Sternheimer shielding using various approximations

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Sternheimer shielding functions $\gamma(r)$ are derived by means of Sternheimer's procedure for a series of elements (Li, Na, K, Rb, F, Cl, Br, I, Cu, Fe, Ag, and Pr) with varying electronic configurations, with and without valence electrons, which are generally included in molecular-orbital calculations with a limited basis set. Direct and exchange contributions to $R = \langle \gamma(r) r^{-3} \rangle / \langle r^{-3} \rangle$ are presented, and the various contributions to $\gamma(r)$ due to angular and radial excitations are discussed. The discrepancy in R values for halides compared to Sternheimer's values is due mainly to an exchange contribution to R which has been omitted by Sternheimer. Self-consistent calculations of $\gamma(r)$ have been performed with and without $X\alpha$ exchange interaction. The general tendency of self-consistent γ_∞ [$= \lim_{r \to \infty} \gamma(r)$] results is that direct Coulomb interaction leads to γ_∞ values more positive than those derived from Sternheimer's procedure (noniterative and excluding exchange interaction), while exchange interaction partly balances this effect. The overall effect in the case of iron is that Sternheimer's value is nearly identical to our self-consistent γ_∞ value including exchange contributions. Self-consistency was obtained only for neutral atoms and positive ions. However, no such self-consistency was obtained for negative ions. Thus the X_α approximation is not very appropriate for the present purpose of calculating $\gamma(r)$ for elements with varying electronic configurations.

I. INTRODUCTION

We have been motivated to calculate Sternheimer shielding functions $\gamma(r)$ by our work on the molecular-orbital (MO) interpretation of experimental quadrupole splittings. In MO or band calculations, which include only valence orbitals within the MO basis set, the electron core of the isotope under study becomes polarized by valence electrons by over-lap or by ligand charges. The amount of polarization depends on $\gamma(r)$ and accounts for shielding [$\gamma(r) > 0$] or antishielding [$\gamma(r) < 0$] effects in deriving the quadrupole coupling constant $e^2 Qq$; e is the elementary charge, Q is the nuclear quadrupole moment, and q is the electric field gradient (EFG) at the nucleus of the isotope. Most of the work with respect to these shielding and antishielding corrections has been reported by Sternheimer,[1-9] therefore these corrections are also termed "Sternheimer corrections." Other workers have contributed to this field, either by using different methods in deriving $\gamma(r)$ (variational method,[10-13] many-body calculations,[14-19]) or by applying Sternheimer's method to specific isotopes.[20-24] Unfortunately most of the publications report only factors R and γ_∞ [for a definition see Eq. (4)], or even only γ_∞. We show below that the appropriate shielding and antishielding corrections of the calculated EFG by MO or band methods require $\gamma(r)$ rather than R and γ_∞ only. Moreover, the required $\gamma(r)$ functions correspond to electronic configurations which exclude the valence orbitals because their contribution to the EFG is already taken care of by the MO's. In Sec. II we follow Sternheimer's method and calculate $\gamma(r)$ for sev-

eral elements, ions, and electronic configurations. In Sec. III we introduce the self-consistency concept and discuss the applicability of the X_α approximation for the exchange interaction in deriving self-consistent $\gamma(r)$ functions.

II. STERNHEIMER METHOD FOR CALCULATING $\gamma(r)$ AND R

A. Physical concept

Sternheimer's procedure for calculating shielding and antishielding corrections of quadrupole coupling constants[2-9] is based on a first-order perturbation treatment of the Schrödinger equation

$$(\mathcal{H}_0 + \mathcal{H}_1 + \mathcal{H}_2)(\psi_0 + \psi_1 + \psi_2) = (E_0 + E_1 + E_2)(\psi_0 + \psi_1 + \psi_2) , \tag{1}$$

with

$$E_i = \langle \psi_0 | \mathcal{H}_i | \psi_0 \rangle , \quad i = 0, 1, 2 .$$

$\mathcal{H}_0$ and ψ_0 describe the electronic structure of the unperturbed system (free atom or ion), while $\mathcal{H}_1$ and $\mathcal{H}_2$ represent the perturbation of the electronic structure by the nuclear quadrupole moment Q and an external charge, respectively. ψ_1 and ψ_2 are the first-order contribution to the wave function. Separation of first-order terms in Q and $1/r^3$ in Eq. (1), with r being the distance of the external charge with respect to the atom or ion under consideration, leads to

$$(\mathcal{H}_0 - E_0)\psi_1 = -(\mathcal{H}_1 - E_1)\psi_0 , \tag{2a}$$

$$(\mathcal{H}_0 - E_0)\psi_2 = -(\mathcal{H}_2 - E_2)\psi_0 . \tag{2b}$$

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The two equations [Eqs. (2a) and (2b)] give the same physical result, only using two different concepts. Equation (2a) describes the perturbation of the spherically symmetric electron charge distribution $|\psi_0|^2$ due to the nuclear quadrupole moment, which produces an induced quadrupole moment Q_{ind} within the electronic shell; the total quadrupole coupling constant is then $e^2(Q+Q_{ind})q$. Equation (2b), on the other hand, describes the perturbation of the spherically symmetric electron charge distribution $|\psi_0|^2$ due to the electric field gradient (EFG) of the external charge, which leads to an induced electric field gradient q_{ind} within the electronic shell; the total quadrupole coupling constant then takes the form $e^2Q(q+q_{ind})$. Sternheimer has shown[8] that both Q_{ind} and q_{ind} include the same proportionality factor $-R^*$, leading to

$$e^2(Qq)_{total}=e^2(Q-QR^*)q=e^2Q(q-qR^*). \qquad (3)$$

From Eq. (3) it follows that Eqs. (2a) and (2b) lead to the same result.

