Shielding and Antishielding of Nuclear Quadrupole Moments*

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The development of the theory of shielding and antishielding of nuclear quadrupole moments is reported. The various contributions to the Sternheimer shielding and antishielding factors are discussed. Also the history of the different calculational techniques is outlined.

My original calculations of shielding and antishielding were started in October 1949. I noticed within the first few weeks that the nuclear quadrupole moment Q induces a moment $Q_{\text{ind}}(n\,l \rightarrow l')$ in each $n\,l$ shell of the core, where l is the angular momentum of the shell in its ground state (with principal quantum number n) and l' is the angular momentum of the excited wave functions, $l' = l \pm 2$ or $l' = l$. It is also obvious that at least for the case of atoms, the problem can be separated into a product of radial and angular factors. The angular factors were calculated first (in 1949) by evaluating the sum over the magnetic quantum numbers m for each type of closed shell having quantum numbers n, l, and m, and for each type of excitation, i.e., $l' = l + 2$, $l' = l$, and $l' = l - 2$.

The perturbation H_1 in the Schrödinger equation is the potential due to Q which is

$$H_1 = -\,Q P_2 / r^3\,, \tag{1}$$

where Q is in units a_{H}^2 (a_{H} = Bohr radius) and r is in units a_{H}. H_1 is then in Rydberg units (1 Ry = 13.60 eV).

My earliest calculations of the radial factors and functions (January to June 1950) were carried out by solving the inhomogeneous Schrödinger equation

$$(H_0 - E_0)\,u_1 = (E_1 - H_1)\,u_0 \tag{2}$$

by means of an expansion of u_1 in terms of the unperturbed wave functions $u_{0,\,n\,l'}$, i.e.

$$u_1 = \sum a_n u_{0,\,n\,l'}\,. \tag{3}$$

Because of the very slow convergence of this series it was soon realized that the continuum states would also make a sizable contribution and would therefore have to be included in the calculations, i.e. (3) becomes

$$u_1 = \sum_{n=1}^{\infty} a_n u_{0,\,n\,l'} + \int_0^{\infty} \mathrm{d}k\, a_k\, u_{0,\,k\,l'}\,, \tag{4}$$

where k is the momentum of the electron at large distances from the nucleus, i.e., $E_{k\,l'} = \hbar^2 k^2 / 2\,m_{\text{e}}$.

A calculation was started for lutetium, Lu, $Z = 71$, because of the large quadrupole moments of the Lu isotopes, and also because there is a large number of different $n\,l$ shells in the atomic core. This turned out, later, to be very important in connection with the calculations of the Sternheimer ionic antishielding factor γ_∞ and its large magnitude for heavy atoms ($Z \gtrsim 50$) and ions.

The calculations for Lu of the atomic antishielding factor R by the method of summation and integration over all excited states (4) became very complicated – and would probably have been beyond the capabilities of the then-existing desk computers. For this reason, I tried to use the Thomas-Fermi model (TF), and it turns out that the TF model gives a fairly reliable estimate of the contributions to R due to the *angular modes* of excitation of the core electron shells, i.e., the excitations $n\,l \rightarrow l + 2$ and $n\,l \rightarrow l - 2$, e.g., ns → d, np → f, nd → s, nd → g, etc.

The idea for the proper formulation of the Q shielding in terms of the TF model occurred to me late in June 1950, and the results were published 35 years ago in a Letter to the Physical Review [1]. It turns out that the angular excitation modes $n\,l \rightarrow l + 2$ always give rise to a *shielding* of Q.

Upon using again the original perturbed wave function approach, the contribution of a single

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$n\,l \rightarrow l'$ mode to the Sternheimer atomic shielding or antishielding factor R is given by

$$R_{\mathrm{D}}(n\,l \rightarrow l') = \frac{c\,(n\,l \rightarrow l')}{\langle r^{-3}\rangle_{n_e l_e}} \times \left\{ \int_0^\infty \omega_e^2 \,\mathrm{d}r \left[\frac{1}{r^3} \int_0^r u_0 v_1 r'^2 \,\mathrm{d}r' + r^2 \int_r^\infty u_0 v_1 r'^{-3} \,\mathrm{d}r' \right] \right\}, \quad (5)$$

where u_0 and v_1 are the radial parts of the unperturbed $n\,l$ and the perturbed $n'\,l'$ wave function (times r), respectively, ω_e is similarly the radial valence electron wave function (times r) and the radial functions are normalized according to

$$\int_0^\infty u_0^2 \,\mathrm{d}r = \int_0^\infty \omega_e^2 \,\mathrm{d}r = 1\,. \quad (6)$$

In (5), $c\,(n\,l \rightarrow l')$ is an angular coefficient, obtained by integration over the angular variables ϑ and φ with respect to the orientation of Q (taken to be along the z axis) and by the subsequent summation over the magnetic substates $m = -l, -l+1 \ldots l-1, l$ of the closed $n\,l$ shell of the core. I have obtained the following values for $c\,(n\,l \rightarrow l')$ (which are independent of n):

8/5 for ns → d; 48/25 for np → p;
72/25 for np → f;
16/7 for nd → d; and 144/35 for nd → g.

