Quadrupole antishielding factors of atoms and ions

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Values of antishielding factor γ_∞ have been obtained for Zn, Cd, In, Fe^{3+}, and Zn^{2+} by solving the appropriate differential equations based on nonorthogonal Hartree-Fock perturbation theory. In the case of Fe^{3+} we have compared our value with that obtained earlier by Sternheimer. While the agreement in the total γ_∞ is excellent, the individual shell contributions, namely γ_∞ $(2p \rightarrow p)$ and γ_∞ $(3p \rightarrow p)$, differ significantly. The reason for this discrepancy is discussed and is attributed to two compensating and exclusion-principle-violating contributions, namely γ_∞ $(2p \rightarrow 3p)$ and γ_∞ $(3p \rightarrow 2p)$, included in Sternheimer values, γ_∞ $(2p \rightarrow p)$ and γ_∞ $(3p \rightarrow p)$, respectively.

I. INTRODUCTION

Since the work of Sternheimer,[1] the first one to calculate the quadrupole antishielding factor, there have been a number of other calculations[2-10] available for the antishielding factor γ_∞. These calculations can be divided into two groups according to the methods of approach used for obtaining γ_∞. The first group of calculations[1-6] have used the perturbation technique, while the second group[7-10] have used the variational approach. The calculation given in Ref. 5 used diagrammatic techniques involving linked-cluster many-body perturbation theory (LCMBPT). In this paper values of γ_∞ have been obtained by solving the appropriate perturbation equations derived in the nonorthogonal formulation[11] of Hartree-Fock perturbation theory (HFPT).

In the latter formulation,[11] the condition that the perturbed orbitals be orthogonal is relaxed to gain some numerical computation advantage in solving the perturbation equations. The solutions so obtained are in general not normalized or orthogonalized. Such conditions are next imposed on the solutions of the starting perturbation equation. The nonorthogonal[11] Hartree-Fock perturbation theory has previously[12] been applied with success to calculate the magnetic hyperfine field in transition metals. The purpose of this paper is therefore twofold: first, to see whether similar success as for the magnetic hyperfine field[12] can be obtained in calculating γ_∞ in the nonorthogonal HFPT; and second, to report results of γ_∞ for neutral atoms Zn, Cd, and In for which the values of γ_∞ are not available. In case of cadmium and indium, we have calculated γ_∞ using Hartree-Fock (HF) and Hartree-Fock Slater (HFS) wave functions separately to see the difference in the values of γ_∞.

Section II discusses the appropriate perturbation equation for obtaining the perturbed wave function. Results and discussion are given in Sec. III. Section IV contains the conclusion.

II. PERTURBED WAVE-FUNCTION CALCULATION

The total γ_∞ consists of contributions arising from radial and angular excitations of the core electrons. By convention an $l \rightarrow l$ excitation is termed radial and an $l \rightarrow l+2$ or $l-2$ excitation is termed angular. The contribution to γ_∞ from angular excitation is usually much smaller than the contribution from radial excitation. The former may therefore be calculated using the approximate Thomas-Fermi model.

A. Radial excitations

Let $\delta\psi'_{nl}$ be the part of the perturbed function of the unperturbed core state ψ^0_{nl} belonging to energy E^0_{nl}. Let H_0 and H_1 be, respectively, the unperturbed Hamiltonian and the perturbation due to nuclear quadrupole moment Q. The function $\delta\psi'_{nl}$ is obtained numerically by solving the following differential equation derived in the nonorthogonal Hartree-Fock perturbation theory discussed earlier in literature[11]:

$$(H_0 - E^0_{nl})\delta\psi'_{nl} = -H_1\psi^0_{nl} + \langle\psi^0_{nl}|H_1|\psi^0_{nl}\rangle\psi^0_{nl} + \sum_{\substack{n'l \\ n'\neq n}} \langle\psi^0_{nl}|H_1|\psi^0_{n'l}\rangle\psi^0_{n'l} + \sum_{\substack{n'l \\ n'\neq n}} \langle\psi^0_{n'l}|\delta\psi'_{nl}\rangle(E^0_{n'l} - E^0_{nl})\psi^0_{n'l}\,. \quad (1)$$

The summation in Eq. (1) is taken over all occupied core states of the same l value as that of the state under perturbation. In atomic units, we have

$$H_0 = -\nabla^2 + V_0 \quad (2)$$

and

$$H_1 = -Q(3\cos^2\theta - 1)/2r^3. \quad (3)$$

The coordinates r, θ are measured with respect

to the axis of the nuclear quadrupole moment. It should be pointed out that the difference between the perturbation equation in the nonorthogonal formulation and the conventional perturbation equation used in other calculations[3] is due to the presence of two additional terms, namely, the third and fourth terms on the right-hand side of Eq. (1).

