

however, on account of the small ratio  $B_{mw}/B_{dc}$ . The effect described in the present paper arises not because of oscillations in time of the charge carrier concentrations, but because of their spatial dependence resulting from the penetration of quantized bundles of flux. Since the variations of  $B_{dc}$  inside hard superconductors are very large, an effect of a different order of magnitude is expected, as we have succeeded in showing in the present investigation, and as was observed by Cardona

*et al.*<sup>9</sup> The two effects may, of course, occur simultaneously, but with the very hard material used in the above mentioned experiments, the one effect is completely hidden by the other.

#### ACKNOWLEDGMENTS

I would like to thank Dr. B. Rosenblum (RCA, Princeton) for extremely interesting and pleasurable discussions.

PHYSICAL REVIEW

VOLUME 135, NUMBER 5A

31 AUGUST 1964

## Quadrupole Antishielding Factors for Rare-Earth and Some Other Heavy Ions

R. E. WATSON

*Bell Telephone Laboratories, Murray Hill, New Jersey*

AND

A. J. FREEMAN

*National Magnet Laboratory,\* Massachusetts Institute of Technology, Cambridge, Massachusetts*

(Received 14 April 1964)

Sternheimer quadrupole antishielding factors ( $\gamma_\infty$ ) are reported for several rare-earth ions and for several ions isoelectronic with  $I^-$  and  $Br^-$ . Radial excitations were obtained using the self-consistent-field unrestricted Hartree-Fock method ("orbitally polarized" H-F method) described previously. Comparisons with perturbation-theory estimates of Sternheimer are presented. It is concluded that a roughly constant value of  $\gamma_\infty \approx -80$  is appropriate for the trivalent rare-earth ions. The relation to experiment of theoretical estimates of  $\gamma_\infty$  for positive and negative ions is discussed.

### I. INTRODUCTION

THE distortion of an ion's closed shells by an external crystalline field and the contributions of such distortions to the electric-field gradient (EFG) at the nucleus of an ion were first investigated by Sternheimer and Foley.<sup>1</sup> The importance of such contributions (called antishielding), which are appreciable in large ions, has been emphasized by recent Mössbauer effect measurements of quadrupole interactions in rare earths.<sup>2</sup> Antishielding effects induced in closed shells by an external crystalline field are incorporated in the Sternheimer antishielding factor  $\gamma_\infty$ , such that the total EFG is  $q_{latt}(1 - \gamma_\infty)$ , where  $q_{latt}$  is the gradient due to the *external* environment. Neglecting refinements, two ways have been commonly used to estimate  $\gamma_\infty$ : (1) by numerical integration of the perturbation equations as is done by Sternheimer and collaborators<sup>1</sup>;

(2) by an analytic variational perturbation technique.<sup>3</sup>

In recent papers<sup>4,5</sup> we described a method, based on the unrestricted Hartree-Fock (UHF) formalism, for calculating these antishielding factors, and it was shown that some of the difficulties associated with the perturbation approach, such as orthogonality, exchange, and self-consistency, were resolved. Since these methods<sup>6</sup> do not yield equivalent results, one purpose of the present paper is to further calibrate and attempt to understand the inconsistencies which arise. Apart from these inconsistencies, the methods all suffer several severe shortcomings when one endeavors to relate results with experiment. A  $\gamma_\infty$  is, by definition, obtained by assuming that the crystalline charge distribution causing  $q_{latt}$  is completely external to the ion. This is an inadequate description of the ion's environment, and there arises the question of how a  $\gamma$  appropriate to experiment differs from a  $\gamma_\infty$ .

In the present paper we report UHF estimates of the antishielding appropriate to rare earths and to several

\* Supported by the U. S. Air Force Office of Scientific Research.

