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1995 J. Phys.: Condens. Matter 7 4855

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# Electron–electron interaction and antishielding constants of core shells of atoms

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Received 6 December 1994, in final form 26 April 1995

**Abstract.** Self-consistent Sternheimer antishielding constants for chemical elements with nuclear charge in the range 2–94 are obtained within the framework of the local density approximation. The dependence of the Sternheimer factors on the ion charge states is discussed. These results can be employed for a prediction of the quadrupole splitting parameters on the basis of pseudopotential electron density calculations.

## 1. Introduction

The interaction between the nuclear quadrupole momentum  $Q$  and electric field gradient (EFG) in a crystal shows itself in nuclear gamma, magnetic and quadrupole resonance (NGR, NMR and NQR). Observation of the nuclear quadrupole interaction (NQI) is one of the most precise experimental methods for chemical bonding investigations. A theoretical description of the splitting, which is connected with the NQI, requires the determination of the values of  $Q$  and EFG.

The value of  $Q$ , in principle, can be obtained from experiments with free nuclei. For a description of the behaviour of the electric field  $E(r)$  in compounds, it is necessary to have information about the charge distribution  $\rho(r)$ . The electron density can be obtained only from *ab initio* self-consistent band structure calculations. They have already become commonly used in the modern theory of solids [1]. However, specific features of NQI make special demands on such computations, and this situation has brought about the comparatively small number of theoretical applications to EFG computations in crystals. These demands arise from the following reasons. The origin of nonzero EFG at the nuclei of ions with closed shells is the nonspherical field of the valence electrons and other ions. This field may be treated as an external field. The EFG, however, induced by core states of a given ion, may be many times greater than the external one. Sternheimer was the first who paid attention to this effect [2]. Thus, in the quest for the EFG acting on nuclei, the reaction of the core states, which do not participate in the formation of chemical bonds, must be considered.

The overwhelming majority of modern band structure calculations are based on the following approaches.

In the first approach, core states are described within the framework of muffin-tin methods. Thanks to the central symmetry and the special properties of the muffin-tin potential, the problem of self-consistency can be solved easily enough, with an accuracy that in many cases is sufficient for the description of electron spectrum features. Appropriate methods are especially effective in their linear versions [3]. NQI methods were developed

in [4–6]. Such methods, in principle, are free of the necessity of taking into account the corrections that are connected with the Sternheimer effect, because the core polarization, induced by the crystal field, can be accounted for automatically. Nevertheless, owing to the great distinction between the locations of core and valence electrons, powerful computers are required for a realization of these methods†.

In another approach, based on the pseudopotential theory, a self-consistent solution is feasible only for a subsystem of valence electrons in the field of ion cores. This approach is cruder than the previous one, but at the same time it has some advantages. The main advantage is the fact that the problem of an electron spectrum description has significantly fewer dimensions, and therefore can be solved with less computational expenditure. Moreover, results obtained in this way are easier to interpret; the interpretation can be done in terms of the charge states of ions and the peculiarities of chemical bonding between these ions.

Since the experimental methods of NQI investigations are widely practiced, the problem of constructing an effective approximate method of EFG computations in crystals becomes important. The application of the pseudopotential theory to these methods seems to be preferable.

In this case the reaction of core shells to the electric field in matter must be investigated separately. It is usually described by means of the Sternheimer constants  $\gamma$  and  $R$  [7]:

$$V_{zz}^{Nuc} = (1 - \gamma)V_{zz}^{Ext} + (1 - R)V_{zz}^{Unfil}. \quad (1)$$

Here  $V_{zz}^{Ext}$  is the EFG created by external valence electrons and ion cores (lattice component),  $V_{zz}^{Unfil}$  describes the polarization of unfilled shells of the considered ion,  $V_{zz}^{Nuc}$  is the EFG at the nucleus.

There are many papers devoted to the problem of  $\gamma$  computations. The starting points and the results of all of them are different. Values for  $\text{Cu}^+$  are  $-15$  [8],  $-17$  [9] and  $-13.77$  [10]. In the case of  $\text{Cu}^{2+}$  the following values were given:  $-25$  [9] and  $-7.59$  [11].