Writing $H_1' = H_1/Q$ and $\delta\psi_{nl}' = Q\delta\psi_{nl}''$, Eq. (1) can be rewritten as

$$(H_0 - E_{nl}^0)\delta\psi_{nl}'' = -H_1'\psi_{nl}^0 + \langle\psi_{nl}^0|H_1'|\psi_{nl}^0\rangle + \sum_{\substack{n'l \\ n'\neq n}} \langle\psi_{nl}^0|H_1'|\psi_{n'l}^0\rangle\psi_{n'l}^0 + \sum_{\substack{n'l \\ n'\neq n}} \langle\psi_{n'l}^0|\delta\psi_{nl}''\rangle(E_{n'l}^0 - E_{nl}^0)\psi_{n'l}^0. \quad (4)$$

The solutions $\delta\psi_{nl}''$ are in general not orthogonal to all occupied orbitals $\psi_{n'l}^0$. However, it is desirable to have a $\delta\psi_{nl}$ which when added to the zero-order functions ψ_{nl}^0 produce normalized, mutually orthogonal orbitals. This is achieved by the Schmidt orthogonalization procedure, namely

$$\delta\psi_{nl} = \delta\psi_{nl}'' - \sum_{\substack{n'l \\ n'\neq n}} \langle\psi_{n'l}^0|\delta\psi_{nl}''\rangle\psi_{n'l}^0. \quad (5)$$

The summation above is taken over all occupied zero-order states of the same l as that of ψ_{nl}^0. Having obtained $\delta\psi_{nl}$, the contribution to γ_∞ from radial excitations $nl \to l$ is obtained from the relation

$$\gamma_\infty(nl \to l) = 4b_l\langle\psi_{nl}^0|r^2|\delta\psi_{nl}\rangle = 4b_l\left(\langle\psi_{nl}^0|r^2|\delta\psi_{nl}''\rangle - \sum_{\substack{n'l \\ n'\neq n}} \langle\psi_{n'l}^0|\delta\psi_{nl}''\rangle\langle\psi_{nl}^0|r^2|\psi_{n'l}^0\rangle\right). \quad (6)$$

The second equality in Eq. (6) results after substituting $\delta\psi_{nl}$ from Eq. (5) in the first line of Eq. (6). The summation above is taken over all zero-order occupied states of the same l value as that of the state from which excitation takes place. Of the constant factor 4 in Eq. (6), a factor of 2 is due to spin degeneracy of the electron state and the remaining factor of 2 is due to the expression for the induced charge density. The factor b_l is a consequence of summation over all the magnetic substates for a given l value. The solutions $\delta\psi_{nl}''$ in Eq. (6) are obtained numerically in a noniterative procedure as described in Ref. 11.

B. Angular excitation

The contribution to γ_∞ from angular excitation could have been also calculated by solving a perturbation equation similar to that for radial excitation. However, since the former contribution is much smaller than the contribution arising from the latter excitation, we have used the Thomas-Fermi model, initially proposed by Sternheimer[1] and later used by Wikner and Das,[8] to get an approximate value for the γ_∞ (ang). Wikner and Das[8] have derived the following formula, based on the Thomas-Fermi model, for the contribution γ_∞(ang).

$$\gamma_\infty(\text{ang}) = \frac{2(1.7707)^{3/2}}{5\pi}\int_0^\infty (\chi x)^{1/2}dx, \quad (7)$$

where the reduced variable x in usual notation is given by

$$x = Z^{1/3}r/0.885\,34a_H. \quad (8)$$

The function χ remains finite at large x, so in order to evaluate the integral $\int_0^\infty(\chi x)^{1/2}dx$ for different atoms, it must be cut off at a distance dependent on the atom. Following Wikner and Das,[8] we obtained the cutoff distance x_0 for various atoms using the tabulated values of atomic radii r by Pauling.[13] The curve $\chi \sim x$ was taken from Messiah.[14] Using the data in the latter curve, another curve of $(\chi x)^{1/2}$ vs x was plotted, from which the value γ_∞(ang) was obtained by finding the area under the curve $(\chi x)^{1/2} \sim x$ between $x = 0$ to $x = x_0$. The results for γ_∞(ang) are given in Tables I and II.