The proportionality factor R^* depends on $\gamma(r)$ by the relation[7]

$$R^*=\langle\gamma(r)\gamma^{-3}\rangle/\langle r^{-3}\rangle, \qquad (4)$$

and hence R^* depends on the distance of the "external" charge from the nucleus under consideration. If the external charge, which produces the EFG q, is a valence electron, then the expectation values in Eq. (4) are derived using the wave function of this valence electron; in this case R^* is denoted by R. If the external charge is far away from the atom or ion under study, $\gamma(r)$ becomes constant and takes the value γ_∞; then R^* reduces to $R^*=\gamma_\infty$.

Assuming that the EFG at the nuclear site of an isotope within a molecule is produced by the valence electrons of the isotope (q_{val}) and additionally by the ligand charges surrounding it (q_{lig}), then the effective EFG is derived[13] according to

$$q_{eff}=(1-R)q_{val}+(1-\gamma_\infty)q_{lig}. \qquad (5)$$

Equation (5) neglects the fact that overlap charges $\langle\phi_a\phi_b\rangle$ between the isotope a and the ligands b contribute in a more sophisticated way to q_{eff} than by simply dividing $\langle\phi_a\phi_b\rangle$ according to a Mulliken population analysis. A better description for $q_{overlap}$ would be[25]

$$q_{overlap}=\int\phi_a[1-\gamma(r)]\hat{q}\,\phi_b\,d\Omega, \qquad (6)$$

where $\hat{q}$ is the electric-field-gradient operator, and where ϕ_a and ϕ_b are the valence orbitals of the isotope and the ligand atom, respectively. Equation (6) indicates that for the evaluation of $q_{overlap}$, the Sternheimer function $\gamma(r)$ has to be known explicitly. As a further argument for the

importance of the knowledge of $\gamma(r)$ for calculating the overall EFG, in the case of heavy isotopes $\gamma(r)$ might not yet have reached its saturation value γ_∞ for interatomic distances of the order 2 or 3 Å. Since in the literature only R and γ_∞ values have been reported [besides[5] $\gamma(r)$ for Cu^+, Cl^-, Rb^+, and Cs^+], we became motivated to calculate $\gamma(r)$ for various atoms and ions. A further motivation for this work has been the necessity of having $\gamma(r)$ and R for the atomic cores only, which are not included within the atomic orbital (AO) basis set for molecular-orbital (MO) calculations. For example, evaluating q_{eff} from MO cluster calculations including Fe $3d$, $4s$, $4p$ AO's for the ferrous ion the relevant Sternheimer function $\gamma(r)$ and factor R have to be derived from the Fe ($1s^2\cdots3p^6$) core rather than from the Fe ($1s^2\cdots3p^63d^5$) core, because the EFG contributions from $3d$ electrons are already included in q_{val}, and the correction $-Rq_{val}$ is only due to the Fe ($1s^2\cdots3p^6$) core.

We followed Sternheimer's procedure in solving Eq. (2a) and in deriving[7] $\gamma(r)$ as

$$\gamma(r)=\sum_{l,l'}C_{ll'}\left(\int_0^r u_{0,l}(r')u_{1,l'}(r')r'^2\,dr'\right.$$
$$\left.+r^5\int_r^\infty\frac{u_{0,l}(r')u_{1,l'}(r')}{r'^3}dr'\right), \qquad (7)$$

where $(1/r)u_{0,l}$ and $(1/r)u_{1,l'}$ are the radial parts of the unperturbed and perturbed part of atomic orbitals, respectively. The $u_{1,l'}(r')$ are derived from the radial part of Eq. (2a). The orbital angular momenta $l\neq l'$ and $l=l'$ describe the appropriate "radial" and "angular excitations" of the atomic orbitals (which were Clementi Hartree-Fock (HF) functions in the present study), due to the perturbation $\mathcal{H}_1$. The coefficients $C_{ll'}$ result from the angular part of Eq. (2a). The numerical procedure[26] in solving Eq. (2a) was slightly different compared to that used by Sternheimer. With the transformation $X=r/(n+r)$ the integration interval in Eq. (7) goes from $[0,\infty]$ to $[0,1]$; 50% of the points are within the r interval $[0,n]$, and the other 50% are within $[n,\infty]$. We varied n from 1 to 3, increased the number of points up to 1440, used various approximations for the integrals (up to seven-point formulas), and neglected areas where u_0 was smaller than 10^{-4}. With $n=3$, for example, the increase of points from 720 to 1440 did not affect $\gamma(r)$ significantly. Details of the calculational procedure are described elsewhere.[26] The calculations we have performed include Li^0, Na^0, K^0, Rb^0, Li^+, Na^+, K^+, Rb^+, F^0, Cl^0, Br^0, I^0, F^-, Cl^-, Br^-, I^-, Cu^0, Cu^+, Fe^0, Fe^{2+}, Fe^{3+}, Ag^0, and Pr^{3+} (some of them with and without valence electrons). [The

reader who is interested in detailed numerical values for $\gamma(r)$ may ask the authors for a supplement to this publication.]

B. $\gamma(r)$ results

As already shown in the literature[4,8] the "angular excitations" $nl \to l'$ ($l \neq l'$) contribute to $\gamma(r)$ with relatively small positive values while the "radial excitations" $nl \to l$ (especially the outer $p \to p$ excitations) contribute with much larger but negative values. Therefore the γ_∞ factor for light atoms (Li, Na, and F) is relatively small (positive or negative) compared with the large and negative γ_∞ factors of heavier atoms (Br, and I). In a series of elements with similar electronic configuration therefore a tendency is that γ_∞ becomes more negative with increasing atomic number, i.e., with increasing number of p electrons (Fig. 1). The values in Fig. 1 are in good agreement with those reported in the literature; only the γ_∞ value for I^- (−254) deviates from values given elsewhere, −138 (Ref. 8) and −39 (Ref. 27). This deviation is due to the use of different basis functions $u_{0,l}$. Since the main contribution to $\gamma_\infty(I^-)$ comes from the $5p \to p$ excitation ($\gamma_\infty^{5p \to p} = -238$), it is obvious that slight modifications within I^- $5p$ wave functions lead to significant changes in $\gamma_\infty(I^-)$.