The majority of theoretical computations are fulfilled within the framework of Hartree–Fock theory. Corrections to wavefunctions have been given either with a straight solution of the inhomogeneous Schrödinger equation [12, 13] or by use of variational perturbation theory [14, 15]. Results, obtained in this way, strongly depend on the type of unperturbed wavefunctions used. Thus, a value  $\gamma = -102.5$  was found for Cs on the basis of Hartree–Fock wavefunctions and  $\gamma = -143.5$  on the basis of Hartree wavefunctions for the same ion [16]. Moreover, results obtained in the framework of variational perturbation theory depend on the flexibility of variation functions [15].

The consideration (coupled Hartree–Fock) or otherwise (uncoupled Hartree–Fock) of self-consistency in the electron–electron interaction plays a significant role in obtaining corrections to wavefunctions. In some papers [17, 18] electron wavefunctions of ions in crystals were obtained within the framework of the Watson sphere approximation [19], because wavefunctions of the external shells may be quite different for free ions and ions in crystals.

Recent papers [17–24] devoted to Sternheimer factor calculations were carried out within the framework of many-body perturbation theory in the spirit of the link-cluster many-body perturbation theory [20].

† The Sternheimer effect demands a high-precision description of small deformations of the close-to-nucleus states. This problem can be relatively easily solved with the perturbation theory method for isolated ions, but meets great difficulties in zone theory methods, which use the basis of Bloch functions.

Thus some works devoted to  $\gamma$  calculations were performed in accordance with Hartree–Fock theory, another calculation was made in the spirit of the Herman–Skillman method [25], and others took into consideration many-electron corrections. The difference in results is caused both by computational details and the starting assumptions.

At the same time, the majority of non-empirical crystal calculations are carried out in the framework of electron density functional theory (DFT) in the local density approximation (LDA). Sternheimer constants, obtained in the same approximation, must be used for constructing a complete theory. Moreover, Sternheimer constants, as a rule, are calculated only for charge states that correspond to chemical valence of ions. The open shells, whose reconstruction in the external field causes the appearance of the second term in (1) were also included in the ion core. However, according to modern pseudopotential theory, electron states of unclosed shells must be treated as the valence ones [26]. It means that in (1) only the first term remains and therefore  $\gamma$  must be recalculated.

In the present work we report the results of calculations of Sternheimer constants, caused by the polarization of the closed shells. These calculations were carried out within the framework of LDF theory both with consideration of the electron–electron interaction and without it. In addition, we discuss the dependence of these constants upon the charge states of ions.

## 2. Model

There are two sources of the polarization of the closed electron shells. The first is the quadrupole nuclear momentum, which creates an appropriate electrical field. The second is the electric field of the environment. A comparison shows that the first source usually can be neglected.

The contribution of the non-spherical component of the nuclear field to the Hamiltonian will be  $\sim Q/r^3$  at a distance  $r$ , and the contribution of the field due to the environment will be  $\sim r^2/A^3$ , where  $A$  is a size of the order of the nuclear distance. For example, for  $^{57}\text{Fe}$ :  $Q \sim 0.14 \text{ b} \sim 0.6 \times 10^{-8} \text{ au}$  [27]† the characteristic value of  $r$  for the M layer, whose contribution to  $\gamma$  is the most important, is  $\sim 0.6$ , and  $A \sim 2.5$ . The ratio of the first contribution to the second is  $\sim 10^{-6}$ .