III. RESULTS AND DISCUSSION

The results for γ_∞ for Fe^{3+}, Zn^{2+} and neutral atoms Zn, In, and Cd are given in Table I. In obtaining the individual shell contribution due to radial excitation, Hartree-Fock atomic functions have been used in all these cases. For the neutral Zn atom and the ion Zn^{2+}, wave functions from Clementi's tables[15] were used and for In and Cd, wave functions from Mann's tables[16] were used. The contribution to γ_∞(ang) in all but Fe^{3+} and Zn^{2+} were calculated in an approximate way from the Thomas-Fermi model as discussed in Sec. II. The γ_∞(ang) for Fe^{3+} and Zn^{2+} are taken, respectively, from the work of Ray and collaborators[5] and Burns and Wikner.[9]

Of the five systems under study in only two cases (Fe^{3+} and Zn^{2+}) are theoretical results by other authors available. We have compared our result γ_∞ for Fe^{3+} with those obtained separately by Sternheimer[3] and by Ray and collaborators.[5] In case of Zn^{2+}, we have compared our result with those of Feiock and Johnson.[4] On comparing the total γ_∞ for Fe^{3+} in our calculation with Ref. 3 (Table I); the agreement is seen to be excellent. But the individual shell contributions, particularly $\gamma_\infty(2p \to p)$ and $\gamma_\infty(3p \to p)$, differ significantly from

TABLE I. Values of $\gamma_\infty(nl \to l)$, γ_∞(ang), and γ_∞(total) from this work, using HF functions, and from Refs. 3 and 4.

	Fe^{3+}		Zn^{2+}		Zn	Cd	In
γ_∞	This work	Ref. 3	This work	Ref. 4	This work	This work	This work
$2p \to p$	−0.39	−0.70	−0.31	•••	−0.31	+0.18	+0.22
$3p \to p$	−8.27	−7.89	−7.60	•••	−7.73	−1.21	−1.14
$4p \to p$	•••	•••	•••	•••	•••	−18.79	−16.93
$3d \to d$	−1.56	−1.59	−4.82	•••	−5.92	−0.31	−0.28
$4d \to d$	•••	•••	•••	•••	•••	−11.76	−8.83
Ang	+0.666	+1.04	+1.19	•••	+1.56	+1.92	+2.01
Total	−9.554	−9.14	−11.54	−12.31	−12.40	−29.97	−24.95

the corresponding values of Sternheimer.[3] However, the value $\gamma_\infty(3d \to d)$ in our calculation compares well with Sternheimer's.

We offer an explanation similar to that of Sternheimer[1] for the above discrepancy. The disagreement is attributed to the nature of the solution $\delta\psi_{nl}$ as obtained by Sternheimer[3] and by our calculation. In Fe^{3+} the core states $2p$ and $3p$ are occupied. Any excitations of the type $2p \to 3p$ and $3p \to 2p$ are excluded by the Pauli principle.

In our calculation $\delta\psi_{2p}$ is orthogonalized to ψ^0_{3p} and similarly $\delta\psi_{3p}$ to ψ^0_{2p} to avoid such exclusion-principle-violating (EPV) excitations. The solutions $\delta\psi_{nl}$ in the Sternheimer[3] calculation, on the other hand, do include such EPV excitations. From perturbation theory it is easy to see that the contribution to γ_∞ from excitation $2p \to 3p$ and that from $3p \to 2p$ are equal in magnitude but opposite in sign. Thus on adding $\gamma_\infty(2p \to p)$ and $\gamma_\infty(3p \to p)$ in the Sternheimer[3] calculation, these EPV contributions cancel, giving a number −8.59 which compares well with the corresponding value −8.66 in our calculation.

From perturbation theory the EPV contribution $\gamma_\infty(2p \to 3p)$ can be calculated from the formula

$$\gamma_\infty(2p \to 3p) = 4\frac{\langle\psi^0_{3p}|1/r^3|\psi^0_{2p}\rangle\langle\psi^0_{2p}|r^2|\psi^0_{3p}\rangle}{E^0_{2p} - E^0_{3p}}. \quad (9)$$

TABLE II. Values of γ_∞ for neutral atoms In and Cd from this work using HFS wave functions.

