Ab initio theory of nuclear-quadrupole antishielding effects in metallic systems—application to zinc and cadmium*

Pratap C. Pattnaik, Michael D. Thompson, and T. P. Das
Department of Physics, The State University of New York at Albany, New York 12222

(Received 8 November 1976)

A first-principles investigation is carried out for the antishielding effects for the field gradients due to conduction electrons in zinc and cadmium. It is found that the field gradient due to conduction electrons external to the core electrons is antishielded in both metals very substantially, by a factor of about 60% of γ_∞ in both cases, while the part of the field gradient due to conduction electrons in the region internal to the core electrons is subject to very little antishielding effect. Our calculated field gradients in the two metals, when combined with the experimental quadrupole coupling constants, lead to quadrupole moments of 0.46 and 0.67 b for $^{67}Zn(9/2)^+$ and $^{111}Cd(5/2)^+$, the latter agreeing well with a value from ionic crystal data.

The understanding of the origin of nuclear quadrupole interaction in metallic systems is a subject of great current interest. The main reason for this is the availability of a variety of experimental techniques which can provide quadrupole coupling data for both ground[1] and excited[2] nuclear states. While the signs of the nuclear quadrupole coupling constants were obtainable before for Mössbauer-active nuclei, the number of nuclei for which the signs can be observed has recently been extended significantly through the utlization of perturbed-angular-correlation techniques.[3] Concurrently with this, the results of theoretical investigations[4] in a number of metals have provided greater insight into the various sources that can contribute to the field gradient and in the case of pure cadmium, one of the first metals for which the sign of the quadrupole coupling constant was experimentally determined, theory[5] and experiment[3] are in agreement.

A crucial factor for the quantative understanding of the field gradients in metallic systems, which had not been critically analyzed so far, is the antishielding effect[6] associated with the field gradient due to conduction electrons. In earlier theoretical investigations,[4] it has been a common practice to incorporate antishielding effects according to the relation

$$q = q_{el}^0 (1 - R) + q_{latt}^0 (1 - \gamma_\infty) , \tag{1}$$

where q_{el}^0 and q_{latt}^0 are, respectively, the field gradients at the bare nucleus due to the conduction electrons and the ions in the lattice, the antishielding effects of the core electrons being incorporated through the factors $(1 - R)$ and $(1 - \gamma_\infty)$, R being the characteristically small factor associated with valence electrons in atoms,[7] and γ_∞ the relatively large factor appropriate for an external charge.[8] Since q_{el} arises from the distributed charge due to the conduction electrons, the antishielded electronic term in (1) represents a rather simplifying approximation and should properly have the form

$$q_{el} = q_{el}^0 - \frac{1}{\Omega} \int q_{el}^0 (\vec{r}) \gamma (\vec{r})\, d^3\vec{r} , \tag{2}$$

Ω being the volume of the crystal over which the integration is carried out; $q_{el}^0 (\vec{r})$, the field gradient due to conduction electrons at position vector $\vec{r}$ with respect to the nucleus, and $\gamma(\vec{r})$, are both functions of $\vec{r}$.

Two compelling developments in this field resulting from recent experimental measurements have motivated us to critically examine the approximation used in Eq. (1) by carrying out a first-principle investigation of $\gamma(\vec{r})$ in metals. The first of these developments is that the quadrupole moment of ^{111}Cd in the excited $\frac{5}{2}^+$ state has recently been inferred[9] from perturbed-angular-correlation measurements in ionic crystals and is in substantial disagreement (by a factor of about 3) with the value of Q derived by combining experimental data in cadmium metal with *ab initio* theoretical calculations[4] of q based on Eq. (1). The second development that has stimulated the present investigation is the discovery of a semiempirical relation[10] of the form

$$q_{el} = X q_{latt} (1 - \gamma_\infty) , \tag{3}$$

found to hold for a number of metals and alloy systems, with X lying between -2 and -3 and γ_∞ referring to the ion containing the nucleus of interest. The relation (3) has also led to a questioning[10] of the choice, assumed in Eq. (1), of the antishielding factor for the conduction-electron field gradient, since such a choice would preclude any relationship between q_{el} and $(1 - \gamma_\infty)$.