Let us observe the problem of a many-electron atom (ion), situated in an external field, in the framework of LDA:

$$V_{\text{ext}}(\mathbf{r}) = Ar^2 Y_{20}(\theta, \varphi). \quad (2)$$

Once we are interested in the linear response,  $A$  may be considered as infinitesimal. The problem thus comes down to a search for a self-consistent solution of a system of Kohn–Sham equations [28]:

$$\left(-\frac{1}{2}\Delta + V_c(\mathbf{r}) + V_{xc}(\mathbf{r}) + V_{\text{ext}}(\mathbf{r})\right)\phi_{nlm}(\mathbf{r}) = \varepsilon_{nl}\phi_{nlm}(\mathbf{r}) \quad (3)$$

where

$$V_c(\mathbf{r}) = -\frac{Z}{r} + \int \frac{\delta\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (4)$$

$$\rho(\mathbf{r}) = \sum_{nlm} |\phi_{nlm}(\mathbf{r})|^2 \quad (5)$$

$$V_{xc}(\mathbf{r}) = \delta E_{xc}[\rho(\mathbf{r})]/\delta\rho(\mathbf{r}). \quad (6)$$

† We use atomic units:  $e = \hbar = m_e = 1$ .

Here  $Z$  is the nuclear charge; only occupied states must be summed. There are many approximate expressions for  $E_{xc}[\rho(\mathbf{r})]$ ; they all provide very similar results. Following [26] we use the expression by Ceperley–Alder [29], taking into account relativistic corrections as proposed by MacDonald and Vosko [30].

We solve equation (3) in first-order perturbation theory. For this, we express  $\phi_{nlm} = \phi_{nlm}^{(0)} + \phi_{nlm}^{(1)} + \dots$ , where  $\phi_{nlm}^{(j)}$  is the correction of the  $j$ th order. To first order we have

$$\left(-\frac{1}{2}\Delta + V_0(\mathbf{r}) - \mathcal{E}_{nl}^0\right)\phi_{nlm}^{(1)}(\mathbf{r}) = (\mathcal{E}_{nl}^1 - V_{ext}(\mathbf{r}) - \delta V(\mathbf{r}))\phi_{nlm}^{(0)}(\mathbf{r}) \quad (7)$$

where

$$\begin{aligned} V_0(\mathbf{r}) &= V_c(\mathbf{r}) + V_{xc}(\mathbf{r}) \\ \delta V(\mathbf{r}) &= \int \frac{\delta\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta V_{xc}(\mathbf{r})}{\delta\rho(\mathbf{r})}\delta\rho(\mathbf{r}) \end{aligned} \quad (8)$$

and  $\mathcal{E}_{nl}^1$  is the average of the sum  $V_{ext}(\mathbf{r}) + \delta V(\mathbf{r})$  over unperturbed functions  $\phi_{nlm}^{(0)}$ . Expanding wavefunctions into spherical harmonics we get

$$\phi_{nlm}^{(0)}(\mathbf{r}) = \frac{1}{r} R_{nl}^0 Y_{lm} \quad \phi_{nlm}^{(1)}(\mathbf{r}) = \frac{1}{r} \sum_{l'm'} R_{nl'l'}^1 Y_{l'm'} B_{l'l'}^{mm'}. \quad (9)$$

We will now omit the obvious index  $n$  of the principal quantum number in the designations of wavefunctions. Separating the radial and angular parts of  $\delta\rho(\mathbf{r})$  we get

$$\begin{aligned} \delta\rho(\mathbf{r}) &= A\delta\rho(r)Y_{20}(\theta, \varphi) \\ \delta\rho(r) &= -\frac{1}{r^2} \sum_{l'm'} \frac{N_l}{2l+1} C_{l'l'} R_{l'l'}^1 R_l^0. \end{aligned} \quad (10)$$

Here  $N_l$  is the number of electrons in the  $l$ th shell

$$C_{l'l'} = 2 \sum_{mm'} \langle Y_{l'm'} | Y_{20} | Y_{lm} \rangle^2 \quad (11)$$

the doubled sum of the squares of Gaunt coefficients [31]. Using occupation numbers we can treat those shells with an insufficient quantity of electrons as closed ones in LDF. The coefficients (11) differ from zero only for even values of  $l+l'$  and for  $|l+l'| \leq l' \leq l+2$ .