As concerns the TF model, it can be easily shown that the angular-mode density of the induced Q is given by [1]

$$\mathrm{d}Q_{\mathrm{ind}} = \frac{3}{10}\, Q\,(\chi x)^{1/2}\,\mathrm{d}x\,, \quad (7)$$

where χ is the TF function [2] and x is the radial distance (from the nucleus) r, expressed in TF units, namely

$$a_{\mathrm{TF}} = \frac{0.88534}{Z^{1/3}}\, a_{\mathrm{H}}\,. \quad (8)$$

The details of the derivation of (7) and the resulting values of R_{ang} (the angular-mode part of R) are given in [1].

In spite of the apparent (and limited) success of the TF model, I felt that it would be much more satisfactory to obtain the complete solutions $u_1\,(n\,l \rightarrow l')$ of the inhomogeneous equation (2).

An important method to accomplish this (without the necessity of the expansion of (4)) occurred to me in September 1950. In essence, the idea is to solve (2) directly and numerically, without calculating the sum and the integral of (4). The resulting radial equation becomes

$$\left(-\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{l'(l'+1)}{r^2} + V_0 - E_0 \right) u_1 = u_0 \left(\frac{1}{r^3} - \langle r^{-3}\rangle_{nl}\,\delta_{ll'} \right), \quad (9)$$

where u_0 and u_1 are the radial parts of ψ_0 and ψ_1, respectively, multiplied by r and with the normalization

$$\int_0^\infty u_0^2 \,\mathrm{d}r = 1\,. \quad (10)$$

The direct numerical integration of (9) took about 2−3 h on a desk calculator for the case $l' = l$, and about 6−7 h for the case $l' = l + 2$. Therefore the calculations using the direct method of integration were eminently feasible on the then-existing desk calculators. Much later, in the middle 1960's, the corresponding calculations for a single $n\,l \rightarrow l'$ mode took about 1−5 min on the CDC 6600 computer, and proportionately less (by about a factor of 6) on the CDC-7600. In 1951, I published a paper entitled "On Nuclear Quadrupole Moments" [3] in which the method of direct solution of (9) was first presented, and was applied to the calculation of R (the *atomic* shielding or antishielding factor) for the valence electrons of Li, Al, and Cl.

For the case of the quadrupole coupling of a valence electron (either in the ground state or in an excited state), there are also important exchange terms which add up to R_{E}, so that the total effective R can be written as

$$R = R_{\mathrm{D}} + R_{\mathrm{E}}\,, \quad (11)$$

where R_{D} is the total term due to the direct electrostatic interaction between the core and the valence electron. It was found in these calculations (1951) that the 2p → p and 3p → p excitations of Al^{3+} and Cl^- result in a net "negative shielding", which I called *"antishielding"* [3].

The procedure of the direct solution of (2), viz. by means of (9) in the present case, which I introduced in 1951 has been very widely used in the past 35 years for a variety of problems in atomic physics and also in other fields of physics (e.g., in solid-state calculations).

In 1951, I extended the present ideas for the nuclear quadrupole coupling e^2qQ/h to the interaction of a nuclear magnetic moment $\boldsymbol{\mu}$ with the valence electron and the core electrons for the magnetic hyperfine structure (hfs). The results of this investigation were published in [4]. In the first paragraph of this paper, the actual physical effect – namely the two different densities at the nucleus for the two spin directions due to the additional exchange interaction with the valence electron for core electrons having spin parallel to that of the valence electron – was clearly described. This effect is usually referred as "core polarization". Furthermore, it was shown in [4] that the $L=0$ part of the exchange interaction (for a valence p electron interacting with a core np^6 shell) is the same for the magnetic hfs as for the nuclear quadrupole coupling, so that the correction factor $(1-R_m)/(1-R)$ for Q extracted from the observed ratio of hfs parameters b_{nl}/a_{nl} is approximately given by $1/(1-\bar{R})$, where $\bar{R} \equiv R - (L=0$ exchange terms). The resulting correction factor for the Q values is usually denoted by C:

$$C \equiv 1/(1-\bar{R}) . \tag{12}$$

The angular factors for the exchange interaction for the quadrupole coupling were originally evaluated by performing the relevant angular integrations (over products $\Theta_{l_1}^{m_1}\Theta_{l_2}^{m_2}$), where Θ_l^m is the normalized spherical harmonic, and then by summing over the magnetic substates m_i of the core electrons in a given closed shell nl. These factors depend upon l, l_1 (for an nl shell excited to l_1 states) and l_v (of the valence electron), and on the multipolarity L of the interaction.

Thus they can be written as

$$C\,(l, l_1, l_v; L) . \tag{13}$$

An extensive table of the $C\,(l, l_1, l_v; L)$ has been given in my paper [5].