The procedure that we have used for the investigation of antishielding effects for conduction electrons is similar to the moment perturbation tech-

nique[11] employed earlier for the study of exchange core polarization effects[12] on Knight shift and relaxation times in metals. Thus we perturb the core wave functions by the nuclear-quadrupole moment and then calculate the sum $(\delta E)_Q$ of the Coulomb and exchange interaction energies between these perturbed core electrons and the conduction electrons, retaining only terms linear in Q. The coefficient of e^2Q in this energy term is the second term in Eq. (2) representing q_{ind}, the induced field gradient arising from antishielding effects. In evaluating the core-conduction interaction energy, one has to include, as in the calculation of the direct field gradient q_{el}^0 due to conduction electrons, the conduction electrons within the entire occupied Fermi volume instead of only those at the Fermi surface as in the case of Knight shifts and relaxation times. Thus

$$(\delta E)_Q = e^2 Q q_{\text{ind}} = \sum_{\vec{k},i} \sum_c \int \psi_c^*(1)\psi_{\vec{k},i}^*(2)\,\frac{1-P_{12}}{r_{12}}\,\delta\psi_c(1)\psi_{\vec{k},i}(2)\,d\vec{r}_1\,d\vec{r}_2\ , \tag{4}$$

P_{12} being the permutation operator, ψ_c and $\psi_c+\delta\psi_c$ the unperturbed and perturbed wave function for the core states c, and $\psi_{\vec{k},i}$ the conduction-electron wave function for the ith band and wave vector $\vec{k}$. The function $\delta\psi_c$ is obtained by solving the perturbation equation:

$$(H_{0c}-E_{0c})\delta\psi_c = -(H'_Q - E_{Qc})\psi_c\ , \tag{5}$$

where

$$H'_Q = e^2Q(3\cos^2\theta - 1)/r^3 \tag{6}$$

with H_{0c} and E_{0c} representing the one-electron Hamiltonian and energy for the core state c, and H'_Q and E_{Qc}, respectively, the perturbation Hamiltonian due to the nuclear-quadrupole moment and its expectation value for the core state c.

For the conduction-electron wave function $\psi_{\vec{k},i}(\vec{r})$, we have used linear combinations of orthogonalized-plane-wave wave functions obtained by the pseudopotential technique as described elsewhere.[5] Since the orthogonalized-plane-wave functions involve both plane-wave (PW) and tight-binding (TB) core-state wave functions, the product of the two functions $\psi_{\vec{k},i}$ in Eq. (4) will involve the sum of PW-PW, PW-core, and core-core components. Since these three types of density components have different degrees of penetration into the core, we expect different antishielding effects for them. We have studied the induced interaction energies for each of these components separately, to analyze the individual antishielding effects associated with each of these components.

The combination of the three induced interaction energies gives the net induced field gradient arising from the interaction of conduction and core electrons. This analysis obviates the need for the choice of an appropriate parameter,[4] like R, for example,[6,7] for the antishielding of the conduction-electron field gradients. However, to obtain added insight into the role of these effects, one can derive antishielding factors appropriate for the net field gradient due to the conduction electrons and also individually from the PW-PW, PW-core, and core-core components, namely, γ, $\gamma_{\text{PW-PW}}$, $\gamma_{\text{PW-core}}$, and $\gamma_{\text{core-core}}$, respectively, by taking the ratios between the total and appropriate contributions from q_{ind} and q_{el} in each case.

The most striking aspect of the results of our *ab initio* antishielding calculation is the large enhancement obtained for the PW-PW component of the field gradient. The contributions to the antishielding effect for this component from individual cores are presented for both zinc and cadmium in Table I. Also shown for useful reference are the corresponding contributions to γ_∞ for an external point charge for both Zn^{+2} and Cd^{+2} ions. To simulate the screening effects on the cores by the conduction electron, the core wave functions employed in the γ_∞ calculation were those for the neutral atoms. The net antishielding factor for the PW-PW component is seen to be two orders of magnitude larger than the typical order[6,7] of 0.1 for R. Also, understandably, this antishielding factor is smaller than γ_∞ for both metals. The reason is that whereas the point charge in γ_∞ calculations[8] is totally external to the cores, the PW-PW component of the conduction-electron density does have partial penetration into the core region and cannot therefore interact effectively with the entire quadrupole moment induced in the cores by the nuclear-quadrupole moment. This effect is also clearly seen from the nature of the individual core contributions in Table I, where there is increasingly greater difference between the contribution to $\gamma_{\text{PW-PW}}$ and γ_∞ as one goes toward the outer cores. The nonorthogonality terms in Table I arise in the Hartree-Fock perturbation theory[13] employed in our work because the perturbed core states are not mutually orthogonal.

The results in Table I are composed of the contributions to the antishielding factors from the Coulomb interaction of core and conduction electrons. We expect a contribution to $\gamma_{\text{PW-PW}}$ of the order of 0.1 from the corresponding exchange effects

TABLE I. Contributions from various cores to the antishielding factor $\gamma_{PW\text{-}PW}$ for the field gradients due to the PW-PW components of the conduction-electron densities compared with the corresponding contributions to γ_∞.