Using (10) and (11), one can show that the change of potential (8) has the form

$$\delta V(\mathbf{r}) = -Ar^2 \gamma_{eff}(r) Y_{20}(\theta, \varphi) \quad (12)$$

where

$$\gamma_{eff}(r) = \gamma(r) + \gamma_{xc}(r) \quad (13)$$

and Coulomb  $\gamma(r)$  and exchange-correlation  $\gamma_{xc}(r)$  contributions in  $\gamma_{eff}(r)$  can be expressed as

$$\gamma(r) = -\frac{4\pi}{3} \left( \frac{1}{r^3} \int_0^r r'^2 \delta\rho(r') dr' + r^2 \int_r^\infty \frac{1}{r'^3} \delta\rho(r') dr' \right) \quad (14)$$

$$\gamma_{xc}(r) = -\frac{\delta V_{xc}}{\delta\rho(r)} r^{-2} \delta\rho(r). \quad (15)$$

Substituting (9) in (7) and considering the definitions (13)–(15), we see that the radial functions  $R_{l\nu}^1$  satisfy the equation

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l'(l'+1)}{2R^2} + V_0(r) - \mathcal{E}_{nl}^0\right) R_{l\nu}^1(r) = [r^2(1 - \gamma_{eff}(r)) - (r^2(1 - \gamma_{eff}(r)))_{nl} \delta_{l\nu}] R_l^0(r). \quad (16)$$

The symbol  $(\dots)_{nl}$  denotes an average over atomic orbitals  $R_l^0(r)$ , which are the solutions of (16) with zero right-hand side. Sternheimer constants  $\gamma = \gamma(0)$ . In the spin variant of the local density theory we draw a distinction between  $\rho_\uparrow(r)$  and  $\rho_\downarrow(r)$ , which causes the appearance of an additional spin index and the necessity of solving (16) with different  $V_{x\sigma}$  for orbitals with spin  $\sigma$ .

### 3. Computational details

In order to solve (16) we have used the finite-difference approximation of derivatives over the set  $r_i$  of radius  $r$  values. This set must converge to zero for a correct reproduction of the deep core states. We have chosen

$$r_i = C[\exp(\lambda i) - 1] \quad i = 1, \dots, N$$

where the parameters  $\lambda$  and  $C$  are determined by the  $r_1$  bound value  $r_\infty \equiv r_{N+1}$  (whose solution must be zero) and the number of nodes  $N$ . It is clear that one must choose  $r_1 \ll 1/Z$ ,  $r_\infty$  much greater than an atomic radius, and in such circumstances the results do not depend on the value of these parameters. Then (16) reduces to a system of algebraic equations of the following type:

$$(A - \mathcal{E})\bar{R} = \bar{B} \quad (17)$$

for the values of the radial function  $R$  in the nodes of a mesh with the three-diagonal matrix  $A$ . Because the mesh is not equidistant, the matrix  $A$  becomes non-symmetrical. Nevertheless, one can show that there exists a transformation  $L$ , such that  $L^{-1}AL$  is a three-diagonal symmetrical matrix. There are many highly-effective numerical methods for solving problems with such matrices [32]. Radial orbitals obtained in this way prove to be normalized to unity in the sense of a trapezium quadrature formula. Therefore we use this formula in all the calculations of integrals. As our results show, a relative precision of order  $10^{-3}$  for  $\gamma$  can be reached in the case  $N \sim 50$  for every electron layer.

Since the orbitals  $R_l^0$  and  $R_{l\nu}^1$  are included both in the left-hand side of equations via  $V_0(r)$  and in the right-hand side via  $\gamma_{eff}$ , the solution should be found self-consistently in the iteration process. It can be carried out in two stages. In the first stage we solve the standard problem of a free ion, and applying the found orbitals  $R_l^0$  we solve the equation for  $R_{l\nu}^1$  considering  $\gamma_{eff} = 0$  in the right-hand side of (16). We then calculate Sternheimer constants by (14) without considering the self-consistent electron–electron interaction. In order to take into account the effect of the electron–electron interaction on  $\gamma(r)$  and  $\gamma(0)$ , we must carry out the second stage of iteration: self-consistent solving of (16) for  $R_{l\nu}^1$  in which  $\gamma_{eff}$  is determined via (13)–(15). A non-self-consistent value of  $\gamma(r)$  can be treated as  $\gamma(r)$ , which was obtained in the first stage of such iterations. It is natural to use the results of every iteration as the starting value for the next iteration. For the optimization

of iteration convergence, it is convenient to use a linear combination of initial data and the result of the previous step with approximately equal weights.

