Position-dependent antishielding factors for the trivalent gallium ion

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We report here the results of our calculation for the position-dependent antishielding factors, $\gamma(r)$ and $\beta(r)$, for the trivalent gallium ion. The dominant part of the contribution which results from the radial mode of excitation of the ion core is calculated in the nonorthogonal Hartree-Fock perturbation theory (NHFPT) of Dalgarno. The less important contribution from the angular mode is evaluated in the Thomas-Fermi (TF) model. The net results of $\gamma(r)$ and $\beta(r)$ show that not only these have the expected variation with respect to distance, but also they correctly reduce to the limiting values at $r=0$ and $r=\infty$. It is hoped that the use of these antishielding factors in the calculation of electric field gradient in Ga metal will provide a better quantitative understanding of quadrupole interaction in this metal than obtained heretofore.

I. INTRODUCTION

Traditionally, it has been the practice[1,2] to express the electric field gradient (EFG) at a nuclear site in a metal as a sum of two contributions, namely, the lattice and conduction electron. The induced effect in the ion core of the given nucleus is included in these calculations[1,2] by multiplying the respective unshielded EFG's from the lattice ions and the conduction electrons by the antishielding factors $1-\gamma_\infty$ and $1-R$. In practice, R is usually much less than unity in magnitude and is therefore approximated[2,3] to be zero. This artificial separation of the net EFG into two such contributions is, however, an approximation to the exact result and holds in the extreme situation where the source charge producing the EFG is outside the given ion core. In metals, where the conduction electrons do penetrate into the core region, the traditional expression[1] for the EFG is certainly inappropriate and its use may lead to significant error in the net EFG in metals. This, in fact, has been observed[4] to be the case in calculations of the EFG in some of the noncubic metals such as Cd and Zn. Thus the need for a more accurate expression than the traditional one for the EFG in a metallic situation is of paramount importance. While some work in this direction had been done in the past,[5] where the net EFG is expressed as an integral over the radial density of the unshielded EFG, antishielded by the radially dependent antishielding factor $1-\gamma(r)$, a more accurate expression than this has recently been worked out by Lodge.[6] The latter expression,[6] in addition to depending on $\gamma(r)$, also contains a different kind of radially dependent antishielding factor, namely, $\beta(r)$ which is, in a sense, dual to $\gamma(r)$. While $\gamma(r)$ measures the induced radial quadrupole moment density at the position r in the core due to the perturbing effect of the nuclear quadrupole moment Q of the nucleus, $\beta(r)$ measures the induced EFG density due to the perturbing effect of the EFG, q of the unshielded source charge.

Results of only $\gamma(r)$ for a number of ions were first reported by Sternheimer and co-workers.[7,8] But recently, by using the nonorthogonal Hartree-Fock perturbation theory[9] (NHFPT), calculations of both $\gamma(r)$ and $\beta(r)$ are reported[10] for the ions Be^{2+}, Mg^{2+}, and Zn^{2+}. Also, using the latter antishielding factors in the expression of Lodge,[6] the effect of distorted core on the EFG of conduction electrons in Be and Mg metals have been calculated.[11] There are two reasons for taking up Ga^{3+} in the present work. First, the radially dependent antishielding factors $\gamma(r)$ and $\beta(r)$ for this ion are not available in the literature, and second, the contribution of the conduction electrons to EFG in Ga metal is not well understood.[6] Since past experience[4] in other noncubic metals shows that the conduction electron contribution to the EFG will be significantly underestimated if proper antishielding factors are not used, we hope that a better understanding of the EFG in Ga metal will follow from the use of the present antishielding factors $\gamma(r)$ and $\beta(r)$.

The details of the NHFPT and its application to antishielding factors are given elsewhere.[9,10,12-14] For the specific problem of $\gamma(r)$ and $\beta(r)$, the reader may refer to the earlier works[10,14] of Rao and Mohapatra. It may be noted here that, as in the previous works,[10,14] the contribution to the antishielding factor from the all-important radial mode is calculated in the NHFPT and that from the less-important angular mode is evaluated in the Thomas-Fermi (TF) model.[7,10]

We would like to remark here that the NHFPT, being an uncoupled-Hartree-Fock procedure,[9,15] the contribution to the antishielding factor resulting from electron self-consistency and correlation effects, cannot be obtained directly in this procedure. However, using the results of many-body perturbation theory,[16] the consistency contribution to first order can be estimated within the NHFPT. The latter contribution in the case of positive polyvalent ions is usually small. For Ga^{3+}, we have estimated the possible error due to the neglect of consistency contribution to $\gamma(r)$ and $\beta(r)$ in Sec. II. Conclusions are summarized in Sec. III.