Core	Zinc		Cadmium	
	Contribution to $\gamma_{PW\text{-}PW}$	Contribution to γ_∞	Contribution to $\gamma_{PW\text{-}PW}$	Contribution to γ_∞
$2p$	5.47	5.75	−0.15	−0.15
$3p$	−16.95	−19.36	44.03	47.72
$3d$	−2.83	−5.92	3.30	3.70
$4p$	...	...	−142.20	−158.48
$4d$	...	...	−10.41	−17.50
Nonorthogonality contribution [a]	5.31	5.56	85.40	92.40
Total	−9.00	−13.97	−20.00	−32.26

[a] See Ref. 13.

from an examination of the magnitudes of the integrals involved. Also, only the effects of the radial excitations[6] of the cores have been included in the antishielding results in Table I, since these are known[6,8] to be the major contributors to γ_∞. The influence of the angular excitations is not expected to change the calculated antishielding factors for the PW-PW components by any more than 10% and therefore should not affect the conclusions of our work significantly.

The net antishielding factors $\gamma_{PW\text{-}PW}$ for zinc and cadmium for the PW-PW components are seen from Table I to be −9 and −20, respectively. Interestingly the values of the ratios $\gamma_{PW\text{-}PW}/\gamma_\infty$, namely, 0.64 and 0.62, are rather close to each other in the two cases. We have also carried out calculations for the antishielding factors for the field gradients due to the TB-TB and TB-PW components in zinc. The values of these factors, 0.02 and 0.06, are very small, closer to the order of magnitude of the atomic antishielding factor.[6,7] This is expected since both these components involve the TB part of the orthogonalized-plane-wave function and are therefore quite internal with respect to the core electrons.

The relatively large antishielding effect for the PW-PW components has profound consequences on both the conduction-electron contributions to q_{el} as well as the total field gradients themselves in both metals as can be seen from Table II. From a comparison of the second, third, and fourth columns for both metals, it is seen that whereas, without the inclusion of the proper γ for the PW-PW component, the contribution to the field gradient from the latter is unimportant compared to the local contribution $q_{TB\text{-}TB}+q_{TB\text{-}PW}$, when one includes $\gamma_{PW\text{-}PW}$, the two contributions become of comparable order of magnitude. The influence of this finding on the net field gradient q_{total} in the eighth column is even more marked because the net electronic and ionic field gradients, q_{el} and q_{ionic}, are opposite in sign. Using the calculated field gradients in Table II, along with the experimental values of the quadrupole coupling constants,[3,14] the quadrupole moments of $^{67}Zn(\frac{5}{2}^+)$ and $^{111}Cd(\frac{5}{2}^+)$ come out as 0.46 and 0.67 b, respectively.[15] The latter is now in good agreement with the value derived from ionic quadrupole coupling data[9] in contrast with the earlier situation when the influence of $\gamma_{PW\text{-}PW}$ on the PW-PW contribution had not been included. For $^{67}Zn(\frac{5}{2}^+)$ we have quoted only the magnitude of Q because the sign of the coupling constant is not available. There is

TABLE II. Contributions [a] to the field gradient in zinc and cadmium including antishielding effects.

	$q_{TB\text{-}TB}+q_{TB\text{-}PW}$	$q_{PW\text{-}PW}$ without antishielding	$q_{PW\text{-}PW}$ with antishielding	q(distant) [b]	q_{el}(total) [c]	q_{ions}	q_{total}	ν_Q(MHz) [d]	Q (barns)
Zinc	150.20	6.69	66.90	−4.98	212.12	−64.40	147.72	49.5	0.46
Cadmium	251.25	7.78	163.38	−13.29	401.34	−119.60	281.74	137.5	0.67

[a] Units of 10^{13} esu/cm^3.

[b] The antishielding factor $(1-\gamma_\infty)$ has been used here. The significance of q(distant) has been explained earlier in the literature (Ref. 4).

[c] For the values of q_{el}(total) listed we have employed the properly antishielded $q_{PW\text{-}PW}$ in column 4.

[d] References 3 and 4.

no other available value for $Q(^{67}\mathrm{Zn}, \frac{9}{2}^+)$ to compare with our result. It would be helpful to have perturbed-angular-correlation data for this level of ^{67}Zn in ionic compounds to obtain a value of Q as in the case of ^{111}Cd, to compare with our present result from the data in the metal.