In 1953, Foley of Columbia University and I did extensive calculations of the Sternheimer ionic antishielding factor γ_∞, which is defined as $-Q_{\text{ind}}/Q$, where Q_{ind} is the *total induced quadrupole moment* obtained by integrating the density of induced moment over all radii r, from 0 to ∞. γ_∞ describes the shielding – or more often the antishielding – of the entire ion when it interacts with a distant external charge, i.e., a charge at a distance R such that both the unperturbed core wave functions $u_0(R)$ and their quadrupole perturbations $u_1(R)$ are very small, i.e., in the exponentially decreasing region where both functions behave approximately as exp $[-\sqrt{|E|}\,r]$, where E is the energy eigenvalue (E_{nl}) of the core electron state. The results of these calculations are published in [6]. It should also be noted that by this time (in 1953) it was obvious to Foley and myself that the large antishielding due to the radial modes, i.e., $u_1(nl \to l)$, (e.g., $u_1(2\mathrm{p} \to \mathrm{p})$, $u_1(3\mathrm{d} \to \mathrm{d})$, etc.) is **not** included in the above-mentioned TF calculations (see (9) and [6]). Furthermore, the TF model gives an over-estimate by about a factor 1.5 for the effect of the angular modes. As a result we have

$$R_{\text{ang}} \approx \frac{R_{\text{TF}}}{1.5}, \quad \text{and} \quad \gamma_{\infty,\,\text{ang}} \approx \gamma_{\infty,\,\text{TF}}/1.5 . \tag{14}$$

In 1951, I also introduced an effective local potential V_{eff} which has to be used for any given core wave function u_{nl} (e.g., a Hartree-Fock HF function), especially for the treatment of the radial modes $nl \to l$, so that V_{eff} is consistent with the choice of u_{nl}. More precisely, the function $V_{\text{eff}} - E_0$ which enters into (9) has to be obtained from the equation

$$V_{\text{eff}} - E_0 = \frac{1}{u_0}\frac{\mathrm{d}^2 u_0}{\mathrm{d}r^2} - \frac{l\,(l+1)}{r^2}, \tag{15}$$

where $u_0 = u\,(nl)$. See [4], Equation (54a).

In particular, in later calculations of the electronic polarizabilities α_d and α_q of the alkali-metal atoms, I used effective wave functions which were better than the corresponding HF wave functions, and included the effect of electron correlations. Therefore it was essential to use (15) in order to calculate $u_1(\mathrm{ns} \to \mathrm{p})$ for α_d (dipole polarizability) and $u_1(\mathrm{ns} \to \mathrm{d})$ for α_q (quadrupole polarizability); see [7] and [8].

The Eq. (15), which defines $V_{\text{eff}} - E_0$, has been widely used in calculations of hyperfine structure, electronic polarizabilities and many other aspects of atomic physics since 1952, when I introduced the equation; see also my papers on α_d of ions [9–12].

In my first paper on the calculation of electronic polarizabilities, namely [9], I have also introduced the electric dipole shielding factor ξ:

$$\xi = N/Z , \tag{16}$$

where Z is the atomic number of the nucleus and N is the number of electrons in the corresponding electronic shells. Obviously when $N = Z$ (neutral atom), we find $\xi = 1$. The proof of (16) is given in Sect. V of [9]. The fact that $\xi = 1$ for a neutral atom was pointed out to me by Foley using the argument that a neutral atom ($N = Z$) does not move when an external field E_{ext} is applied, and therefore the total field at the nucleus: $E_{\text{ext}} + E_{\text{ind}} = 0$. Since $\xi = -E_{\text{ind}}/E_{\text{ext}}$, this implies that $\xi = 1$ for a neutral atom. The generalization to an ion with net charge $q = Z - N$ is easily accomplished; see [9], Equation (113).

The result of (16) can be readily used as a test of the unperturbed wave functions $u_{0,nl}$ of the core electrons and the resulting perturbations $u_1(nl \to l')$ caused by the presence of an external electric field E_{ext}. It can be readily seen that because of the dipole character of the potential V_{ext} pertaining to $\boldsymbol{E}_{\text{ext}}$, namely

$$V_{\text{ext}} = e E_{\text{ext}}\, r \cos \vartheta\,, \tag{17}$$

we must have $l' = l \pm 1$, i.e., the following perturbations will be encountered: ns → p, np → s, np → d, nd → p, nd → f, nf → d, nf → g. Thus the angular coefficients $C(nl \to l_1)$ will be the same as for the calculation of α_d; however, in the radial integral involving the factor $u_0(nl)\, u_1(nl \to l')$ the factor r must be replaced by $1/r^2$. Similarly for the induced quadrupole moment arising from Q, where the radial integral has a factor r^2, the corresponding electric field gradient EFG at the nucleus due to the induced charge density of the core has the radial factor r^{-3}. This is a general result. The angular factors $C(l, l_1; L)$ due to the induced moment density arising from a distant electric charge are the same as for the corresponding L-type shielding-antishielding factors. However, the radial factor pertaining to a particular multipole interaction L is changed from r^L (for the L-type multipole polarizability (2^L)) to r^{-L-1} for the corresponding L-type shielding or antishielding factor.

Another set of calculations which were encouraged by the importance of R and γ_∞, pertains to the antishielding (and in some cases the shielding) of nuclear electric hexadecapole (2^4) moments H. These calculations were started by myself in January 1961, and preliminary results were published in [13]. The ionic hexadecapole antishielding factor has been denoted by η_∞, in analogy to γ_∞ for Q. Thus we have

$$H_{\text{ion}} = H + H_{\text{ind}} = (1 - \eta_\infty)\, H\,. \tag{18}$$

The nuclear hexadecapole moment (HDM) is defined as

$$H = \sum_p \langle r_p^4 (35 \cos^4 \vartheta_p - 30 \cos^2 \vartheta_p + 3) \rangle_{m_I = I}\,, \tag{19}$$

where r_p is the distance of a proton (in the nucleus) from the center of the nucleus. H is expected to be non-zero for any nucleus with spin $I \geqq 2$. The potential due to H acting on an atomic electron (core electron) is

$$V_H = e H P_4(\vartheta)/8 r^5 \tag{20}$$

or in Rydberg units

$$V_H = -H P_4(\vartheta)/(4 r^5)\ \text{Ry}\,, \tag{21}$$

where r is in units a_H, and H is in units a_H^4. $P_4(\vartheta)$ is the Legendre polynomial.