In Fig. 2(a) we show $\gamma(r)$ for Cu^+ which is in good agreement with Sternheimer's result.[5] Similar $\gamma(r)$ curves are found for the other atoms and ions presently under study; in Figs. 2(b) and 2(c) we present as examples the results for Na^+ and $Fe^{3+(2+)}$. The general tendency that $\gamma(r)$ is positive for small r values ($r \lesssim 1$ a.u.) reflects the dominant positive contributions to $\gamma(r)$ due to inner angular excitations in this range.

The shape of $\gamma(r)$ for elements with outer s electrons deviates to some extent from $\gamma(r)$ for elements which do not have an outer s electron. This is illustrated by Fig. 3(a), which represents $\gamma(r)$
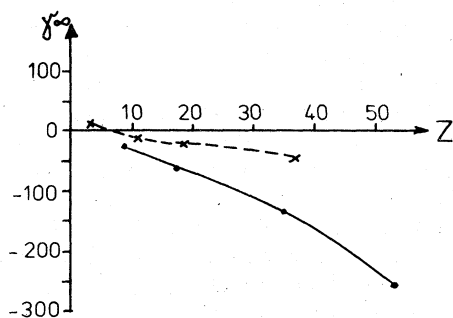
for Na^0. Comparing Fig. 3(a) (Na^0) with Fig. 2(b) (Na^+) one realizes that $\gamma^{Na^0}(r)$ at about 3 a.u. becomes more negative than the γ_∞ value. This minimum in $\gamma(r)$ is due to the considerable positive contribution to $\gamma(r)$ from the $3s \to d$ angular excitation for large r values, which to some extent compensates the dominant negative contribution from the $2p \to p$ radial excitation. In Fig. 3(b) we show the contributions to $\gamma^{Na^0}(r)$ due to various angular and radial excitations.

In connection with the MO interpretation of nuclear quadrupole coupling constants we were also interested in Sternheimer shielding functions of atomic cores which do not include the valence or-
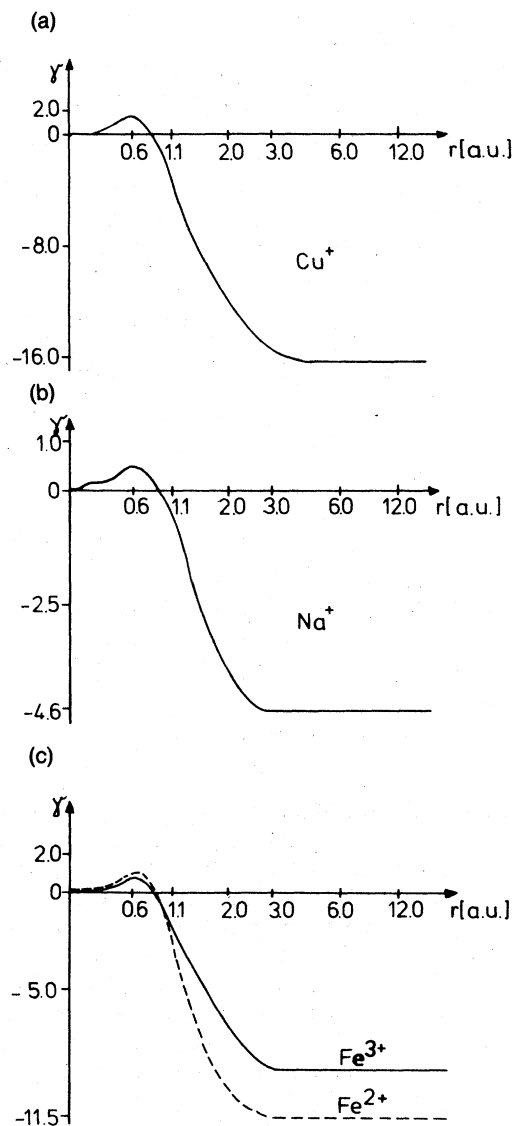

FIG. 1. Sternheimer shielding factor γ_∞ depending on the atomic number Z of elements. (×) Li^0, Na^0, K^0, Rb^0; (●) F^-, Cl^-, Br^-, I^-.

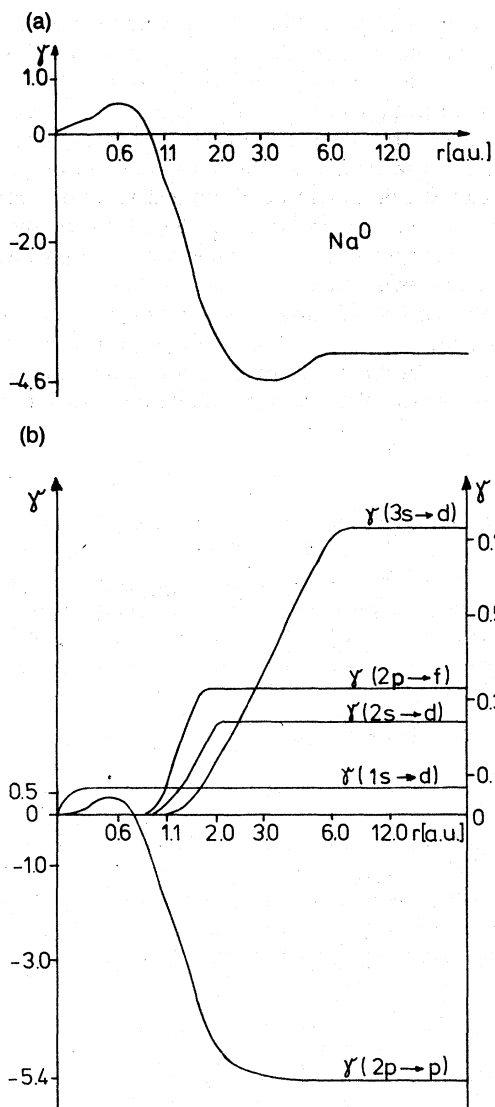FIG. 2. Sternheimer shielding function $\gamma(r)$ for (a) Cu^+, (b) Na^+, (c) Fe^{3+} (solid line), and Fe^{2+} (dashed line).