<sup>1</sup> R. M. Sternheimer and H. M. Foley, *Phys. Rev.* **92**, 1460 (1953); H. M. Foley, R. M. Sternheimer, and D. Tycko, *ibid.* **93**, 734 (1954); R. M. Sternheimer, *ibid.* **96**, 951 (1954); **80**, 102 (1950); **84**, 244 (1954); **86**, 316 (1952); **95**, 736 (1954); **105**, 158 (1957); R. M. Sternheimer and H. M. Foley, *ibid.* **102**, 731 (1956).

<sup>2</sup> E.g., see S. Hüfner, M. Kalvius, P. Kienle, W. Wiedemann, and H. Eicher, *Z. Physik* **175**, 416 (1963); R. G. Barnes, E. Kankleit, R. L. Mössbauer, and J. M. Poindexter, *Phys. Rev. Letters* **11**, 253 (1963); R. L. Cohen (to be published); P. Kienle (to be published); R. Bauminger, L. Grodzins, and A. J. Freeman (to be published).

<sup>3</sup> T. P. Das and R. Bersohn, *Phys. Rev.* **109**, 360 (1958).

<sup>4</sup> R. E. Watson and A. J. Freeman, *Phys. Rev.* **131**, 250 (1963), designated as I.

<sup>5</sup> A. J. Freeman and R. E. Watson, *Phys. Rev.* **132**, 706 (1963), designated as II.

<sup>6</sup> See also A. Dalgarno, *Proc. Roy. Soc. (London)* **A251**, 282 (1959); *Advan. Phys.* **11**, 281 (1962).

TABLE I. Individual shell  $\gamma_{l \rightarrow l}$  values and total ion  $\gamma_{\infty}$  values for  $\text{Br}^-$ ,  $\text{Rb}^+$ ,  $\text{I}^-$ ,  $\text{Cs}^+$ , and  $\text{La}^{3+}$ .

	$\text{Br}^-$	$\text{Rb}^+$	$\text{I}^-$	$\text{Cs}^+$	$\text{La}^{3+}$
$\gamma_{2p \rightarrow p}$	- 4.7	- 2.2	- 4.8	- 2.7	- 1.8
$\gamma_{3p \rightarrow p}$	- 13.3	- 7.1	- 8.2	- 5.1	- 3.7
$\gamma_{4p \rightarrow p}$	- 85.5	- 42.2	- 23.1	- 15.2	- 11.5
$\gamma_{5p \rightarrow p}$			- 143.0	- 86.8	- 59.0
$\gamma_{3d \rightarrow d}$	- 2.2	- 1.4	- 1.1	- 0.8	- 0.6
$\gamma_{4d \rightarrow d}$			- 4.0	- 3.1	- 2.6
Estimated total $\gamma_{l \rightarrow l \pm 2}$	+ 6	+ 3	+ 8	+ 4	+ 3
Total $\gamma_{\infty}$	- 100	- 50	- 175	- 110	- 76

ions isoelectronic with  $\text{I}^-$  and  $\text{Br}^-$  and discuss some of the above questions.

## II. ORBITALLY POLARIZED H-F METHOD AND RESULTS

In the UHF approach, quadrupole polarizabilities and antishielding factors are obtained by relaxing several restrictions generally associated with the usual Hartree-Fock self-consistent field formalism. Briefly, the "angular" excitations are obtained by relaxing the usual restriction that the spatial part of the one-electron functions be separable into a radial function times an angular function; relaxing the restriction that electrons of the same shell, but differing in magnetic quantum number ( $m_l$ ), have the same radial function yields the "radial" excitations. Full details have been given in I and II. Formally, this scheme is a natural extension of the spin or exchange polarized H-F method used in estimates of magnetic hyperfine effects.<sup>7</sup> We may, in the same way, refer to the  $m_l$  UHF scheme as the "orbitally polarized" H-F method.

In the present paper, the contributions to a  $\gamma_{\infty}$  arising from the *radial* distortions of closed  $p$  and  $d$

TABLE II. Comparison of individual shell  $\gamma_{l \rightarrow l}$  contributions for  $\text{I}^-$  and  $\text{Cs}^+$  as obtained in the present calculations and by Sternheimer (Ref. 8).