The induced HDM density arising from the nd → d and nf → f (radial) modes is given by

$$H_{\text{ind,rad}}(r)\, dr = H r^4 \left[\frac{80}{63} \sum_n u_0(\text{nd})\, u_{1,H}(\text{nd} \to \text{d}) + \frac{112}{99} \sum_n u_0(\text{nf})\, u_{1,H}(\text{nf} \to \text{f}) \right] dr\,, \tag{22}$$

where $u_{1,H}$ is determined by the inhomogeneous equation, similar to (9),

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_0 - E_0 \right] u_{1,H}(nl \to l) = u_0(nl) \left[\frac{1}{r^5} - \left\langle \frac{1}{r^5} \right\rangle_{nl} \right] \tag{23}$$

and by the orthogonality condition

$$\int_0^\infty u_0(nl)\, u_{1,H}(nl \to l)\, dr = 0\,. \tag{24}$$

Incidentally, the same type of orthogonality condition as (24) holds also for the quadrupole case. The angular factors 80/63 and 112/99 result from the integration over the angular parts of the wave functions (Θ_l^m = spherical harmonic) and the summation over the magnetic substates m of the closed nl shell. The resulting coefficients $C_H(nl \to l)$ are obtained from

$$C_H(nl \to l) = 8 \sum_{m=-l}^{l} \left[\int_0^\pi (\Theta_l^m)^2 P_4(\vartheta) \sin \vartheta\, d\vartheta \right]^2. \tag{25}$$

Thus the term η_∞ (nd → d) pertaining to the hexadecapole excitation of the nd shell is given by

$$\eta_\infty(\mathrm{nd}\to\mathrm{d}) = \frac{80}{63}\int_0^\infty u_0(\mathrm{nd})\, u_{1,\mathrm{H}}(\mathrm{nd}\to\mathrm{d})\, r^4\,\mathrm{d}r\,. \quad (26)$$

In addition to the antishielding effects due to nd → d and nf → f, we expect some shielding due to the excitations of the angular modes of the core electrons, i.e., ns → g, np → h, nd → g and nd → i. The sum of the effects of these angular modes can be obtained from the TF model (cf. [1] for the quadrupole effects). By the same analysis as for the quadrupole case, I have obtained for the density of the induced HDM (see [13]):

$$H_{i,\mathrm{ang}}(x)\,\mathrm{d}x = \tfrac{1}{6} H (\chi x)^{1/2}\,\mathrm{d}x\,, \quad (27)$$

where χ and x are the TF function and the radial distance r expressed in terms of the TF unit radius, as given in (8) above.

Thus $H_{i,\mathrm{ang}}(x)$ involves the same function, namely $(\chi x)^{1/2}$ as does the $Q_{i,\mathrm{ang}}(r)$ of my earlier letter ([1], 1950), the only difference being that the coefficient 3/10 for $Q_{i,\mathrm{ang}}$ is replaced by 1/6 for $H_{i,\mathrm{ang}}$. The general expression for the coefficient C_L pertaining to a nuclear 2^L-moment is

$$C_L = \frac{3/2}{(2L+1)}\,. \quad (28)$$

Upon integrating over x in (27), I obtain

$$H_{i,\mathrm{ang}} = \tfrac{1}{6} H \int_0^\infty (\chi x)^{1/2}\,\mathrm{d}x\,. \quad (29)$$

The total $Q_{i,\mathrm{ang}}$ has been obtained by means of wave function calculations (see (9)) for several ions. Thus $\gamma_{\infty,\mathrm{ang}} = 0.60$ for Na^+, 1.05 for K^+, 1.4 for Cl^-, and 2.9 for Cs^+. Upon multiplying by the factor $(1/6)/(3/10) = 5/9$, I obtain $\eta_{\infty,\mathrm{ang}} = 0.33$ for Na^+, 0.58 for K^+, 0.78 for Cl^-, and 1.6 for Cs^+.

Accurate values of η_∞ (using the solution of the inhomogeneous equation (23) above) have been calculated in a subsequent paper [14]. The following values of η_∞ were obtained: $\eta_\infty(\mathrm{Cu}^+) = -1200$, $\eta_\infty(\mathrm{Ag}^+) = -8050$, and $\eta_\infty(\mathrm{Hg}^{2+}) = -63000$. The last value is probably an overestimate because Hartree functions for the Hg^{2+} ion were used to obtain $u_0(nl)$ and $u_{1,\mathrm{H}}(nl\to l)$, instead of HF functions (including the exchange effects) which were not available for Hg^{2+} in 1961. Additional calculations of η_∞ can be found in [15]. See also [16] and [17] for additional calculations of γ_∞.