FIG. 3. Sternheimer shielding function $\gamma(r)$ (a) for Na^0, (b) for the various angular and radial excitations in Na^0. [Note the different scale for γ $(2p \rightarrow p)$].

FIG. 4. Sternheimer shielding function $\gamma(r)$ for Fe^{3+} (solid line) and Fe^{2+} (dashed line) derived after neglecting $3d \rightarrow d$ radial and $3d \rightarrow s$, $3d \rightarrow g$ angular excitations. These $\gamma(r)$ curves may be used for EFG core corrections of MO results if Fe $3d$ AO's are part of the basis set of the MO calculations.

bitals entering the MO basis set. The procedure was simply to neglect the contributions to $\gamma(r)$ due to the valence orbitals. In the case of iron, where the $3d$ valence orbitals would be part of a cluster for MO calculations, the relevant core corrections of the EFG at the nuclear site of iron $[-Rq_{val}$, $-\gamma_\infty q_{11g}$, $\int_a(1 - \gamma(r)\hat{q}\,\phi_b\,d\Omega]$ from Eqs. (5) and (6) would be derived by neglecting the contributions to $\gamma(r)$ due to the $3d \rightarrow d$ radial excitation and the $3d \rightarrow s$ and $3d \rightarrow g$ angular excitations. The resulting $\gamma(r)$ curves for Fe^{2+} and Fe^{3+} (without $3d$ excitations) are drawn in Fig. 4. In the case of halides the change of $\gamma(r)$ by including or neglecting the outer s and p excitations is drastic as il-
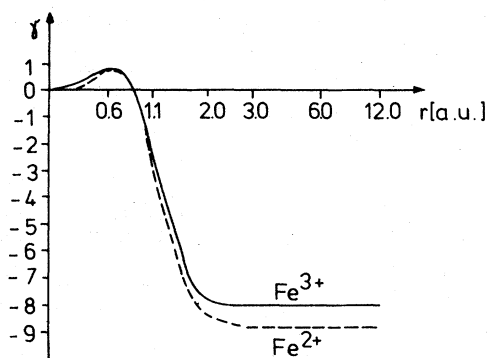
lustrated by the γ_∞ values given in Table I; this is due to the large and negative contributions from outer $p \rightarrow p$ radial excitations.

C. R results

R is derived from Eq. (4) using a valence orbital (in the case of Fe^{2+}: Fe $3d$ AO) for calculating the expectation values $\langle \gamma(r)r^{-3} \rangle$ and $\langle r^{-3} \rangle$. This R value, however, does not include the contributions due to the exchange interaction of the excitation $nl \rightarrow l'$ with the valence electron. Therefore we distinguish two different contributions to R. The "direct contribution" (R_D) is identical to that derived from Eq. (4), and the other represents the exchange effect (R_E)

$$R = R_D + R_E. \tag{8}$$

Sternheimer has discussed extensively[8,9] the influence of exchange interaction upon R. We repeated his calculations and found some deviations from his results: The exchange interaction between the $m = 0$ hole and the $m = 0$ electron within the p valence shell is zero; it takes however, a finite value concerning the exchange between the $m = 0$ electron of the p valence shell and the $m = 0$ electrons of the core. Comparable arguments hold for the direct Coulomb interaction. Therefore a series of R_D and R_E coefficients are different for the valence-valence interaction compared to the valence-core interaction (Table II). Sternheimer has omitted these differences and used the R_D and R_E coefficients of the first column in Table II throughout.[28-31] (If we recalculate our R values under the same condition we derive results close to Sternheimer's.) Since F^0 has no inner p orbitals the second column of Table II does not enter the calculations in this case; therefore it is evi-

TABLE I. Sternheimer shielding factors γ_∞ for neutral and negative halides with and without the contributions due to ns, np valence orbitals.

Element	Present work		Literature	
	Neutral atom	Negative ion	Neutral atom	Negative ion
F	−7.1	−22.3	−8.51 [b]	−22.5 [c]
Cl	−25.4 (−1.2) [a]	−55.4 (−1.2) [a]	−30.14 [b]	−46.5 [d] −57.1 [e]
Br	−66.0 (−6.2) [a]	−133.0 (−6.2) [a]	−78.36 [b]	−123.0 [c]
I	−136.0 (−16.9) [a]	−254.0 (−16.7) [a]		−138.4 [e] −396.1 [f]
				(−16.8) [a,f]

[a] Values in parentheses correspond to electronic configuration excluding ns, np valence orbitals.
[b] Reference 28.
[c] R. M. Sternheimer, Phys. Rev. <u>132</u>, 1637 (1963).
[d] Reference 5.
[e] Reference 8.
[f] Reference 27.

dent that ours and Sternheimer's $R(F^0)$ values have to be comparable (0.0805 and 0.10075, respectively). For Cl^0 and Br^0, however, our R values deviate considerably from Sternheimer's: $R(Cl^0)$ $= -0.078$, $R(Br^0) = -0.114$ (this work), $R(Cl^0)$ $= +0.043$, and $R(Br^0) = +0.004$ (Ref. 28).

In Table III we summarize our results for B^0, F^0, Cl^0, Br^0, I^0, Fe^{2+}, and Pr^{3+} and compare them with values from the literature. For Fe^{2+} and I^0 we tabulate the various contributions to R, thus one can calculate MO-relevant R values for Fe $3p^6$ and I $4d^{10}$ configurations by omitting contributions $3d \rightarrow s,d,g$ and $5s \rightarrow d$, $5p \rightarrow p,f$, respectively. Our R value for Pr^{3+} deviates from the values reported in the literature.[24] These deviations are not due to the arguments mentioned above, be-

cause the electronic configuration of Pr^{3+} is $4f^2$. The deviations are due to the use of different wave functions $u_{0,l}$ (in the present work Hartree-Fock wave functions reported by Synek and Timmons[32] have been used), which illustrates that R values significantly depend on the choice of $u_{0,l}$.