	$\text{I}^-$		$\text{Cs}^+$	
	This paper	Sternheimer (Ref. 8) (preliminary result)	This paper	Sternheimer (Ref. 8) (preliminary result)
$\gamma_{2p \rightarrow p}$	- 4.8	- 0.3	- 2.7	- 0.3
$\gamma_{3p \rightarrow p}$	- 8.2	- 1.8	- 5.1	- 1.7
$\gamma_{4p \rightarrow p}$	- 23.1	- 10.8	- 15.2	- 10.0
$\gamma_{5p \rightarrow p}$	- 143.0	- 122.4	- 86.8	- 91.0
$\gamma_{3d \rightarrow d}$	- 1.1	- 0.4	- 0.8	- 0.4
$\gamma_{4d \rightarrow d}$	- 4.0	- 3.5	- 3.1	- 2.9
Total $\gamma_{l \rightarrow l}$ contribution to $\gamma_{\infty}$	- 184	- 139	- 114	- 106

<sup>7</sup> For a review with a complete list of references see A. J. Freeman and R. E. Watson, in *Treatise on Magnetism*, edited by G. Rado and H. Suhl (Academic Press Inc., New York, 1964).

shells ( $\gamma_{l \rightarrow l}$ ) have been obtained self-consistently using this method. The less important angular terms ( $\gamma_{l \rightarrow l \pm 2}$ ) have been estimated crudely.

Results for the closed shell ions,  $\text{Br}^-$ ,  $\text{Rb}^+$ ,  $\text{I}^-$ ,  $\text{Cs}^+$ , and  $\text{La}^{3+}$  are given in Table I. These were obtained using analytic H-F methods (see I and II). Computational considerations mainly involving the size of basis sets have made the  $\text{I}^-$  sequence calculations somewhat inferior to those for  $\text{Br}^-$  and  $\text{Rb}^+$ . The UHF results differ by as much as thirty percent from other estimates (when available) for the same ions.<sup>8-10</sup> Table II compares our results with those of Sternheimer<sup>9</sup> for  $\text{I}^-$  and  $\text{Cs}^+$ . In both investigations the same conventional Hartree-Fock functions were used as the starting point. This point is important in making comparisons since antishielding estimates tend to be sensitive to details of the unperturbed wave functions. The inner shell contributions obtained by us are consistently larger than those obtained by Sternheimer. This is typical of all the uhf results which have been obtained and is caused, we believe, by the fact that the inner shells were allowed to feel the influence of the more severely distorted outer shell (such repercussions being accounted for in a self-consistent treatment of the antishielding problem). In addition to the observation that the innermost shells are most appreciably enhanced,<sup>11</sup> the fact that the ion with the larger (in magnitude) value of  $\gamma_{5p}$  shows greater inner shell enhancement supports this view. Efforts to estimate this enhancement with perturbation techniques have yielded conflicting results,<sup>12</sup> and the situation is far from clarified.

The variations between UHF and perturbation estimates of outer shell contributions show no clear pattern. It is currently not possible to say how such factors as self-consistency, exchange, and the implementation of orthogonality requirements, which cause the UHF method to differ from its perturbation theory counterparts (see I), contribute to these outer shell variations. It is, in fact, dangerous to ascribe these variations as being entirely due to differences in the methods rather than (in part) to details of how the methods have actually been carried out. On the other hand, the inner shell enhancement, which appears to be associated with the self-consistent procedure of the UHF approach, tends to be the most important contributor to differ-

<sup>8</sup> R. M. Sternheimer, Phys. Rev. **132**, 1637 (1963).

<sup>9</sup> R. M. Sternheimer, Bull. Am. Phys. Soc. **8**, 24 (1963); and (to be published).

<sup>10</sup> E. G. Wikner and T. P. Das, Phys. Rev. **109**, 360 (1958).