Finally, I may note that an accurate calculation of the Sternheimer *atomic* R_H for the holmium atom ^{165}Ho was carried out in [18]. The final value of R_H for holmium was found to be $R_\mathrm{H} = +0.32$, indicating a shielding of the nuclear HDM. The relatively small value of R_H, i.e. $R_\mathrm{H} < 0.4$ is similar to the corresponding results found for the atomic factors R, namely in general I have found that $-0.3 \leqq R \leqq +0.2$.

In the early 1970's, I performed a recalculation of R, first for the excited np states of the alkali-metal atoms Li, Na, K, Rb and Cs [19] and then for several atomic ground states, [20] and [21]. Seven atomic ground states from $\mathrm{F}(2\mathrm{p}^5)$ to $\mathrm{Br}(4\mathrm{p}^5)$ were included in the calculations. In this region of the Periodic Table, R is generally positive (shielding) and of the order of +0.1, except for Al(3p) and Ga(4p) on account of the 2p → p and 3p → p perturbations of the core electrons, 2p and 3p, respectively. The resulting correction factors $C = 1/(1-R)$ have been applied to the (uncorrected) Q of 11 nuclear isotopes, namely ^{27}Al, ^{35}Cl, ^{36}Cl, ^{37}Cl, ^{63}Cu, ^{65}Cu, ^{67}Ga, ^{68}Ga, ^{69}Ga, ^{71}Ga, and ^{72}Ga.

In an outstanding example of the relevance and accuracy of my calculations of $R(nl)$, I have computed $R(3\mathrm{d})$ and $R(4\mathrm{p})$ for the case of Cu. The apparent spectroscopic moments (without introducing the factor $C(nl)$) differ by a factor ~ 1.4. When the appropriate correction factors $[1-R(3\mathrm{d})]^{-1}$ and $[1-R(4\mathrm{p})]^{-1}$ are applied, the resulting Q values are equal, to within the small experimental uncertainties. These results are reported in [5].

A similar situation exists for an isotope of terbium, ^{159}Tb, as was noted by Childs [22]. In this case it is necessary to calculate $[1-R(4\mathrm{f})]^{-1}$ and $[1-R(5\mathrm{d})]^{-1}$. The application of these factors brings the two differing values of $Q_{\mathrm{spectr.}}$ (i.e., the uncorrected Q values) which differ by a factor 1.4, into excellent agreement for the "true" value of Q.

It may be noted here that from the point of view of the k ordering which I introduced in 1977, and where $k = n + l$ [23], the two atomic states which are compared both for Cu and Tb have the same value of k. Thus for Cu: $k = 3 + 2\,(3\mathrm{d}) = 4 + 1\,(4\mathrm{p}) = 5$. For Tb, $k = 4 + 3\,(4\mathrm{f}) = 5 + 2\,(5\mathrm{d}) = 7$. These equalities explain, in part, the fact that these ground states and the corresponding excited states (e.g., 3d and 4f for Cu) have approximately the same energy E_{nl}. The $(1 - R_{nl})$ values for ^{159}Tb and the resulting $Q\,(^{159}\mathrm{Tb})$ are discussed in [19].

Among the earlier calculated values of $R(nl)$ I would recommend those derived in [5] plus those of my papers published in 1971 and 1972 [19–21]. A later paper [24] gives estimates of $R(\mathrm{n\,d})$ for the excited nd states of the alkali-metal atoms, in particular for Rb.

Concerning the calculations of the ionic antishielding factor γ_∞, the first such calculations were carried out by Foley et al. [6]. Revised values were published by Sternheimer and Foley [25]. In 1956, Das and Bersohn also published values of γ_∞ for Na^+ and Al^{3+}, based on a variational method for evaluating the perturbations $u_1(nl \to l')$, see [26] and a subsequent paper by Wikner and Das [27].

Since November 1962 I had been using the BNL (Brookhaven National Laboratory) IBM-704 computer to calculate the perturbations $u_1(nl \to l)$, i.e., the large antishielding excitation modes of the core ($l' = l$). As a result it was possible for me to obtain reliable values of γ_∞ for several additional ions. These calculations were published in three papers:

(i) [28], in which I first calculated $\gamma_\infty(\mathrm{Fe}^{3+}) = -9.14$, $\gamma_\infty(\mathrm{Na}^+) = -4.56$, $\gamma_\infty(\mathrm{K}^+) = -17.32$, $\gamma_\infty(\mathrm{Mn}^{2+}) = -11.37$, $\gamma_\infty(\mathrm{Ga}^{3+}) = -9.50$ and $\gamma_\infty(\mathrm{Ag}^+) = -34.87$. All of these calculations were carried out using HF wave functions $u_0(nl)$. The value $\gamma_\infty(\mathrm{Fe}^{3+}) = -9.14$ has been very widely used in evaluating Mößbauer quadrupole effects using the probe nucleus $^{57\mathrm{m}}\mathrm{Fe}$.

(ii) A second paper by myself [29] gave $\gamma_\infty(\mathrm{F}^-) = -22.53$, $\gamma_\infty(\mathrm{Br}^-) = -123.0$, $\gamma_\infty(\mathrm{Rb}^+) = -47.2$, all three values having been obtained using HF wave functions $u_0(nl)$ and the corresponding perturbations $\gamma_\infty(nl - l')$. I also obtained $\gamma_\infty(\mathrm{Pr}^{3+}) = -78.5$ and $\gamma_\infty(\mathrm{Tm}^{3+}) = -74.0$, using the Hartree functions of Ridley [29], which were the best ones available at that time (1963). The effect of exchange on the inner and outer wave functions of the trivalent rare-earth ions is expected to be small. In fact the "best" value of $\gamma_\infty(\mathrm{RE}^{3+})$ throughout the rare-earth region is ≈ -80.