The following situation must also be observed:  $l' = l$  in (16). In this case the matrix  $(A - \mathcal{E})$  becomes degenerate. As soon as the right-hand side is orthogonal to the appropriate eigenvector, a solution exists. It can be found with sufficient accuracy as the average of solutions (17) with  $\mathcal{E}$  replaced by  $\mathcal{E} \pm \Delta$ , where  $\Delta \sim 10^{-7}$ – $10^{-9}$  (square root from the precision of the performance of real numbers in 8–10 bytes).

#### 4. Results and discussion

The results of calculations of Sternheimer factors for elements with nuclear charge up to  $Z = 94$  are given in table 1. The upper values are calculated in a non-self-consistent manner; the lower ones are self-consistent. We consider the polarization of electron shells from the state  $1s^2$  to the state pointed out in the table. Taking into account these core shells corresponds to the natural chemical valence of such elements as ( $\text{Li}^+$ ,  $\text{Be}^{2+}$ ,  $\text{Mg}^{2+}$ , ...). To define the cores of other elements we use the criteria which are used in constructing the norm-conserving pseudopotentials [26]: we consider as a core all electron shells except external (valence) and unclosed d- and f-shells. In the first case computations can be carried out for the above-mentioned 'chemical' charge states of isolated ions. In the other cases such computations are meaningless because the appropriate degrees of ionization significantly exceed those ones that can be realized in compounds. Core states become closer to the nucleus than in the crystal case. Therefore, we have always calculated electron states of a neutral atom self-consistently, but have considered only core-shell polarization in our  $\gamma(r)$  and  $\gamma_{eff}(r)$  computations. Thus the shells that do not contribute to  $\gamma$  only model the spherically averaged field that they produce in the vicinity of the core in compound. Later we shall discuss the problem of the influence of the ion charge on the obtained Sternheimer factors, but here we notice that the functions  $\gamma(r)$  and  $\gamma_{eff}(r)$  display a strong space dispersion, which reflects the shell structure of ion.

The Sternheimer factors gathered in table 1, calculated without taking into account the changes of the potential of the electron–electron interaction, which are due to the electron cloud polarization  $\delta V(r)$ , are similar to the values given in [15, 22], despite the difference between the approximations used in these works and the LDA. However, we cannot say the same about the self-consistent factors (i.e. factors obtained without neglecting  $\delta V(r)$ ).

Some papers report that a weak influence of the electron–electron interaction on  $\gamma$  values is about 1% for Rb and Cs [21] and self-consistency changes the factors by not more than 15–20% in all cases [17]. Our results do not confirm these inferences. In the case of Rb and Cs, self-consistency, as shown in table 1, changes  $\gamma$  values by 13–15%. The influence of self-consistency on He and the elements of the second row of the periodic table is not significant ( $\sim 1$ –2%). This influence increases with row number and reaches 20–25% for closed d-shells. As one can see in table 1, the influence of the electron–electron interaction is a maximum for Tl and Hg (i.e. when the external core shell is 5d), reaching 35% and 41% accordingly.