<sup>11</sup> It may appear surprising that an outer shell  $\gamma_{l \rightarrow l}$  of, say, -100 does not lead to a similar enhancement of inner shell  $\gamma$  contributions by the outer shell's field. This enhancement does not occur because the radial interaction operator is  $r^2 < / r^2 >$  (< and > denoting lesser and greater, respectively). The nucleus, being completely inside the electron shells, feels the brunt of the outer shell distortion, while the overlap between shells greatly reduces the effect of the distortion on other  $\gamma$  terms (see I for further discussion of this point). The reduction is least for the innermost shells.

<sup>12</sup> Analytic variational estimates yielded an enhancement (Ref. 3) but numerical integration a reduction (Ref. 9) for  $\text{Cl}^-$ .

TABLE III. Individual shell  $\gamma_{l \rightarrow l}$  values and total ion  $\gamma_\infty$  values for  $\text{Yb}^{3+}$ ,  $\text{Ce}^{3+}$ ,<sup>a</sup> and  $\text{La}^{3+}$  (second calculation). See discussion in text concerning the role of outer orbital behavior on these estimates.

	$\text{La}^{3+}$	$\text{Ce}^{3+}$	$\text{Yb}^{3+}$
$\gamma_{2p \rightarrow p}$	- 1.4	- 1.5	- 1.2
$\gamma_{3p \rightarrow p}$	- 4.0	- 4.0	- 3.3
$\gamma_{4p \rightarrow p}$	-10.9	-11.0	- 9.2
$\gamma_{5p \rightarrow p}$	-51.4	-54.0	-66.0
$\gamma_{3d \rightarrow d}$	- 0.6	- 0.5	- 0.4
$\gamma_{4d \rightarrow d}$	- 2.7	- 2.5	- 2.0
Estimated total $\gamma_{l \rightarrow l \pm 2}$	+ 3	+ 3	+ 3
Total $\gamma_\infty$	-68	-71	-79

<sup>a</sup> Ref. 5.

ences in the total estimated antishielding. To the extent to which this enhancement occurs, we believe the UHF approach to be, of necessity, superior.

The presence of the open  $4f$  shell complicates UHF estimates of  $\gamma_\infty$  for the rare earths since one wishes to separate the antishielding associated with  $q_{\text{latt}}$  from that associated with the  $4f$  shell and its electric-field gradient,  $q_{4f}$ . To estimate  $\gamma_\infty$  we follow the procedure of II, and obtain UHF solutions for an ion where the  $4f$  shell is not allowed to contribute to the self-consistent aspherical potential distorting the other shells (cf. calculation C of II). The  $\gamma_\infty$  value for  $\text{Yb}^{3+}[(4f)^{13}]$  has been obtained in this way and is listed, along with the previously obtained<sup>5</sup> estimate for  $\text{Ce}^{3+}[(4f)^1]$ , in Table III. The  $\text{Yb}^{3+}4f$  shell was constrained to have a single radial function and therefore makes no contributions to  $\gamma_\infty$ . The capacity of the H-F computer programs allowed less variational freedom (i.e., smaller basis sets) than was obtained for the  $\text{I}^-$  sequence. For meaningful comparison,  $\text{La}^{3+}$  results of equivalent variational freedom to those for  $\text{Ce}^{3+}$  and  $\text{Yb}^{3+}$  have also been obtained. These are given in Table III. We see that the value of  $\gamma_{5p \rightarrow p}$  for  $\text{La}^{3+}$ , and in turn that the value  $\gamma_\infty$ , is smaller than the values of Table I. Such a variation is typical of the sensitivity of  $\gamma_\infty$  estimates to details of outer electron wave function behavior and suggests that the results of Table III should be some 10 units greater in magnitude than the values listed. These results are to be compared with perturbation estimates of -105 and -62 by the analytic variation-perturbation method,<sup>14</sup> and of -81 and -75 by numerical integration<sup>9</sup> for  $\text{Pr}^{3+}$  and  $\text{Tm}^{3+}$ , respectively.<sup>15</sup> These various results suggest that an essentially constant value for  $\gamma_\infty \sim -80$  is appropriate to the rare earths. The analytic variation-perturbation results conform most poorly to this rule and this may be due

<sup>13</sup> The total ion energy is 0.1 a.u. or 0.002% poorer for the Table III  $\text{La}^{3+}$  function.