(iii) The third paper, [30], gives a rather comprehensive review of the various shielding-antishielding factors which I have introduced, including in particular R and γ_∞ for the quadrupole hyperfine structure, R_H and η_∞ for the hexadecapole hyperfine structure, the dipole shielding factor ξ (introduced and evaluated in 1954) and also calculations of the crystal-field-splitting shielding factors σ_2, σ_4 and σ_6 for the rare-earth ions which had been originally considered by Burns [31] and which were reliably calculated in my 1966 paper [30] and also in a paper by Ghatikar et al. [32]. [30] is quite detailed and gives several specific examples of the Pasternack-Sternheimer selection rule involving integrals over the *hydrogenic* wave functions $u_0(nl)$ and $u_1(nl')$, i.e. integrals of the form

$$K_{nll',s} \equiv \int_0^\infty r^{-s} u_6(nl)\, u_0(nl')\, \mathrm{d}r\,. \tag{30}$$

These integrals are zero in a large number of cases, namely for all s values in the range from $s = 2$ to $s = l - l' + 1$, where I have assumed that $l > l'$. The original paper on this selection rule was published by Pasternack and Sternheimer [33]. I will discuss several aspects of this paper later on in the present review article.

I shall now discuss the two cases (Cu and Tb) for which the correction factor $C_1 \equiv (1 - R_{n_1 l_1})^{-1}$ and $C_2 \equiv (1 - R_{n_2 l_2})^{-1}$ are essential in order to obtain a reliable and unique value of Q.

The case of copper is especially interesting because the Q values differ considerably depending upon whether the hfs is measured in the $3\mathrm{d}^9 4\mathrm{s}^2$ excited states $^2\mathrm{D}_{3/2}$ and $^2\mathrm{D}_{5/2}$ [34] or in the excited state $3\mathrm{d}^{10}4\mathrm{p}\,(^2\mathrm{P}_{3/2})$ [35]. Thus the values of $Q(^{65}\mathrm{Cu})$ uncorrected for the factors C_1 and C_2 were found to be -0.161 ± 0.003 b and -0.228 ± 0.005 b, respectively.

In [5] I calculated that R gives a net shielding for $3\mathrm{d}^9 4\mathrm{s}^2$ and has the value $R_{3\mathrm{d}} = +0.179$, whereas R is antishielding for $3\mathrm{d}^{10}4\mathrm{p}$, with $R_{4\mathrm{p}} = -0.175$. Upon applying the correction factors $C_{3\mathrm{d}} = (1 - R_{3\mathrm{d}})^{-1} = 1.218$ and $C_{4\mathrm{p}} = (1 - R_{4\mathrm{p}})^{-1} = 0.851$ to the preceding values of $Q(^{65}\mathrm{Cu})_{\mathrm{spectr.}}$ the resulting corrected values of $Q(^{65}\mathrm{Cu})$ are in excellent agreement with each other, namely -0.196 ± 0.004 b from $3\mathrm{d}^9 4\mathrm{s}^2$ and -0.194 ± 0.004 b from $3\mathrm{d}^{10}4\mathrm{p}$. The final average value of $Q(^{65}\mathrm{Cu}) = -0.195 \pm 0.004$ b leads to $Q(^{63}\mathrm{Cu}) = -0.211 \pm 0.004$ b upon using the known ratio $Q(^{63}\mathrm{Cu})/Q(^{65}\mathrm{Cu})$. The close agreement of the two corrected values of $Q(^{65}\mathrm{Cu})$ provides a very good confirmation of the existence and the methods of calculation of the Sternheimer atomic shielding and antishielding effects; see [5].

A second direct confirmation of my calculations for R_{nl} for different atomic states arose a few years later as a result of the work of Childs [22]. Childs had investigated the hfs of 17 low-lying atomic levels of $^{159}\mathrm{Tb}$ for both the configurations $4\mathrm{f}^9 6\mathrm{s}^2$

and $4f^85d6s^2$. For the second configuration ($4f^85d6s^2$) the magnetic dipole (a_{nl}) and nuclear quadrupole (b_{nl}) coupling constants are obtained both for the 4f and 5d valence electrons (the situation is similar to that for Cu 3d and 4p). It was found by Childs that, whereas

$$a_{4f}/a_{5d} = \langle r^{-3}\rangle_{4f}/\langle r^{-3}\rangle_{5d} = 2.96\,, \tag{31}$$

the ratio b_{4f}/b_{5d} is only 2.02:

$$b_{4f}/b_{5d} = \langle r^{-3}\rangle_{4f}(1-R_{4f})/[\langle r^{-3}\rangle_{5d}(1-R_{5d})] = 2.02\,, \tag{32}$$

and is thus smaller than a_{4f}/a_{5d} (31) by a factor

$$(1-R_{5d})/(1-R_{4f}) = 2.96/2.02 = 1.47\,. \tag{33}$$

The result 1.47 of (33) can thus be regarded as the "experimental value" of $(1-R_{5d})/(1-R_{4f})$.