In summary then, our first-principles investigations of antishielding effects for conduction electrons in metals have shown that, contrary to earlier ideas in the literature, the field gradients from different components of the conduction-electron distributions are antishielded very differently. In particular, the PW-PW component is subject to very sizeable antishielding effects found to be about $0.6\,\gamma_\infty$ in both metals, zinc and cadmium, indicating that an antishielding effect of this order probably applies to all metals. To confirm this point, similar investigations need to be carried out in other metals. In any case, the very substantial size of the antishielding effects for the PW-PW component and the influence it has on the net field gradient in the metal lead to the conclusion that such effects must be included in not only the study of metals under ideal conditions, but also in alloys and for variations of the field gradients in metalic systems with respect to temperature and pressure.

Finally, our results provide support for the empirical relation [Eq. (3)] found recently[10] between q_{el} and q_{latt}. Whereas in Eq. (1), there was no possibility for a dependence of q_{el} on $(1-\gamma_\infty)$, our result that at least an important part of q_{el}, namely, $q_{\mathrm{PW\text{-}PW}}$, is related to γ_∞ does provide qualitative support for Eq. (3). Our calculated values of q_{el} and q_{latt} lead to values of the parameter X in Eq. (3) of -3.3 and -3.4 for zinc and cadmium close to the upper limit in the range of -2 to -3 found empirically.[10]

---

*Supported by NSF.

[1]See, for example, W. D. Knight and R. R. Hewitt, Phys. Rev. Lett. 3, 18 (1959); W. W. Simmons and C. P. Slichter, Phys. Rev. 121, 1580 (1961); D. E. Barnaal, R. G. Barnes, B. R. McCart, L. W. Mohn, and D. R. Torgeson, *ibid.* 157, 510 (1967).

[2]See, for example, *Hyperfine Interactions in Excited Nuclei*, edited by C. Goldring and R. Kalish (Gordon and Breach, New York, 1971); P. Raghavan, E. N. Kaufmann, R. S. Raghavan, E. J. Ansaldo, and R. A. Naumann, Phys. Rev. B 13, 2835 (1976).

[3]R. S. Raghavan, P. Raghavan, and E. N. Kaufmann, Phys. Rev. Lett. 31, 111 (1973); 31, 802(E) (1973); Phys. Rev. C 12, 202 (1975); R. S. Raghavan and P. Raghavan, Phys. Lett. A 36, 313 (1971).

[4]T. P. Das, Phys. Scr. 11, 121 (1975), and references therein.

[5]N. C. Mohapatra, C. M. Singal, and T. P. Das, Phys. Rev. Lett. 31, 630 (1973). See also Ref. 4.

[6]R. M. Sternheimer and R. F. Peierls, Phys. Rev. A 4, 1722 (1971); R. M. Sternheimer, Phys. Rev. 146, 140 (1966).

[7]S. N. Ray, T. Lee, and T. P. Das, Phys. Rev. A 8, 1748 (1973); James E. Rodgers, Ribha Roy, and T. P. Das, *ibid.* 14, 543 (1976).

[8]S. N. Ray, T. Lee, and T. P. Das, Phys. Rev. A 9, 1108 (1974); M. Vajed-Samii, S. N. Ray, and T. P. Das, Phys. Rev. B 12, 4591 (1975).

[9]R. S. Raghavan, P. Raghavan, and J. M. Friedt, Phys. Rev. Lett. 30, 10 (1973).

[10]R. S. Raghavan, E. N. Kaufmann, and P. Raghavan, Phys. Rev. Lett. 34, 1280 (1975).

[11]G. D. Gaspari, Wei-Mei Shyu, and T. P. Das, Phys. Rev. 134, A852 (1964).

[12]S. D. Mahanti and T. P. Das, Phys. Rev. B 3, 1599 (1971).

[13]K. J. Duff and T. P. Das, Phys. Rev. 167, 660 (1968); S. N. Ray, Taesul Lee, R. M. Sternheimer, S. K. Sen, and R. P. Gupta, Phys. Rev. A 11, 1804 (1975).

[14]H. Bertschat, E. Recknagel, and B. Spellmeyer, Phys. Rev. Lett. 32, 18 (1974).

[15]These values are reasonably close to the values of the quadrupole moments that were estimated in our earlier work [N. C. Mohapatra, P. C. Pattnaik, M. D. Thompson, and T. P. Das, Bull. Am. Phys. Soc. 21, 105 (1976)] using antishielding factors of $0.5\gamma_\infty$ for the field gradients due to the PW-PW components of the conduction electrons in both metals. These latter antishielding factors were estimated by intuitive analyses of the overlaps of the core and conduction-electron distributions in the two metals.