<sup>14</sup> E. G. Wikner and G. Burns, Phys. Letters 2, 225 (1962).

<sup>15</sup> These estimates are based on E. C. Ridley's [Proc. Cambridge Phil. Soc. 56, 41 (1960)] Hartree functions for  $\text{Pr}^{3+}$  and  $\text{Tm}^{3+}$ .

to shortcomings<sup>16</sup> of the method when dealing with heavily noded functions. (In this procedure, a variation function is constrained to have the same nodes as its parent.)

Roughly constant rare earth  $\gamma_\infty$  behavior (say to  $\pm 5$ ) should not be surprising since these ions are very similar in size. On going to larger  $Z$ , the inner part of the  $p$  shells contracts, enhancing their interaction with the nucleus and tending to increase  $\gamma_\infty$ . At the same time, the outer part of the  $5p$  shell contracts slightly, decreasing its interaction with the crystal potential and thereby opposing the tendency to increase  $\gamma_\infty$ .

The various  $\gamma_\infty$  estimates reported, and referred to, are based on nonrelativistic wave functions. One expects severe relativistic contractions of the inner loops of the  $p$  shells for all the ions discussed here, and while there would be repercussions in the outer regions of the ions we expect that relativistic estimates of  $\gamma_\infty$  would yield larger values than those reported in this paper.

### III. RELATION TO EXPERIMENT

In the preceding section we concentrated on how one estimate of a  $\gamma_\infty$  would differ from another and why one might be the more appropriate result. Let us now revert to the problem indicated in the Introduction, namely: How do these  $\gamma_\infty$  values differ from the antishielding parameters appropriate to experiment?

Experience<sup>17</sup> with the smaller ions, such as  $\text{Cu}^+$  and  $\text{Cl}^-$ , suggests that the computed  $\gamma_\infty$  values are roughly appropriate for the positive ions, while overestimating the effect by perhaps as much as a factor of five for the negative ions. The comparatively good agreement for the positive ion arises from errors which are relatively less severe and which we believe tend to cancel. The most important of these is the inadequate description of the crystalline environment. Considering only inter-electronic and nuclear Coulomb effects, the potential of quadrupolar symmetry is

$$V_q(r, \cos\theta) = \frac{eP_2(\cos\theta)}{2\pi} \int_0^{2\pi} \int_{-1}^1 \left[ \int_0^r \rho(\mathbf{x}) \frac{x^2}{r^3} dx + \int_r^\infty \rho(\mathbf{x}) \frac{r^2}{x^3} dx \right] P_2(\cos\theta') d\varphi d(\cos\theta'),$$

where  $\rho(\mathbf{x})$  is the charge density of the rest of the crystal and  $P_2(\cos\theta)$  is a Legendre function. Assuming  $\rho(\mathbf{x})$  to be completely external to the ion, as is done in obtaining  $\gamma_\infty$  estimates,  $V_q$  becomes  $V_{q,\infty}(r, \cos\theta) = eq_{\text{latt}} r^2 P_2(\cos\theta)$ . The large  $\gamma_\infty$  values for negative ions such as  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  are due to the stronger

<sup>16</sup> We were unable to obtain a stable  $\gamma_\infty$  value for  $\text{Ce}^{3+}$  with this method.