II. RESULTS AND DISCUSSIONS

The unperturbed wave functions for the core electrons, which have been used in the present work, are those determined by Clementi[17] for the neutral Ga atom. This choice of the wave functions corresponding to neutral atom configuration in preference to the trivalent ionic configuration is exercised for the following reason. The core electron wave functions in the neutral atom being determined in the pres-

TABLE I. Radially dependent antishielding factors $\gamma(r)$ and $\beta(r)$ for Ga^{3+}.

$n(r)$	$\gamma_{ang}(r)$	$\gamma_{rad}(r)$	$\gamma(r)$	$\beta_{ang}(r)$	$\beta_{rad}(r)$	$\beta(r)$
1	0.000 01	0.000 00	0.000 01	0.797 66	−11.331 01	−10.533 3
2	0.000 01	0.000 00	0.000 01	0.797 66	−11.318 13	−10.520 46
10	0.000 02	0.000 00	0.000 02	0.797 66	−11.257 94	−10.460 27
20	0.000 05	0.000 00	0.000 05	0.797 66	−11.221 57	−10.423 92
30	0.000 13	0.000 00	0.000 13	0.797 66	−11.197 45	−10.399 84
50	0.000 71	0.000 00	0.000 71	0.797 28	−11.123 79	−10.326 50
70	0.003 65	0.000 02	0.003 67	0.795 68	−10.706 77	−9.911 08
80	0.008 14	0.000 33	0.008 48	0.793 20	−10.009 40	−9.216 19
90	0.017 97	0.003 17	0.021 14	0.787 72	−8.629 02	−7.841 30
100	0.038 96	0.019 47	0.058 43	0.775 78	−6.546 56	−5.772 78
110	0.082 39	0.045 01	0.127 40	0.750 39	−4.441 76	−3.691 37
117	0.136 48	0.003 13	0.139 61	0.717 88	−3.312 26	−2.594 38
118	0.146 45	−0.006 82	0.139 63	0.711 79	−3.166 86	−2.455 06
120	0.168 42	−0.021 95	0.146 46	0.698 27	−2.877 90	−2.179 62
122	0.193 32	−0.020 46	0.172 85	0.682 81	−2.585 29	−1.902 48
123	0.206 97	−0.009 10	0.197 86	0.674 25	−2.436 00	−1.761 74
124	0.221 46	0.011 56	0.233 03	0.665 13	−2.284 37	−1.619 24
129	0.307 99	0.271 93	0.579 92	0.609 45	−1.504 40	−0.894 95
134	0.421 18	0.517 42	0.938 60	0.533 58	−0.787 31	−0.253 72
138	0.531 79	0.050 52	0.582 31	0.454 55	−0.364 99	0.089 55
139	0.561 79	−0.232 76	0.329 02	0.431 83	−0.286 35	0.145 47
141	0.623 42	−1.027 55	−0.404 13	0.382 51	−0.160 88	0.221 63
146	0.765 02	−4.082 16	−3.317 13	0.233 99	−0.000 63	0.233 35
151	0.797 67	−7.391 39	−6.593 72	0.044 14	0.030 02	0.074 16
156	0.797 67	−9.651 59	−8.853 92	0.000 00	0.020 02	0.020 02
161	0.797 67	−10.768 42	−9.970 75	0.000 00	0.008 41	0.008 41
166	0.797 67	−11.190 61	−10.392 94	0.000 00	0.002 71	0.002 71
176	0.797 67	−11.305 43	−10.507 76	0.000 00	0.000 19	0.000 19
196	0.797 67	−11.305 93	−10.508 26	0.000 00	0.000 01	0.000 01
209	0.797 67	−11.305 93	−10.508 26	0.000 00	0.000 00	0.000 00