III. SELFCONSISTENT CALCULATIONS OF $\gamma(r)$

A. Procedure

In the following we discuss the self-consistent solution[33,34] of the perturbed Schrödinger Eq. (2a). Because we are also interested in directly taking care of exchange interactions, we start from the X_α Hartree-Fock equation (in a.u.)

TABLE II. R_D and R_E coefficients [a] for valence-electron–valence-electron interaction and valence-electron–core interaction in the case of elements with p^5 configuration.

Coefficients		Valence-valence [b]	Valence-core [c]
R_D	$c(p \rightarrow p)$	$\frac{16}{25}$	$\frac{48}{25}$
	$c(p \rightarrow f)$	$\frac{288}{175}$	$\frac{72}{25}$
R_E	$c(p \rightarrow p;p;L=0)$	0	4
	$c(p \rightarrow p;p;L=2)$	$-\frac{12}{25}$	$\frac{4}{25}$
	$c(p \rightarrow f;p;L=2)$	$\frac{144}{175}$	$\frac{36}{25}$

[a] R_D and R_E coefficients were calculated from

$$c_D(nl \rightarrow l') = 8 \sum_{m=-l}^{l} [C_0^{(2)}(lm;l'm)]^2,$$

$$c_E(nl \rightarrow l';p;L) = 4 \sum_{m=-l}^{l} \frac{c_0^{(2)}(lm;l'm)c_0^{(L)}(lm;pm_p)c_0^{(L)}(l'm;pm_p)}{c_0^{(2)}(pm_p;pm_p)},$$

where p and m_p are the orbital and the magnetic quantum number of the valence electron (Ref. 8).
[b] Summation over $m=0$ in (a) omitted.
[c] Summation over $m=0$ in (a) included.

$$\left[-\tfrac{1}{2}\vec{\nabla}_j^2 - \frac{Z}{r} + \int \frac{\rho_0(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}' - 3\alpha\left(\frac{3}{8\pi}\rho_0(r)\right)^{1/3}\right]\psi_{0,j}(\vec{r}) = E_{0,j}\psi_{0,j}(\vec{r}).$$ (9)

Introducing perturbation $\mathcal{H}_1$, we derive (see Appendix):

$$(\mathcal{H}_{0,j} - E_{0,j})u_{1,j}(r) = \frac{u_{0,j}(r)}{2r^3}\left[1 - \gamma(r) + r^3\left(\frac{3}{8\pi}\rho_0(r)\right)^{1/3}\alpha\frac{2\Delta V(r)}{\rho_0(r)} - r^3\langle r^{-3}\rangle\delta_{ll'} + r^3\left\langle\frac{\gamma(r)}{r^3}\right\rangle\delta_{ll'}\right.$$
$$\left. - r^3\left\langle\left(\frac{3}{8\pi}\rho_0(r)\right)^{1/3}\alpha\frac{2\Delta V(r)}{\rho_0(r)}\right\rangle\delta_{ll'}\right].$$ (10)

TABLE III. Sternheimer shielding factors R and their direct (R_D) and exchange (R_E) contributions. For Fe^{2+} and I^0 additionally the various contributions to R due to different angular and radial excitations are included.

Element	Excitations	$10^2 R_D$ [a]	$10^2 R_E$ [a]	$10^2 R$ [a]	$10^2 R$
B^0		+14.169	−9.104	+5.029	+4.80 [b]
F^0		+10.000	−1.944	+8.055	+10.07 [b]
Cl^0		+3.891	−11.675	−7.779	+4.30 [b]
Br^0		−1.452	−9.968	−11.420	+0.42 [b]
I^0	$1s \to d$	1.133	−0.616	0.517	
	$2s \to d$	0.211	−0.017	0.194	
	$3s \to d$	0.116	−0.005	0.111	
	$4s \to d$	0.082	−0.009	0.073	
	$5s \to d$	0.099	−0.111	−0.012	
	$2p \to f$	0.485	−0.147	0.338	
	$3p \to f$	0.256	−0.049	0.207	
	$4p \to f$	0.218	−0.028	0.190	
	$5p \to f$	0.049	−0.024	0.025	
	$3d \to g$	0.297	−0.034	0.264	
	$3d \to s$	−0.049	0.022	−0.027	
	$4d \to g$	0.270	−0.026	0.244	
	$4d \to s$	0.151	−0.055	0.096	
	$2p \to p$	−0.246	−2.441	−2.687	
	$3p \to p$	−1.761	−2.947	−4.708	
	$4p \to p$	−5.211	−6.539	−11.750	
	$5p \to p$	2.289	1.716	4.005	
	$3d \to d$	−0.460	0.012	−0.448	
	$4d \to d$	−1.751	0.893	−0.858	
	Total	−3.8	−10.4	−14.2	
Fe^{2+}	$1s \to d$	2.719	−0.116	2.603	
	$2s \to d$	4.807	−1.382	3.425	
	$3s \to d$	2.129	−0.827	1.302	
	$2p \to f$	7.054	−1.609	5.445	
	$3p \to f$	3.542	−1.388	2.154	
	$3d \to g$	1.940	···	1.940	
	$3d \to s$	−0.982	···	−0.982	
	$2p \to p$	−35.512	26.618	−8.894	
	$3p \to p$	20.694	−19.190	1.504	
	$3d \to d$	4.127	···	4.127	
	Total	+10.518	+2.106	+12.624	+12.10 [c] +11.90 [d]
Pr^{3+}		−1.36	+8.18	+6.82	+13.08 [c] +11.83 [d]

[a] This work.
[b] Reference 28.
[c] Reference 8.
[d] Reference 24.

Starting the calculation, the function $\gamma(r)$ is set equal to zero and $u_{1,l'}$ is derived from Eq. (10). $\gamma(r)$, in zeroth iteration $[\gamma^0(r)]$, then follows from Eq. (7). Inserting $\gamma^0(r)$ in Eq. (9) leads to $u_{1,l'}$ from the first iteration and this through Eq. (7), to $\gamma^{(1)}(r)$. Self-consistency is obtained when $\gamma^{(n)}(r)$ and $\gamma^{(n+1)}(r)$ are practically equal (within 0.1%). Taking $\alpha = 0$ Eq. (10) reduces to the self-consistent solution of the perturbed Schrödinger equation as has been used by Sternheimer[8] to calculate $\gamma^{(1)}(r)$. In the present study we went to real self-consistency, which was obtained within ten iterations.

