared to the values calculated by means of Hartree wave functions. These ratios ρ are as follows: $\rho(3p\rightarrow p)=3.93/4.4=0.893$; $\rho(3d\rightarrow d)=1.23/1.4=0.879$; $\rho(4p\rightarrow p)=43.8/66.6=0.658$. Here the γ_∞ values for Rb^+ in the denominators are those obtained in Ref. 3 using Hartree wave functions. As would be expected, the percentage reduction is largest for the outermost shell ($4p$), which is the most loosely bound and, therefore, the most sensitive to the contraction of the wave function as a result of exchange effects.

In Table I, the values of the term γ_∞(ang) for Br^- and Rb^+, due to the angular modes of excitation ($ns\rightarrow d$, $np\rightarrow f$) have been obtained from Ref. 3. They are based essentially on the Thomas-Fermi treatment of γ_∞(ang), as derived by Sternheimer.[9]

We note that the present value of $\gamma_\infty(2p\rightarrow p)$ for F^- practically coincides with that obtained by Burns[10] using the variational method of Das and Bersohn,[11] (−23.30 as compared to −23.22). The result that the variational method works very well in this case probably arises from the fact that the $2p$ radial wave function has no node, and therefore, the approximation made in this method that u_1' is given by u_0' times a polynomial in r does not introduce any artificial nodes into u_1', unlike the case when the unperturbed wave function u_0' has one or more nodes. The value of γ_∞(ang)$=+0.77$ for F^- which is given in Table I is based in part on the variational results of Burns (see footnote 27 of Ref. 10), and in part on a comparison of the variational[11] with the numerical results[12] for the terms of γ_∞(ang) for the isoelectronic Na^+ ion. Of course, γ_∞(ang) is very small compared to the total γ_∞ which is almost entirely due to $\gamma_\infty(2p\rightarrow p)$.

For the cases of Pr^{3+} and Tm^{3+}, we have calculated only the dominant terms $\gamma_\infty(4p\rightarrow p)$ and $\gamma_\infty(5p\rightarrow p)$. We note that a calculation of γ_∞ for these ions using the variational method has been recently carried out by Wikner and Burns.[13] The present results differ from those of Ref. 13 by amounts which are of the order of the uncertainties associated with the variational method. It should be pointed out that for a given unperturbed wave function u_0', the method of direct solution of the inhomogeneous Schrödinger equation [Eq. (2)] which has been used here gives results which are generally accurate to within 3%.

From the work of Wikner and Burns,[13] it is seen that

[5] C. Froese, Proc. Cambridge Phil. Soc. **53**, 206 (1957).
[6] R. E. Watson and A. J. Freeman, Phys. Rev. **124**, 1117 (1961).
[7] E. C. Ridley, Proc. Cambridge Phil. Soc. **56**, 41 (1960).
[8] Tables of the perturbed wave functions $u_1'(nl\rightarrow l)$ obtained in the present work are given in a supplementary paper "Wave Functions for Quadrupole Antishielding Factors." This supplementary paper has been deposited as Document No. 7675 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 $2.50 for photoprints or $1.75 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.
[9] R. M. Sternheimer, Phys. Rev. **80**, 102 (1950).
[10] G. Burns, Phys. Rev. **115**, 357 (1959); see footnote 27.
[11] T. P. Das and R. Bersohn, Phys. Rev. **102**, 733 (1956).
[12] R. M. Sternheimer, Phys. Rev. **115**, 1198 (1959); see p. 1205.
[13] E. G. Wikner and G. Burns, Phys. Letters **2**, 225 (1962).

the radial terms not calculated in the present paper [i.e., $\gamma_\infty(2p\rightarrow p)$, $\gamma_\infty(3p\rightarrow p)$, $\gamma_\infty(3d\rightarrow d)$, and $\gamma_\infty(4d\rightarrow d)$] are very small compared to $\gamma_\infty(5p\rightarrow p)$, and will approximately cancel the effect of γ_∞(ang), which is shielding. γ_∞(ang) is of the order of $+2$ to $+3$, as can be estimated from our result for the neighboring Cs^+ ion, namely $+2.9$ (see Table I of Ref. 3). Thus, even allowing for an appreciable percent error of the variational results, one can safely conclude that the sum of the terms which have not been calculated in Table I, will be less than ~ 2. The results for γ_∞ given in the last row of Table I represent just the sum of $\gamma_\infty(4p\rightarrow p)$ and $\gamma_\infty(5p\rightarrow p)$, and will, therefore, have an uncertainty of $\sim\pm 2$ on account of the terms which have been neglected. This error is probably somewhat smaller than that which arises from the use of Hartree wave functions, although it should be noted that for the trivalent rare-earth ions, the outermost $(5p)$ electrons are rather strongly bound, so that the contraction of the $5p$ wave function which would arise from including exchange is expected to be a relatively small effect. The resulting decrease of $|\gamma_\infty(5p\rightarrow p)|$ might therefore be expected to be of the order of only 15–20% (as compared to 34% for $Rb^+ 4p\rightarrow p$). This would give values of $\gamma_\infty(Pr^{3+})$ and $\gamma_\infty(Tm^{3+})$ of the order of -65 to -70. We note that very recently, Freeman and Watson[14] have made detailed calculations of γ_∞ for the Ce^{3+} ion, using the unrestricted Hartree-Fock method. This method automatically includes the effect of the distortion of the $5p$ shell (for example, by an external electric field) on the distortions of the inner shells. The authors have shown that such effects may be important for the determination of the total γ_∞ of the ion.