ence of valence electrons are believed to be more appropriate to a metallic situation than those determined in ionic configuration. The perturbed core functions V_1' and $\bar{V}_1'$ (see Ref. 10) are obtained as solutions of the standard[10] differential equations in the NHFPT. These solutions are carried out on the IBM 370 system of the Indian Institute of Technology, Madras. The functions V_1' and $\bar{V}_1'$ as well as $\gamma(r)$ and $\beta(r)$ are calculated each at 209 mesh points, generated in a logarithm scale

$$r_n = z^{-1}\exp[-4.5+(n-1)h] \ ,$$

where z is the atomic number of gallium and h is the mesh size. The latter is chosen in the present work to be 0.054 81. In calculating $\gamma_{ang}(r)$ and $\beta_{ang}(r)$ from the TF model,[10] the value used for the core radius r_c is taken from the work of Pauling.[18]

The results of $\gamma(r)$ and $\beta(r)$ at some representative points are summarized in Table I. In column 1 of this table, the index n of the mesh point is given, which one may use to calculate the r value from the logarithm scale mentioned above. In columns 2–4 the contributions $\gamma_{ang}(r)$ and $\gamma_{rad}(r)$, and the total $\gamma(r)$ are listed, respectively. Similarly, columns 5–7 list the respective values of $\beta_{ang}(r)$ and $\beta_{rad}(r)$, and the total $\beta(r)$. In Table II, we list the individual shell contributions to the values of the Sternheimer antishielding factor obtained separately from the quadrupole moment-perturbed core states and from the EFG-perturbed core states. For brevity, we shall refer to these two cases as Q perturbation and q perturbation. The antishielding factor obtained in q perturbation is denoted by $\bar{\gamma}_\infty$ and that in Q perturbation by γ_∞. The values of γ_∞ and $\bar{\gamma}_\infty$ are, respectively, given by the radial integrals of $\gamma(r)$ and $\beta(r)$ over all space.

From Table I as also from Fig. 1 [where total $\gamma(r)$ and $\beta(r)$ are plotted], it is to be noticed that the radial variation of $\gamma(r)$ and $\beta(r)$ have qualitatively the same features as observed previously[10] in the case of Be^{2+}, Mg^{2+}, and Zn^{2+} ions. These qualitative features include: (a) a steeper variation of $\beta(r)$ relative to $\gamma(r)$, (b) the saturation value of $\gamma(r)$ at large r, equal to γ_∞, and (c) the satisfaction of the end-point relations $\gamma(\infty)=\beta(0)=\gamma_\infty$ and $\gamma(0)=\beta(\infty)=0$.

The relative importance of the individual shell contributions of the core electrons to $\gamma(r)$ and $\beta(r)$ can be studied by calculating them separately for each shell. This, in fact, has been done in the present work. But for reasons of brevity of space, we have decided not to list the individual shell contribution to $\gamma(r)$ and $\beta(r)$. However, the same relative

TABLE II. Values of antishielding factors γ_∞ and $\bar{\gamma}_\infty$ for Ga^{3+} ion in Q and q perturbations.

Term	Q perturbation	q perturbations
$2p \rightarrow p$	−0.29	−0.40
$3p \rightarrow p$	−7.06	−6.97
$3d \rightarrow d$	−3.95	−3.95
γ_∞(ang)	0.79	0.79
Total	−10.51	−10.53

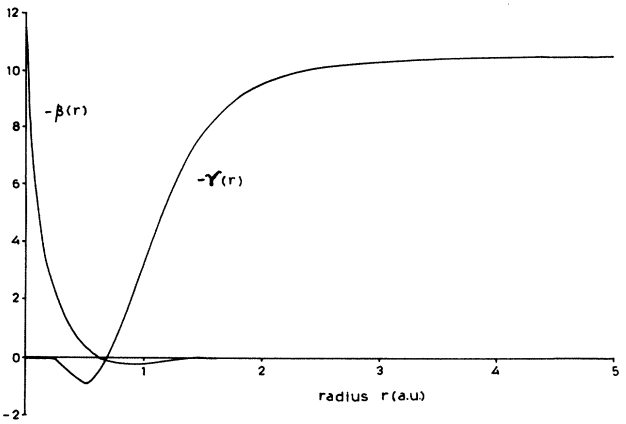

FIG. 1. Total radially dependent antishielding factors $-\gamma(r)$ and $-\beta(r)$ for Ga^{3+}.

importance of the individual shell contributions can be seen on an average from Table II. The latter table shows that the contribution from the $2p$ shell is the least and that from the $3p$ shell is the largest. This is understandable in view of a relatively loose binding and hence of larger deformability of the $3p$ electrons than the $2p$ electrons.