B. Self-consistent $\gamma(r)$ results without exchange

The general tendency of self-consistent $\gamma(r)$ results is that γ_∞ becomes more positive, in the case of I^- for example, γ_∞ changes from $\gamma_\infty^{(0)} = -254$ to $\gamma_\infty^{(10)} = -209$; in the case of $Fe^{2+(3+)}$ from $\gamma_\infty^{(0)} = -11.51$ (-9.44) to $\gamma_\infty^{(10)} = -7.57$ (-7.26), and in the case of Cl^- from $\gamma_\infty^{(0)} = -55.3$ to $\gamma_\infty^{(10)} = -44.3$. Because Sternheimer calculated $\gamma^{(n)}(r)$ only up to $n = 1$ for Cl^-, we can only compare $\gamma_\infty^{(0)}$ and $\gamma_\infty^{(1)}$: $\gamma_\infty^{(1)} = -42.1$ from the present study, and $\gamma_\infty^{(1)} = -45.9$ ($\gamma_\infty^{(0)} = -57.1$) from Ref. 8.

In addition the shape of $\gamma(r)$ is modified (see, for example, Fig. 2(c) and Fig. 5 for $Fe^{2+(3+)}$). These changes are explained by the fact that without iterative procedure the perturbation $u_{1,l'}^{(0)}$ of the orbital wave functions is only due to the nuclear quadrupole moment, while in the self-consistent procedure ($n > 0$) the perturbation $u_{1,l'}^{(n)}$ additionally contains the mutual polarization of perturbed orbitals. This higher-order polarization effect may even become dominant over the zeroth-order polarization effect, which is illustrated by the $\gamma^{(0)}(r)$ and $\gamma^{(10)}(r)$ curves for Ag^0 in Fig. 6. The perturbation of the Ag $5s^1$ electron by the induced quadrupole moment Q_{ind} of the elec-

FIG. 6. Sternheimer shielding functions $\gamma^{(0)}(r)$ (solid line), $\gamma^{(10)}(r)$ ($\alpha = 0$, dashed line), and $\gamma^{(10)}(r)$ (including exchange, dotted line) for Ag^0.

tron core ($Ag\ 1s^2 \cdots 4d^{10}$) is considerably larger than the perturbation of this electron by the nuclear quadrupole moment Q. Since the angular excitation $5s \to d$ contributes with a positive value to $\gamma^{(10)}(r)$ ("shielding effect") the negative contributions ("antishielding effects") due to $2p \to p$, $3p \to p$, $4p \to p$ radial excitations can be balanced at large distances r from the nucleus leading to a positive $\gamma^{(10)}$ value for Ag^0. Because the $5s$ electron is located "outside" the $2p$, $3p$, $4p$ electrons, the antishielding effects due to the $2p \to p$, $3p \to p$, $4p \to p$ radial excitations became dominant at smaller distances r over the shielding effect due to the $5s \to d$ angular excitation; thus $\gamma^{(10)}(r)$ becomes negative below about $r = 6$ a.u. The tendency that an outer s electron produces considerable shielding effects in self-consistent calculations is also reflected in other cases which we investigated, Na^0, K^0, Rb^0, and Cu^0, with the only difference being that $\gamma_\infty^{(n)}$ is considerably reduced compared with $\gamma_\infty^{(0)}$, but remains negative. In addition to the $\gamma^{(0)}(r)$ values for the elements listed in Sec. II A, a supplement to this publication, which is available to readers, also contains the self-consistent results $\gamma^{(n)}(r)$.

C. Self-consistent calculations in X_α approximation

Including exchange interaction in our calculational concept through the X_α exchange potential, we came to a self-consistent solution of the perturbed Schrödinger equation (10) by the iterative procedure described in Sec. III A. The relevant α parameters for the various elements and ions under study were taken from the literature.[35]

A general feature of our results is that $\gamma_\infty^{(n)}$ derived from self-consistent calculations including exchange becomes more negative compared with self-consistent values excluding exchange. This finding is consistent with what we have described in Sec. III B, i.e., the general tendency of self-consistent $\gamma(r)$ results excluding exchange but in-
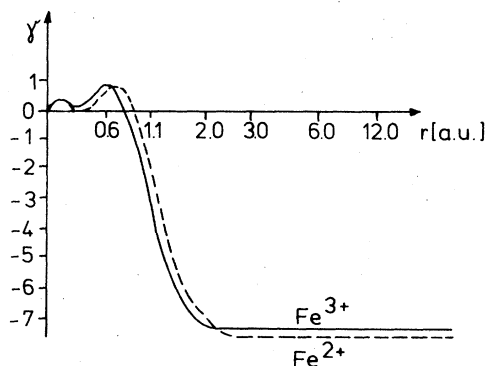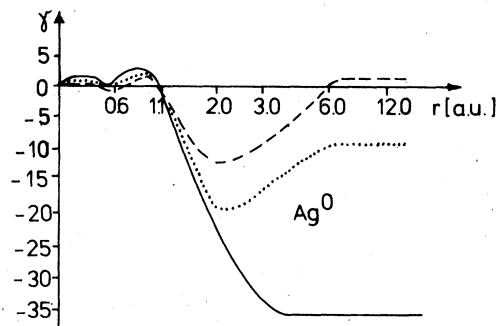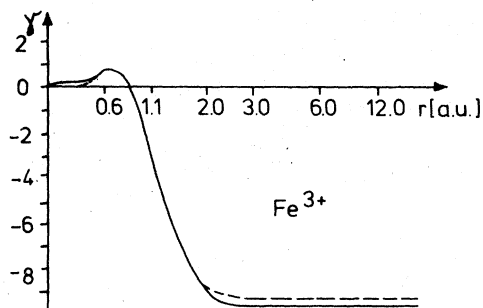

FIG. 5. Sternheimer shielding function $\gamma^{(10)}(r)$ obtained from a self-consistent solution of the perturbed Schrödinger equation for Fe^{2+} and Fe^{3+} ($\alpha = 0$).