On the other hand, upon using $R_{4f} = +0.10 \pm 0.05$ and $R_{5d} = -0.3$, which I calculated on the basis of my results in [30] and [5], I find the following theoretical value for the ratio:

$$(1-R_{5d})/(1-R_{4f}) = 1.3/(0.90 \pm 0.05) = 1.44 \pm 0.08\,, \tag{34}$$

which is in very good agreement with the result 1.47 of (33).

The magnitude of the effect $(1-R_{5d})/(1-R_{4f})$ is very similar to that previously found for Cu, in which case $(1-R_{4p})/(1-R_{3d}) = 1.429$. If we denote by $n_1 l_1$ the values of nl pertaining to the R factor in the numerator, and by $n_2 l_2$ the values of nl in the denominator, the two atomic states are related by $n_2 = n_1 - 1$ and $l_2 = l_1 + 1$ in both cases, i.e., the state with the larger n value and the smaller l value shows an *antishielding* effect, while the other state gives rise to a *shielding* of the nuclear Q. I may note again the connection with the k ordering of atomic structure, as discussed above [23]; both states 1 and 2 have the same value of $k = n + l$.

A third way of checking the importance of the correction factor $C_{nl} = (1-R_{nl})^{-1}$ is to compare the *corrected values* of $Q(^{131}\mathrm{Cs})$ as obtained from the 6p and 7p state hyperfine structures (the constants b_{nl}) by zu Putlitz and his coworkers [36]. Thus

$$Q_{\mathrm{corr}}(^{131}\mathrm{Cs}, 6p) = -0.572\,(10)\cdot 0.807/0.791 = -0.583\,(10)\ \mathrm{barn}\,, \tag{35}$$

where $-0.572\,(10)\,b = -0.572 \pm 0.010\,b$ is the uncorrected value obtained by Ackermann et al. [36] and 0.807/0.791 is the ratio of the revised value of C_{6p} [20] to the previously calculated value [37] of C_{6p}. (Actually the factor $0.807/0.791 = 1.020$ is not very different from 1, indicating that my earlier calculations of 1957 were almost as accurate as the later ones of 1970.)

Similarly upon correcting the value of Ackermann et al. [36] for $Q(^{131}\mathrm{Cs}, 7p)$, we find

$$Q(^{131}\mathrm{Cs}, 7p) = -0.562\,(8)\cdot 0.829/0.817 = -0.570\,(8)\ \mathrm{barn}\,, \tag{36}$$

where 0.829/0.817 is the ratio of the corresponding factors C_{7p}.

The two corrected values of $Q(^{131}\mathrm{Cs}, 7p)$ and $Q(^{131}\mathrm{Cs}, 6p)$ are in good agreement with each other, and the final value of $Q(^{131}\mathrm{Cs})$ is

$$Q(^{131}\mathrm{Cs}) = -0.575 \pm 0.006\ \mathrm{barn}\,. \tag{37}$$

It should be emphasized that the *uncorrected* values of $Q(^{131}\mathrm{Cs}, 6p)$ and $Q(^{131}\mathrm{Cs}, 7p)$ differ appreciably from each other, since they are given by

$$Q_{\mathrm{uncorr}}(^{131}\mathrm{Cs}, 6p) = -0.572/0.791 = -0.723\,b\,, \tag{38}$$

$$Q_{\mathrm{uncorr}}(^{131}\mathrm{Cs}, 7p) = -0.562/0.817 = -0.688\,b\,. \tag{39}$$

The ratio of the two uncorrected values ((38) and (39)) is 1.051, i.e. a 5.1% deviation. A large part of the deviation is removed by the application of the correction factors C_{6p} and C_{7p}. (This has been called the Sternheimer *differential* correction effect.) Of course, a much larger correction arises from the application of the factor C_{nl} itself. Thus, without the factor $(1-R_{nl})^{-1} = C_{nl}$, $Q(^{131}\mathrm{Cs})$ would be approximately

$$Q_{\mathrm{uncorr}}(^{131}\mathrm{Cs}) = -0.575/0.818 = -0.703\,b\,, \tag{40}$$

i.e. it would be 22% larger than the corrected value $-0.575\,b$ of (37).

It is not known to me whether even at present (1985) the available nuclear models (e.g. the nuclear shell model) would be able to distinguish between these two Q values for the case of ^{131}Cs. However, from conversations with a few nuclear physicists interested in quadrupole deformations of the nuclear core, I conclude that the answer is "probable not", i.e. the present calculations of nuclear structure are not accurate enough to predict a 22% difference in the value of $Q(^{131}\mathrm{Cs})$.

The complete results of my 1970 calculations for R, $C = (1-R)^{-1}$, and the resulting Q values of the alkali-metal isotopes are summarized in Tables XI, XII, and XIV of my paper [19], see pages 843, 845 and 846 of this paper.

A further confirmation of the necessity of the $(1-R_{nl})^{-1}$ correction factor has been obtained by Bucka et al. [38]. They have shown that for the rubidium isotopes ^{85}Rb and ^{87}Rb

$$Q_{5\mathrm{p,\,exp}}/Q_{7\mathrm{p,\,exp}}\,(^{85}\mathrm{Rb},\,^{87}\mathrm{Rb}) = 1.07 \pm 0.03\,, \qquad (41)$$

where the Q_{exp} are not corrected for antishielding effects. However, the ratio of the correction factors $C_{7\mathrm{p}}/C_{5\mathrm{p}} = 0.840/0.796 = 1.055$ brings the two values of Q ($Q_{5\mathrm{p}}$ and $Q_{7\mathrm{p}}$) into very good agreement. It may be mentioned that extensive work on my corection factors R_{nl} for the Rb isotopes was carried out by Schüssler [39].