<sup>17</sup> E.g., see the discussion in I, and also G. Burns and E. G. Wikner, Phys. Rev. 121, 155 (1961).

interaction of the more diffuse outer  $p$  shells with  $V_{q,\infty}$ . Significant contributions to  $\gamma_\infty$  arise from the charge density of these shells in regions which, for a typical environment, would be several layers of near neighboring nuclei out from the parent nucleus.  $V_{q,\infty}$  is clearly inappropriate to such a region, as is the free ion function itself. The remedy does not lie in estimating  $V_q$  and evaluating an antishielding factor with it alone, for one must account for repercussions from other terms in the crystal potential,<sup>16</sup> and for interionic exchange, overlap and, on occasion, covalent and/or conduction electron effects from the environment. At the minimum one would be involved with the as yet incompletely understood matter of crystal field effects. We should note that an analytic uhf (and if need be many-centered) approach would be particularly adept for coping with the above complications.

We believe the  $\text{Br}^-$  and  $\text{I}^-$   $\gamma_\infty$  values to appreciably overestimate the antishielding appropriate to experiment, though very likely less severely than is the case

for  $\text{Cl}^-$ . The overestimate could easily be a factor of two for these ions.

Of greater interest to us is the case of rare-earth antishielding. One would like to think, from experience with positive ions such as  $\text{Cu}^+$ , that a  $\gamma_\infty$  of  $-80$  is appropriate to experiment. Such a value is in good agreement with current Mössbauer effect estimates.<sup>2</sup> (Actually, any value between  $-30$  and  $-150$  would not be in serious disagreement with experiment.) Whether  $\gamma_\infty \approx -80$  or not, external-field antishielding in rare-earth ions appears to be substantial, making the lattice electric-field gradient an experimentally significant quantity (see II).

#### ACKNOWLEDGMENTS

We are grateful to Dr. R. M. Sternheimer for conversations and for allowing us to quote his preliminary results. We are indebted to Mrs. Anna Hansen of the U. S. Army Materials Research Agency for help with some of the computations.

## Atomic Absorption Cross Section of Sodium Vapor Between 2400 and 1000 Å

R. D. HUDSON

*Aerospace Corporation, El Segundo, California*

(Received 8 April 1964)

The continuous atomic absorption cross section of sodium vapor has been measured using photoelectric techniques from the  $3s\ ^2S \rightarrow np\ ^2P^0$  series limit at 2412.6 Å, down to 1000 Å. The bandwidth of the monochromator was 1 Å, and values of the cross section were obtained at about 2-Å intervals. The best value for the atomic absorption cross section at the series limit was  $0.130 \pm 0.018$  Mb. A zero minimum was observed at 1950 Å, in agreement with theoretical predictions but conflicting with previous experimental results. The reasons for this conflict are discussed, and a description is given of the experimental procedures adopted.

### I. INTRODUCTION

THE alkali metals form one group in which theory and experiment can be compared most favorably. Ditchburn and Öpik<sup>1</sup> have recently summarized the results obtained for the continuous absorption cross section of these metals and conclude that the agreement between theory and experiment is good for photon energies up to about 2 eV above the ionization limit. The agreement is not good at higher energies for, with the exception of lithium, the balancing of the positive and the negative contributions to the transition integral is so close that unless the initial wave functions chosen are exact, accurate calculations are almost impossible.

It would not be fair, however, to dismiss any disagreement that now exists between theory and experiment as being due only to the theory. It was therefore

decided to measure the continuous absorption cross section of the alkali metals using improved techniques. This paper is an account of the results obtained for sodium.

### II. DETERMINATION OF THE ATOMIC ABSORPTION CROSS SECTION OF METALLIC VAPORS

#### A. Absorption Cross Section

The absorption cross section  $\sigma(\lambda)$  of a single species in the gaseous or vapor state is defined as follows:

$$\ln \frac{I_0(\lambda)}{I(\lambda)} = N\sigma(\lambda) \frac{273}{T} \frac{p}{760} L, \quad (1)$$

where  $I_0(\lambda)$  and  $I(\lambda)$  are, respectively, the intensity incident on and transmitted through the column of vapor or gas, of length  $L$ , at a pressure of  $p$  mm Hg and at an absolute temperature  $T$ , and where  $N$  is Loschmidt's number.

<sup>1</sup>R. W. Ditchburn and V. Öpik, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962).