Table 2 illustrates the dependence of Sternheimer factors of several ions on their charge states. We consider the polarization of the same shells that are specified in table 1. The values obtained from a self-consistent process are shown in brackets. These results show that the change in factors due to the change of ion charge is insignificant and, as a rule, can be neglected. In computations that are carried out for higher ion charges and which aspire to a quantitative description of experiments, this dependence, of course, must be taken into

Table 1. Sternheimer constants of chemical elements.

| State     | Element |       |       |       |       |       |        |        |        |
|-----------|---------|-------|-------|-------|-------|-------|--------|--------|--------|
|           | He      | Li    | Be    | B     | C     | N     | O      | F      | Ne     |
| $1s^2$    | 0.439   | 0.266 | 0.192 | 0.149 | 0.122 | 0.104 | 0.0899 | 0.0794 | 0.0711 |
|           | 0.428   | 0.262 | 0.189 | 0.148 | 0.121 | 0.103 | 0.0892 | 0.0788 | 0.0706 |
| $2p^6$    | Ne      | Na    | Mg    | Al    | Si    | P     | S      | Cl     | Ar     |
|           | -10.7   | -5.91 | -3.95 | -2.88 | -2.25 | -1.83 | -1.54  | -1.33  | -1.16  |
|           | -10.1   | -5.59 | -3.76 | -2.76 | -2.17 | -1.78 | -1.50  | -1.29  | -1.13  |
| $3p^6$    | Ar      | K     | Ca    | Sc    | Ti    | V     | Cr     | Mn     | Fe     |
|           | -33.3   | -22.1 | -16.4 | -14.3 | -12.9 | -11.8 | -11.6  | -10.3  | -9.67  |
|           | -32.1   | -21.0 | -15.5 | -13.6 | -12.2 | -11.2 | -11.0  | -9.77  | -9.20  |
|           | Co      | Ni    | Cu    | Zn    |       |       |        |        |        |
|           | -9.15   | -8.69 | -8.66 | -7.92 |       |       |        |        |        |
|           | -8.72   | -8.30 | -8.28 | -7.58 |       |       |        |        |        |
| $3d^{10}$ | Zn      | Ga    | Ge    | As    | Se    | Br    | Kr     |        |        |
|           | -16.7   | -12.3 | -9.99 | -8.52 | -7.47 | -6.66 | -6.02  |        |        |
|           | -9.88   | -9.03 | -7.97 | -7.09 | -6.39 | -5.81 | -5.32  |        |        |
| $4p^6$    | Kr      | Rb    | Sr    | Y     | Zr    | Nb    | Mo     | Tc     | Ru     |
|           | -85.4   | -59.9 | -46.0 | -39.4 | -35.0 | -33.1 | -30.4  | -27.0  | -26.3  |
|           | -73.8   | -52.3 | -40.4 | -34.8 | -31.1 | -29.5 | -27.2  | -24.3  | -23.7  |
|           | Rh      | Pd    | Ag    | Cd    |       |       |        |        |        |
|           | -24.7   | -24.1 | -22.2 | -20.4 |       |       |        |        |        |
|           | -22.4   | -21.9 | -20.2 | -18.6 |       |       |        |        |        |
| $4d^{10}$ | Cd      | In    | Sn    | Sb    | Te    | I     | Xe     |        |        |
|           | -35.0   | -28.9 | -25.0 | -22.1 | -19.9 | -18.1 | -16.7  |        |        |
|           | -24.4   | -21.9 | -19.9 | -18.1 | -16.7 | -15.4 | -14.3  |        |        |
| $5p^6$    | Xe      | Cs    | Ba    |       |       |       |        |        |        |
|           | -162.   | -120. | -95.0 |       |       |       |        |        |        |
|           | -138.   | -103. | -81.2 |       |       |       |        |        |        |
| $4d^{10}$ | La      | Ce    | Pr    | Nd    | Pm    | Sm    | Eu     | Gd     | Tb     |
|           | -13.3   | -12.8 | -12.7 | -12.3 | -11.9 | -11.6 | -11.3  | -10.8  | -10.7  |
|           | -11.7   | -11.3 | -11.2 | -10.9 | -10.6 | -10.3 | -10.1  | -9.70  | -9.63  |
|           | Dy      | Ho    | Er    | Tm    | Yb    | Lu    |        |        |        |
|           | -10.4   | -10.2 | -9.98 | -9.77 | -9.57 | -9.26 |        |        |        |
|           | -9.42   | -9.22 | -9.04 | -8.86 | -8.69 | -8.43 |        |        |        |
| $5p^6$    | Hf      | Ta    | W     | Re    | Os    | Ir    | Pt     | Au     | Hg     |
|           | -68.3   | -62.6 | -58.0 | -54.1 | -50.9 | -48.1 | -47.0  | -44.8  | -41.5  |
|           | -60.4   | -55.3 | -52.0 | -48.9 | -45.9 | -43.4 | -42.5  | -40.5  | -37.6  |
| $5d^{10}$ | Hg      | Tl    | Pb    | Bi    | Po    | At    | Rn     |        |        |
|           | -69.9   | -59.0 | -51.9 | -46.6 | -42.4 | -39.0 | -36.2  |        |        |
|           | -40.9   | -38.9 | -36.6 | -34.3 | -32.2 | -30.4 | -28.7  |        |        |
| $6p^6$    | Rn      | Fr    | Ra    | Ac    | Th    | Pa    | U      | Np     | Pu     |
|           | -294.   | -222. | -179. | -157. | -142. | -148. | -145.  | -142.  | -151.  |
|           | -249.   | -188. | -151. | -133. | -119. | -125. | -123.  | -120.  | -129.  |