The results of $\gamma(r)$ and $\beta(r)$ for Ga^{3+} from other calculations are not available in the literature for comparison with the present results. However, results for the total Sternheimer antishielding factor γ_∞ are available.[16,19] The angular contribution to γ_∞ in the work of Sternheimer[19] is the same as in the present work. This is because the TF model is used to estimate the angular contribution in both these works. The contributions from the radial mode are, however, different, the present value of -11.30 being a little larger in magnitude than the Sternheimer's value[19] of -10.29. This difference is attributed to the use of two different unperturbed core-electron wave functions in these works. While Sternheimer[19] has used the wave functions for the ion obtained from the work of Piper,[20] the wave functions used in the present work are those of Clementi[17] corresponding to neutral atom configuration. Since the core-electron wave functions in the neutral atom are likely to be more loosely bound than those in the ion, the magnitude of γ_∞ in the former case is expected to be larger than that in the latter.

Another aspect of the result, which we would like to point out, is that the results of γ_∞ obtained in Q and q perturbation are not identical and that γ_∞ is slightly smaller in magnitude than $\bar{\gamma}_\infty$. However, in principle, these should be identical in view of the fact that the operators $1/r^3$ and r^2 are simultaneously present in both the procedures for obtaining γ_∞. We attribute the difference between γ_∞ and $\bar{\gamma}_\infty$ in the present work to the local approximation[15] to the electron potential, which has been assumed while solving the perturbation equations in NHFPT. That γ_∞ will be different from $\bar{\gamma}_\infty$ and also that for positive ions $|\bar{\gamma}_\infty|$ is larger than $|\gamma_\infty|$ can be explained on the assumption that the local approximation overestimates the exchange part of the potential. This can be seen from the following argument. The exchange interaction in atoms being attractive, an overestimation of this will amount to a pulling in of the core-electron wave functions towards the nucleus. Since the integrals for γ_∞ and $\bar{\gamma}_\infty$ are weighted[10] according to r^2 and $1/r^3$, respectively, such contraction of wave functions would give a larger magnitude of $\bar{\gamma}_\infty$ and a smaller magnitude of γ_∞ than the value if exchange were not approximated. Further in this approximation, one would also expect a smaller discrepancy between γ_∞ and $\bar{\gamma}_\infty$ for isoelectronic positive ions with larger ionicity. This is because, as the ionicity increases, the Coulomb interaction becomes more dominant than exchange and therefore any local approximation to the latter would produce a relatively small effect. Conversely, the discrepancy is expected to increase for isoelectronic positive ions with decrease of their ionicity. That this is actually the case has recently been observed[21] in some of the isoelectronic positive ions.

We now estimate the error in $\gamma(r)$ and $\beta(r)$ due to the neglect of electron self-consistency effect. From a recent work on the electron self-consistency effect[16] on the antishielding factor, we find that the contribution to γ_∞ from the self-consistency effect in Ga^{3+} is roughly 15% of the total γ_∞ obtained in an uncoupled Hartree-Fock procedure. Since radial dependence of the self-consistency contribution to γ and β are not available, we use this 15% of the consistency effect in total γ_∞ as an estimated error in the total $\gamma(r)$ and $\beta(r)$ in the present work.

III. CONCLUSIONS

The radially dependent antishielding factors $\gamma(r)$ and $\beta(r)$ for Ga^{3+} are calculated in the NHFPT. The error due to the self-consistency effect is estimated to be less than 15%. The small but negligible discrepancy between γ_∞ and $\bar{\gamma}_\infty$ can be accounted if one assumes that the local approximation to the electron potential overestimates the exchange interaction. The results for $\gamma(r)$ and $\beta(r)$ have been calculated by using core wave functions of the Ga neutral atom rather than those of the Ga^{3+} ion and as such are believed to be more appropriate for the metallic situation. It is hoped that use of these antishielding factors in the calculation of EFG in gallium metal will help towards a quantitative understanding of the quadrupole interaction in this metal.

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