In connection with the results of Table I for $\gamma_\infty(F^-)$, $\gamma_\infty(Br^-)$, and $\gamma_\infty(Rb^+)$, one can calculate the ratios $\gamma_\infty(F^-)/\gamma_\infty(Na^+)$, $\gamma_\infty(Cl^-)/\gamma_\infty(K^+)$, and $\gamma_\infty(Br^-)/\gamma_\infty(Rb^+)$, in order to obtain the effect of the increased binding upon increasing Z by 2 for these three pairs of isoelectronic ions. Upon using the results of Table III of Ref. 4, one obtains:

$$\gamma_\infty(F^-)/\gamma_\infty(Na^+)=22.53/4.56=4.94\,, \tag{5}$$

$$\gamma_\infty(Cl^-)/\gamma_\infty(K^+)=56.6/17.32=3.27\,, \tag{6}$$

$$\gamma_\infty(Br^-)/\gamma_\infty(Rb^+)=123.0/47.2=2.61\,. \tag{7}$$

[14] A. J. Freeman and R. E. Watson, Phys. Rev. **132**, 706 (1963).

It is seen that the ratios decrease with increasing Z of the pair, with a particularly large decrease in going from $F^- - Na^+$ to $Cl^- - K^+$. A similar comparison has been previously made by Wikner and Das.[15] These authors have also calculated values of γ_∞ for Rb^+ and Br^-. However, their results cannot be directly compared to those given here, since they used Hartree wave functions and, moreover, the variational method was employed.

In Table II, we have listed the values of $\gamma_\infty(nl\rightarrow l)$, $\langle r^{-3}\rangle_{nl}$, and $J(nl\rightarrow l)$ for the various perturbations considered in the present work. The integral $J(nl\rightarrow l)$ is defined by:

$$J(nl\rightarrow l)\equiv\int_0^\infty u_0' u_1'(nl\rightarrow l)r^{-3}dr\,. \tag{8}$$

As discussed previously,[16] $J(nl\rightarrow l)$ enters into the calculation of the second-order quadrupole effect for the hyperfine structure (energy $\propto Q^2$). In general, the values of $J(nl\rightarrow l)$ are estimated to be accurate to 10%. However, for the cases of $Rb^+ 4p\rightarrow p$ and $Tm^{3+} 5p\rightarrow p$, the accuracy is only ~ 30 percent. For $Pr^{3+} 4p\rightarrow p$ and Tm^{3+} $4p\rightarrow p$, values of $J(4p\rightarrow p)$ have not been obtained.

TABLE II. Values of $\gamma_\infty(nl\rightarrow l)$, $\langle r^{-3}\rangle_{nl}$, and $J(nl\rightarrow l)$ for the F^-, Br^-, Rb^+, Pr^{3+}, and Tm^{3+} ions. $\langle r^{-3}\rangle_{nl}$ is in units a_H^{-3}. All values of $J(nl\rightarrow l)$ are positive.

Perturbation	$\gamma_\infty(nl\rightarrow l)$	$\langle r^{-3}\rangle_{nl}$	$J(nl\rightarrow l)$
$F^- 2p\rightarrow p$	-23.30	6.401	50.88
$Br^- 3p\rightarrow p$	-4.51	181.3	4545
$Br^- 3d\rightarrow d$	-1.63	23.08	66.50
$Br^- 4p\rightarrow p$	-118.7	10.24	281.5
$Rb^+ 3p\rightarrow p$	-3.93	228.1	6006
$Rb^+ 3d\rightarrow d$	-1.23	30.61	89.70
$Rb^+ 4p\rightarrow p$	-43.8	20.21	$\sim$520
$Pr^{3+} 4p\rightarrow p$	-8.81	285.6	...
$Pr^{3+} 5p\rightarrow p$	-69.7	40.10	1306
$Tm^{3+} 4p\rightarrow p$	-6.79	518.2	...
$Tm^{3+} 5p\rightarrow p$	-67.2	61.87	$\sim$5600

ACKNOWLEDGMENTS

I wish to thank Dr. M. Blume and Miss E. Wolfson for help in obtaining the wave functions of Ref. 6.

[15] E. G. Wikner and T. P. Das, Phys. Rev. **109**, 360 (1958).
[16] R. M. Sternheimer, Phys. Rev. **127**, 812 (1962).