γ_∞	Cd	In
$2p \to p$	−0.48	−0.12
$3p \to p$	−0.45	−1.09
$4p \to p$	−18.47	−17.05
$3d \to d$	−0.001	+0.55
$4d \to d$	−13.37	−6.00
Ang	+1.92	+2.01
Total	−30.85	−21.70

For Fe^{3+}, by actual calculation[17] the value $\gamma_\infty(2p \to 3p)$ was found to be −0.316. Correspondingly $\gamma_\infty(3p \to 2p)$ is equal to +0.316. Adding these values of $\gamma_\infty(2p \to 3p)$ and $\gamma_\infty(3p \to 2p)$, respectively, to our values of $\gamma_\infty(2p \to p)$ and $\gamma_\infty(3p \to p)$, we get the numbers −0.706 and −7.954, which compare well with the respective values −0.70 and −7.89 of Sternheimer[3] for $\gamma_\infty(2p \to p)$ and $\gamma_\infty(3p \to p)$. Since there is no other occupied d shell than $3d$ in Fe^{3+}, the question of EPV contribution does not arise. Therefore it is not surprising that the value $\gamma_\infty(3d \to d)$ in Sternheimer's calculation[3] agrees well with ours. We would like to remark here that in a recent calculation by Ray and collaborators,[5] the individual shell contributions $\gamma_\infty(nl \to l)$ for Fe^{3+}, obtained by orthogonalizing the Sternheimer-type solution $\delta\psi_{nl}$ to occupied core states of the same l value, agree excellently with the corresponding

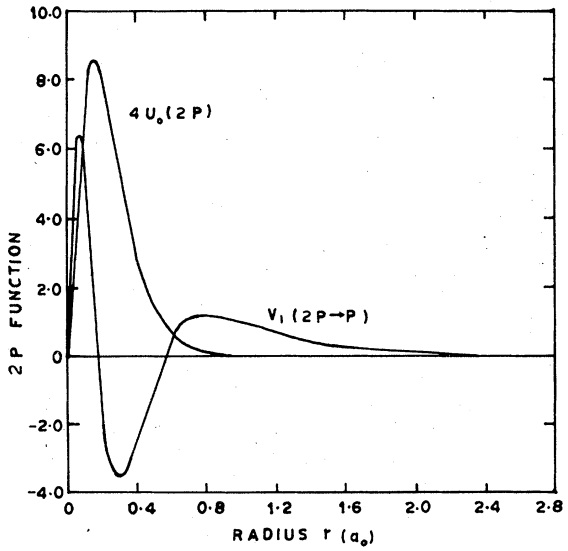

FIG. 1. The perturbed function $V_1(2p \to p)$ and the $2p$ function $U_0(2p)$ for Zn.

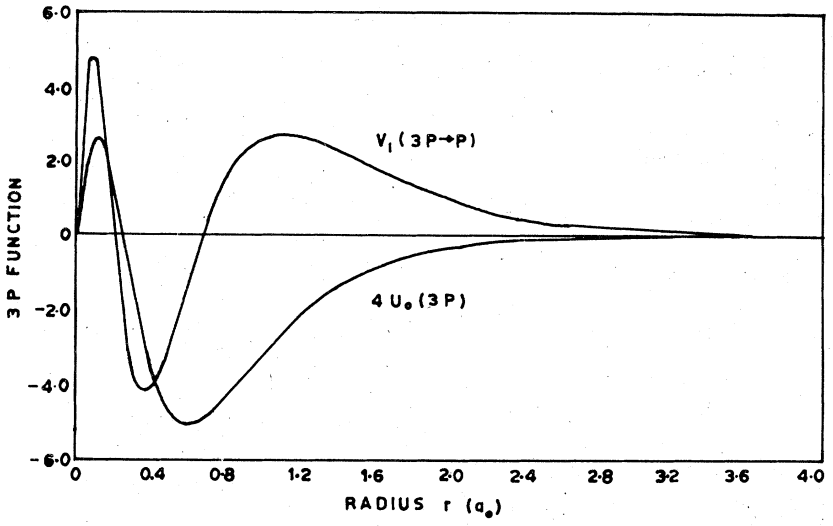

FIG. 2. The perturbed function $V_1(3p \rightarrow p)$ and the $3p$ function $U_0(3p)$ for Zn.

values in our calculation. The novelty in our calculation is, however, that we have orthogonalized the solution $\delta\psi_{nl}$ obtained in the nonorthogonal formulation of the Hartree-Fock perturbation equation.

