Sternheimer antishielding factors for core electrons in metals: Comparison with free-ion results

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The Sternheimer antishielding factor γ_∞ has been calculated using nonrelativistic Hartree-Fock-Slater core-electron wave functions for several metallic elements in the third, fourth, and fifth rows of the Periodic Table assuming the ground-state electronic configuration for the transition-metal atoms to be $3d^n4s^1$, $4d^n5s^1$, and $5d^n6s^2$, respectively. These values have been compared with the available γ_∞ values based on the free-ionic-core-electron wave functions. For the elements in the intermediate region of each row, the presently calculated γ_∞ values are found to be significantly different from the frequently used free-ion values corresponding to the core-electron configuration.

I. INTRODUCTION

The electric field gradient (EFG) in metals and alloys has been traditionally interpreted as

$$eq = (1-\gamma_\infty)eq_{\text{latt}} + (1-R)eq_{\text{cond}} \quad (1)$$

where eq_{latt} and eq_{cond} are the contributions to the EFG due to the lattice charges and conduction electrons, respectively. The Sternheimer shielding-antishielding factors,[1] γ_∞ and R, arise due to the quadrupolar polarization of the core electrons. Values of $1-\gamma_\infty$ have so far been calculated generally using free-ion wave functions and are found to be ~10–100. The calculated values of $1-R$ are also generally based on wave functions of free atoms and ions and are found to be ~1.

Recently, Raghavan *et al.*,[2] have analyzed the available experimental data on the EFG in metallic systems and shown that, in general, the antishielding-corrected lattice field gradient is linearly related to the conduction-electron contribution. In light of such a universal correlation, it appears that the shielding-antishielding-corrected conduction-electron field gradient in metallic systems is not fully understood at present.

In their first-principles calculations of the EFG in Zn and Cd metals, Das and co-workers[3] have shown that, whereas the field gradient due to the tight-binding component of the conduction-electron density is shielded by the traditional valence shielding factor $1-R$, the plane-wave component is "antishielded" by a factor closer to $1-\gamma_\infty$. In particular, the plane-wave component is found to have an antishielding of 64% and 62% for Zn and Cd metal, respectively.

From the above considerations it becomes essential to have a knowledge of accurate theoretical values of the first term in Eq. (1). The eq_{latt} values are often computed fairly accurately by standard lattice summation methods.[4,5] For γ_∞, however, values calculated[6] for free ions have been frequently employed.[3]

On the basis of rigorous band-structural calculations,[7] atoms in the third, fourth, and fifth rows, transition metals, are commonly represented by (Ar)$3d^n4s^1$, (Kr)$4d^n5s^1$, and (Xe)$5d^n6s^2$ configurations, respectively. The free-ionic values of γ_∞ are less accurate since they do not incorporate the shielding effects of conduction electrons on the core. A more accurate value of γ_∞ to be used in Eq. (1) can be calculated by using the core-electron wave functions corresponding to the neutral atom in the electronic configuration appropriate to the metal. The purpose of this paper is to report the results of our calculation of γ_∞ values for a large number of cases using Hartree-Fock-Slater[8] (HFS) wave functions corresponding to the ground-state neutral-atom configuration which leads to a more realistic potential experienced by the core electrons in actual metals as compared to the closed-shell free-ionic cases. A quantitative estimate of the repercussions of the conduction-electron shielding effects on γ_∞ in several cases has also been obtained by comparing the presently calculated values of γ_∞ with the free-ionic γ_∞ values available in the literature.

II. METHOD OF CALCULATION

The method of calculation adopted in the present work is same as that described in our previous work.[9] Thus, for the unperturbed state we have used 441-point-mesh HFS wave functions corresponding to the neutral atoms using a modified version of the Herman-Skillman program.[8] As mentioned earlier, the transition-metal atoms of the third, fourth, and fifth row in the Periodic Table have been assumed to be in (Ar)$3d^n4s^1$, (Kr)$4d^n5s^1$, and (Xe)$5d^n6s^2$ configurations, respectively. The nuclear quadrupole moment-perturbed radial wave functions $u_1'(nl \to l')$ have been obtained by directly solving the first-order

TABLE I. Sternheimer antishielding factor γ_∞ corresponding to the closed shells and γ_∞ per d electron in the elements of third, fourth, and fifth row of the Periodic Table. The transition-metal elements have been assumed to have $3d^n4s^1$, $4d^n5s^1$, and $5d^n6s^2$ electron configurations, respectively.