account. In the case of Gd, however, this dependence is absent. For Gd all 18 electrons, which belong to 4f, 5s, 5p, 5d and 6s shells must be considered as the non-core ones, and a relatively small change in their value does not influence the strongly coupled core states. Naturally, in similar cases the dependence of antishielding factors on the ion charge states is not essential.



Table 2. The dependence of the Sternheimer factors of some ions on their charge states.

| Z  | Y             | Gd            | Fe            | Cu            |
|----|---------------|---------------|---------------|---------------|
| 0  | -34.8 (-39.4) | -9.70 (-10.8) | -9.20 (-9.67) | -8.28 (-8.66) |
| +1 | -34.0 (-38.6) | -9.70 (-10.8) | -9.16 (-9.62) | -8.30 (-8.69) |
| +2 | -32.5 (-37.0) | -9.70 (-10.8) | -9.04 (-9.50) | -8.21 (-7.84) |
| +3 | -28.9 (-33.0) | -9.70 (-10.8) | -8.24 (-8.56) | —             |

Table 3. The contribution of the electronic shells of Fe ions to Sternheimer constants.

| Shell | Fe     | Fe <sup>+</sup> | Fe <sup>2+</sup> | Fe <sup>3+</sup> |
|-------|--------|-----------------|------------------|------------------|
| 1s    | 0.0979 | 0.0949          | 0.0939           | 0.0878           |
| 2s    | 0.0594 | 0.0591          | 0.0589           | 0.0567           |
| 3s    | 0.144  | 0.144           | 0.144            | 0.140            |
| 2p    | -0.337 | -0.338          | -0.338           | -0.332           |
| 3p    | -9.16  | -9.12           | -9.00            | -8.20            |
| Total | -9.20  | -9.16           | -9.04            | -8.24            |

As mentioned above, the main contribution to Sternheimer factors comes from the outermost core shells. In table 3 the contributions of several shells to the values of self-consistent antishielding constants of Fe ions are displayed.

## 5. Conclusions

(1) Sternheimer factors of core shells have been found in the framework of LDF theory. As in modern pseudopotential theory, only entirely closed shells have been classified as core shells. Therefore, the accepted values can be used in computations of the EFG at nuclei, which are based on non-empirical calculations of only the valence electron density distribution.

(2) The influence of the electron-electron interaction upon shielding constants has been investigated. It changes from a few per cent (for the ions of the first and second rows of the periodic table) to 30–40% (in the case of d external shells).

(3) Information about the dependence of Sternheimer factors upon the charge states of ions has been reported.

## Acknowledgments

This work was supported by the International Science Foundation (through grant #U1G000), and by the International Soros Scientific and Educational Program (through grant #GSU042069).

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