FIG. 7. Sternheimer shielding functions for Fe^{3+}; the solid line is identical to that of Fig. 2(c), and the dashed line represents $\gamma^{(10)}(r)$ including exchange interaction in Eq. (10) through the X_α exchange potential.

cluding direct Coulomb interaction is that $\gamma_\infty^{(n)}$ becomes more positive compared with $\gamma_\infty^{(0)}$. The overall effect of this is that the contributions $\gamma(r)$ due to exchange and direct Coulomb interaction in self-consistent calculations partly cancel each other, leading to the interesting fact that self-consistent $\gamma^{(n)}(r)$ curves including exchange may be close to the simpler $\gamma^{(0)}(r)$ results presented in Sec. II B.

The considerable effect of the Ag $5s^1$ electron upon the self-consistent γ_∞ value (it is positive neglecting exchange) described in Sec. III B is reduced after including exchange; the self-consistent γ_∞ for Ag^0 now takes the value -9.32 (Fig. 6). Taking Fe^{3+} as an additional example we compare $\gamma^{(0)}(r)$ from Fig. 2c with $\gamma^{(10)}(r)$ including exchange (Fig. 7) and find that the values derived in Sec. II may be considered thoroughly as valuable. Comparing our results obtained for heavier elements (for example Pr^{3+}) with those derived from many-body perturbation calculations[19] we find significant deviations. $\gamma_\infty^{(10)}$ for Pr^{3+} from the present study takes the value -59.29, while the self-consistent γ_∞ reported by Ahmad and Newman[19] is -142.12. (For further comparison: $\gamma_\infty^{(0)} = 56.51$ from the present work, $\gamma_\infty^{(0)} = -60.02$ reported by Das and Raychaudhuri,[36] and $\gamma_\infty^{(0)} = -66.82$ reported by Ahmad and Newman[19]).

Applying Eq. (10) to negative ions no self-consistency was obtained. Because it is known from practical applications of the X_α theory that the exchange interaction tends to be overestimated at large distances r from the nucleus in the case of negative ions, we tried to restrict the exchange potential to smaller r values by an appropriate "cutoff"; however, this procedure also did not lead to a self-consistent solution of Eq. (10).

The discrepancies mentioned above and the limitations with respect to negatively charged ions indicate that the X_α approximation for the exchange interaction in Eq. (10) is not very useful

for deriving reliable self-consistent Sternheimer shielding functions $\gamma(r)$.

IV. CONCLUSION

We briefly described Sternheimer's method, which we followed mainly in calculating $\gamma(r)$ and R. Calculations were performed for a series of elements with varying electronic configuration, including core configurations which are eliminated in molecular-orbital calculations with limited basis set: $Li^{0,1+}$, $Na^{0,1+}$, $K^{0,1+}$, $Rb^{0,1+}$, $F^{0,1-}$, $Cl^{0,1-}$, $Br^{0,1-}$, $I^{0,1-}$, $Cu^{0,1+}$, $Fe^{0,1+,2+,3+}$, Ag^0, Pr^{3+}. The various contributions to $\gamma(r)$ due to angular and radial excitations were discussed. Direct and exchange contributions (R_D and R_E) to R were presented; in connection with this the discrepancy between ours and Sternheimer's R (Cl^- and Br^-) values was explained on the basis of R_E valence-core contributions, mainly $c(p \to p; p; L = 0)$, which were omitted in Ref. 28.

We investigated the influence of direct Coulomb interaction and X_α exchange interaction upon $\gamma(r)$. We found that both contribute with opposite sign to $\gamma(r)$, and in the case of iron even cancel each other; thus $\gamma^0(r)$ and self-consistent results $\gamma^{(n)}(r)$ (including the X_α approximation) are nearly identical in the case of iron. For heavier elements (Pr^{3+}) the X_α approximation yields γ_∞ which deviates considerably from results having been obtained with a more reliable approximation[19]; in addition our X_α calculations, when applied to negative ions, led to divergent $\gamma(r)$ results.

Because many Mössbauer spectroscopists still use the iron value 0.68 for $1 - R$ in Eq. (5) we want to emphasize, that the correct value is 0.88.[28] For MO calculations with limited basis set (Fe $3d$, $4s$, $4p$ AO's), however, the appropriate value would be 0.92. Taking this value instead of 0.68, which we have used so far in our MO work,[37] the nuclear quadrupole moment of iron can be recalculated.

We find $Q(Fe) = 0.15 \pm 0.03$ b which is significantly different from the value 0.20 ± 0.03 b, which was reported earlier.[38]

For readers who are interested in detailed numerical values for $\gamma(r)$ a supplement to this publication is available.

APPENDIX

Introducing perturbation $\mathcal{H}_1$ we get modified wave functions $\phi_j(\vec{r}) = \phi_{0,j}(\vec{r}) + \phi_{1,j}(\vec{r})$, where

$\phi_{0,j}(\vec{r})$ and $\phi_{1,j}(\vec{r})$ are defined by

$$\phi_{0,j}(\vec{r}) = [u_{0,j}(r)/r]Y_m^l(\theta, \varphi) ,$$

$$\phi_{1,j}(\vec{r}) = \frac{Qu_{1,j}(r)}{r} \langle Y_{m'}^{l'} | C_0^2 | Y_m^l \rangle Y_{m'}^{l'}(\theta, \varphi) . \tag{A1}$$

C_0^2 depends on θ and φ:

$$C_m^k(\theta, \varphi) = [4\pi/(2k-1)]^{1/2} Y_m^k(\theta, \varphi) . \tag{A2}$$