Ion	Core (Ar)	Contribution per 3d electron	Ion	Core (Kr)	Contribution per 4d electron	Ion	Core (Xe)	Contribution per 5d electron
K	−17.86	•••	Rb	−49.34	•••	Cs	−99.65	•••
Ca	−13.67	•••	Sr	−38.93	•••	Ba	−81.07	•••
Sc	−13.37	−4.57	Yt	−36.00	−9.12	La	−72.66	−5.42
Ti	−12.21	−2.93	Zr	−32.51	−5.54	Hf	−61.50	−5.11
V	−11.29	−2.21	Nb	−29.75	−3.97	Ta	−56.9	−4.92
Cr	−10.53	−1.80	Mo	−27.57	−3.09	W	−52.83	−4.15
Mn	−9.90	−1.53	Tc	−25.65	−2.56	Re	−49.60	−3.52
Fe	−9.34	−1.38	Ru	−24.10	−2.20	Os	−46.83	−3.09
Co	−8.85	−1.27	Rh	−22.59	−1.93	Ir	−44.29	−2.77
Ni	−8.43	−1.17	Pd	−21.55	−1.73	Pt	−42.23	−2.51
Cu	−8.04	−1.10	Ag	−20.52	−1.57	Au	−40.28	−2.30
Zn	−7.33	−0.58	Cd	−18.98	−1.07	Hg	−38.52	−2.13
Ga	−6.64	−0.31	In	−17.28	−0.79	Tl	−35.22	−1.66
Ge	−6.03	−0.27	Sn	−16.18	−0.63	Pb	−33.27	−1.32
As	−5.51	−0.21	Sb	−14.76	−0.52	Bi	−31.03	−1.12
Se	−5.06	−0.17	Te	−13.70	−0.45	Po	−29.14	−0.96

Schrödinger equation

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

An iterative computer code for solving Eq. (2) via the difference equation has been developed in our laboratory. γ_∞ is obtained as

$$\gamma_\infty=\sum_{nl} c(nl\to l')\int_0^\infty u_1'u_0'r^2dr, \quad (3)$$

where the constants $c(nl\to l')$ have been tabulated by Sternheimer.[10] In the cases of atoms with incomplete d shells, $c(nl\to l')$ values have been multiplied by 0.1, and the values of γ_∞ per d electron have been obtained by summing the contributions from $nd\to s$, $nd\to g$, and $nd\to d$ perturbations. All integrals have been evaluated by using the formula for integration through adjacent intervals including fourth-order differences.[11]

III. RESULTS AND CONCLUSIONS

In Table I, we have presented the results of our calculations of γ_∞ corresponding to the core and the single d electron for the cases of third-, fourth-, and fifth-row elements in the Periodic Table. The core configurations in these three cases correspond to the ground-state electronic configurations of Ar, Kr, and Xe, respectively. The combined screening effects of the valence electrons are expected to give rise to more external core-electron wave functions as compared to the free ions. This means that $|\gamma_\infty|$, using neutral-atom wave functions, should be larger than the corresponding free-ionic value, and the difference should increase with the increase in ionic charge. We note here that calculations of γ_∞ using neutral-atom HFS wave functions have been reported by Sternheimer[12] in the cases of In, Bi, and Am. Our calculations[13] using ionic HFS wave functions for In^{3+}, Bi^{3+}, Bi^{5+}, and Am^{2+} show, as expected, that the use of neutral-atom wave functions increase $|\gamma_\infty|$ by ~5–10%. Das[3] has recently arrived at similar conclusions in the cases of Be, Mg, Zn, and Cd.

For a few cases of the atoms in the intermediate region of the transition-metal elements in the Periodic Table, we have earlier calculated[14] γ_∞ using ionic HFS wave functions. In the cases of Sc, Yt, and La, the use of ionic wave functions underestimates $|\gamma_\infty|$ by ~20%, 14%, and 10%. Comparing the $|\gamma_\infty|$ values corresponding to the metal cores of M^{4+}, M^{5+}, and M^{6+}, having $3d$ and $4d$ electrons with the present values, we find that for Ti^{4+} and Zr^{4+}, the underestimation is ~28% and 20%, respectively, while for V^{5+} and Nb^{5+} it is 34% and 25%, respectively, and for Cr^{6+} and Mo^{6+} 39% and 30%, respectively.

In view of such significant differences observed in the cases of these metals and in absence of the calculations of γ_∞ including the screening effects due to the conduction electrons on the core in general, we recommend the use of the presently calculated γ_∞ values in interpreting the EFG data on metallic systems. Our present results should also be useful in ascertaining the net relativistic ef-

fects on γ_∞ when calculations of γ_∞ using relativistic HFS wave functions corresponding to the neutral atoms become available. The calculations of r-dependent antishielding factors for the atomic systems considered here are in progress.

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