Since the individual shell contributions $\gamma_\infty(nl \rightarrow l)$ in the case of Zn^{2+} are not reported in the calculation of Feiock and Johnson,[4] we have compared our total γ_∞ with their corresponding value. Our value of total γ_∞ is a little larger than their value. This is possibly due to the combined influence of relativitistic effects and the use of HFS wave functions on their calculation. On comparing our result for the neutral zinc atom with that for Zn^{2+}, we find that the result for the ion is smaller in magnitude than the value for the neutral atom. This is understandable because in the ion, because of the relatively strong attraction, the orbitals are drawn inward more than in the atom. As a result the induced quadrupole moment in the ion is less than in the neutral atom and hence the antishielding is small.

The results for γ_∞ for neutral Cd and In atoms using HFS atomic functions[18] are given in Table II. Comparing the former results with the corresponding HF results given in Table I, we find that except for small differences in individual shell contributions, the total γ_∞ agrees within 3% in cadmium and within 15% in indium. The difference is mainly due to the local exchange used in HFS atomic wave functions in contrast to nonlocal exchange used in HF functions.

The spatial variations of the solution $\delta\psi_{nl}$ in the case of neutral zinc atoms have been shown in Figs. 1, 2, and 3 for the states $2p$, $3p$, and $3d$, respectively. In each figure we have plotted $V_1(nl \rightarrow l)$ and $U_0(nl)$ against r, where the former function is obtained by taking the product of r with the radial part of $\delta\psi_{nl}$ and the latter is r times the radial part of the unperturbed function ψ^0_{nl}. The functions $V_1(2p \rightarrow p)$, $V_1(3p \rightarrow p)$ and $V_1(3d \rightarrow d)$ behave, as far as nodes are concerned, like excited $4p$, $4p$, and $4d$ states, respectively. Since for large r the product of $V_1(nl \rightarrow l)$ and $U_0(nl)$ is negative, the effect is therefore antishielding.

IV. CONCLUSION

The motivation of the present paper has been to show how well the quadrupole antishielding factors

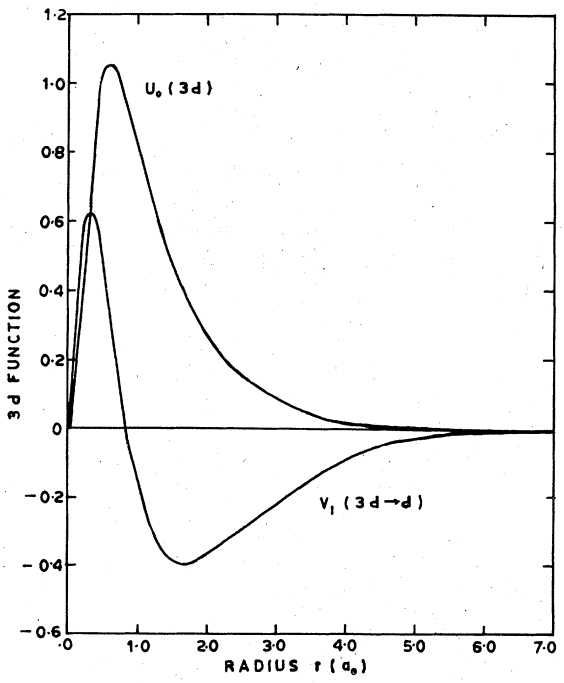

FIG. 3. The pertubed function $V_1(3d \rightarrow d)$ and the $3d$ function $U_0(3d)$ for Zn.

obtained in the nonorthogonal Hartree-Fock perturbation theory compare with those obtained in other methods. In view of the excellent agreement between the results obtained in this paper and those obtained by others, we conclude that one can use the nonorthogonal Hartree-Fock perturbation theory with confidence to calculate antishielding factors in other ions and neutral atoms.

The difference between the individual shell contributions of various $\gamma_\infty(nl \to l)$ in our procedure and the corresponding ones in Sternheimer's procedure is traced to being due to exclusion-principle-violating contributions included in the latter procedure. The spatial variations of the perturbed part of the wave function seem to have the right behavior as far as the number of nodes is concerned.

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