The modified energies and electron densities are $E_j = E_{0,j} + E_{1,j}$ and $\rho(\vec{r}) = \rho_0(\vec{r}) + \Delta\rho(\vec{r})$. Thus the perturbed X_α Hartree-Fock equation (9) becomes

$$\left[-\tfrac{1}{2}\vec{\nabla}_j^2 - \frac{Z}{r} + \int \frac{\rho_0(\vec{r}') + \Delta\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' - 3\alpha \left(\frac{3}{8\pi} \rho_0(r) \right)^{1/3} \left(1 + \frac{\Delta\rho(r)}{\rho_0(r)} \right)^{1/3} + \mathcal{K}_{1,j} \right] [\phi_{0,j}(\vec{r}) + \phi_{1,j}(\vec{r})]$$

$$= (E_{0,j} + E_{1,j})[\phi_{0,j}(\vec{r}) + \phi_{1,j}(\vec{r})] , \tag{A3}$$

where $\mathcal{K}_{1,j} = QC_0^2(\theta, \varphi)/2r^3$. Using the expansion

$$\left(1 + \frac{\Delta\rho(r)}{\rho_0(r)} \right)^{1/3} = 1 + \frac{\Delta\rho(r)}{3\rho_0(r)} + \cdots$$

up to first order in $\Delta\rho/\rho_0$ and the unperturbed Schrödinger equation [Eq. (9)] Eq. (A3) takes the form

$$\left[-\frac{1}{2}\vec{\nabla}_j^2 - \frac{Z}{r} + \int \frac{\rho_0(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' - 3\alpha \left(\frac{3}{8\pi} \rho_0(r) \right)^{1/3} - E_{0,j} \right] \phi_{1,j}(\vec{r})$$

$$= -\left[\mathcal{K}_{1,j} - E_{1,j} + \int \frac{\Delta\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' - \alpha \left(\frac{3}{8\pi} \rho_0(r) \right)^{1/3} \frac{\Delta\rho(r)}{\rho_0(r)} \right] \phi_{0,j}(\vec{r}) . \tag{A4}$$

The charge densities are derived from

$$\rho_0(\vec{r}) = \sum_j n_j | \phi_{0,j}(\vec{r}) |^2 , \tag{A5}$$

$$\Delta\rho(\vec{r}) = 2\sum_j n_j \phi_{0,j}(\vec{r})\phi_{1,j}(\vec{r})$$

$$= 2Q \sum_j \sum_{ll'} n_j \frac{u_{0,j}(r)u_{1,j}(r)}{r^2} Y_m^l(\theta, \varphi)Y_{m'}^{l'}(\theta, \varphi)$$

$$\times \langle Y_{m'}^{l'} | C_0^2 | Y_m^l \rangle . \tag{A6}$$

(n_j is the population of orbital ϕ_j.) Because $\mathcal{K}_1$ induces a quadrupole moment within the electron shell, $\Delta\rho(r)$ can be represented also by

$$\Delta\rho(\vec{r}) = \Delta V(r)C_0^2(\theta, \varphi) . \tag{A7}$$

$\Delta V(r)$ is obtained from Eqs. (A6) and (A7) by multiplication with C_0^2 and integration over $\cos\theta$ and φ:

$$\Delta V(r) \iint C_0^2(\theta, \varphi)C_0^2(\theta, \varphi) d(\cos\theta) d\varphi$$

$$= 2Q \sum_j \sum_{ll'} n_j \frac{u_{0,j}u_{1,j}}{r^2} \sum_{m,m'} \langle Y_{m'}^{l'} | C_0^2 | Y_m^l \rangle$$

$$\times \langle Y_{m'}^{l'} | C_0^2 | Y_m^l \rangle , \tag{A8}$$

$$\Delta V(r) = \frac{5}{8\pi} Q \sum_j \sum_{ll'} \frac{n_j}{2(2l+1)} C_{ll'} \frac{u_{0,j}u_{1,j}}{r^2} , \tag{A9}$$

with

$$C_{ll'} = 8 \sum_{m=-l}^{l} (\langle Y_{m'}^{l'} | C_0^2 | Y_m^l \rangle)^2 .$$

Using the abbreviation $C_{m'}^{(k)}(lm, l'm)$ for the Gaunt integral $\langle Y_m^l | C_{m'}^k | Y_{m'}^{l'} \rangle$ we are within the same notation as Sternheimer[8]:

$$C_{ll'} = 8 \sum_{m=-l}^{l} [C_0^{(2)}(lm, l'm)]^2 .$$

The term

$$\int \frac{\Delta\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'$$

in Eq. (A4) can be replaced by[8]

$$\int \frac{\Delta\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' = \frac{Q\gamma(r)}{2r^3} C_0^2(\theta, \varphi) . \tag{A10}$$

With the effective perturbation operator

$$\mathcal{K}_1^{\text{eff}} = -\frac{1}{2} \left\{ Q/r^3 - \gamma(r)/r^3 \right.$$

$$\left. + \left[\frac{3}{8\pi} \rho_0(r) \right]^{1/3} \alpha \frac{2\Delta V(r)}{\rho_0(r)} \right\} C_0^2(\theta, \varphi) , \tag{A11}$$

the energy

$$E_{1,j} = \langle \phi_{0,j} | \mathcal{K}_1^{\text{eff}} | \phi_{0,j} \rangle$$

is calculated to be

$$E_{1,j} = \sum_{l,m} \frac{1}{2} \langle Y_m^l | C_0^2 | Y_{m'}^l \rangle$$

$$\times \left[-\left\langle \frac{Q}{r^3} \right\rangle_j + \left\langle \frac{Q\gamma(r)}{r^3} \right\rangle_j \right.$$

$$\left. - \left(\frac{3}{8\pi} \right)^{1/3} \alpha Q \langle \rho_0^{-2/3}(r) 2\Delta V(r) \rangle_j \right] . \tag{A12}$$

[The expectation values in (A12) are derived from the radial part of the unperturbed wave function $\phi_{0,j}(r)$]. Combining Eqs. (A4) and (A9)–(A12) we finally come to the expression represented by Eq. (10).

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