Early estimates of R_{nl}, especially for the rare earths, were carried out by Murakawa [40].

Following the publication of my paper with Peierls [19], I carried out extensive additional calculations on the Q shielding and antishielding factors for seven atomic ground states ranging from F 2p^5 to Br4p^5. The results were published in [21]. See in particular Table VIII of this paper, which shows that R is generally positive (shielding) for the ground states of these light atoms (i.e. B, O, F, Cl, Sc, Fe^{3+}, Cu(3d) and Br) with the exception of Al ($R = -0.063$) and the excited state Cu(4p) ($R = -0.175$) and also the ground state of Ga ($R = -0.129$). The resulting corrected quadrupole moments for 11 nuclear isotopes (ranging from ^{27}Al to ^{73}Ga) are presented in Table IX of the paper [21].

Similar calculations for some atomic or ionic states, using the formalism which I had developed (especially the papers [30] and [5]) were subsequently carried out by Sen and Gupta [41].

An extension of my work for atoms with one valence p electron outside a core of closed shells or one "valence" p hole (i.e., a configuration np^5) was attempted for the case of a valence d electron. The results are reported in [42].

A hydrogenic treatment of the various shielding and antishielding effects was carried out by Foley et al. in 1953 [6]. Of course, we realized at the time (1953) that the use of hydrogenic wave functions, with any arbitrary effective Z, Z_{eff}, would be very unreliable, except for one and two-electron systems. (This was also confirmed when I carried out the first calculations of the hexadecapole antishielding factors, in 1961, see [13] and [14].) Nevertheless the use of hydrogenic wave functions is an interesting exercise and led to new insights into the various shielding and antishielding effects. In particular, Foley pointed out to me that there would be special difficulties in carrying out the calculations of the 3s → d excitations, since the 3s and 3d states are energy-degenerate in the hydrogen atom.

In April 1962 I started to consider this problem in detail. Therefore I calculated the matrix element 3s → 3d via the nuclear Q interaction, i.e. the potential due to the Q moment, which is $-QP_2/r^3$ Ry (cf. (1)). This matrix element involves the radial integral $\int_0^\infty u_0(3\mathrm{s})\,u_0(3\mathrm{d})\,r^{-3}\,\mathrm{d}r$, where $u_0(nl) = r$ times the radial wave function pertaining to the hydrogenic state nl. To my surprise this integral was found to be zero. Wondering whether this is the indication of a more general phenomenon, I also calculated $\int_0^\infty u_0(4\mathrm{s})\,u_0(4\mathrm{d})\,r^{-3}\,\mathrm{d}r$ (again using hydrogenic wave functions), and again the integral = 0. Similar results were found for $u_0(5\mathrm{s})\,u_0(5\mathrm{d})$ and also for $u_0(4\mathrm{p})\,u_0(4\mathrm{f})$, which would arise if we were to consider an electron in a hydrogenic 4p shell and its excitation to f states via the quadrupole interaction H_{Q}. Thus again

$$\int_0^\infty u_0(4\mathrm{p})\,u_0(4\mathrm{f})\,r^{-3}\,\mathrm{d}r = 0\,. \qquad (42)$$

The same property holds for the 5p and 5f states, etc. In view of my earlier work on η_∞ (1961; [13] and [14]) I also calculated matrix elements which pertain to the HDM and which could in principle be calculated using hydrogenic wave functions. Again I found similar zero results. As an example:

$$\int_0^\infty u_0(5\mathrm{s})\,u_0(5\mathrm{g})\,r^{-5}\,\mathrm{d}r = 0\,. \qquad (43)$$

(Note that the radial factor r^{-3} for the quadrupole interaction is replaced by r^{-5} for the hexadecapole interaction.)

Pasternack obtained a general proof of these results by using the generating function of the associated Laguerre polynomials [43].

The general statement of the theorem (or selection rule) is that

$$K_{nll',s} \equiv \int_0^\infty r^{-s}\,u_0(nl)\,u_0(nl')\,\mathrm{d}r = 0\,, \qquad (44)$$

provided that $s = 2, 3, \ldots, l - l' + 1$ (with the convention that $l > l'$).

In the above example of (43), $l = 4$, $l' = 0$, so that $l - l' + 1 = 5$. Thus all integral inverse powers from $s = 2$ to 5 (i.e., $s = 2, 3, 4, 5$) will give a zero integral. The theorem and its proof were published by Pasternack and Sternheimer [33].

In connection with the solution of the inhomogeneous equation for $u_1(nl \to l')$ (9), I should note that it is essential to use a value of $V_0 - E_0$ at each grid point r_0 (see (9)), which is consistent with the unperturbed radial function $u_0(nl)$ used in the calculations. As I pointed out in 1952 [4], this can be done by inverting the Schrödinger equation for $u_0(nl)$, namely

$$\left[-\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{l(l+1)}{r^2} + V_0 - E_0\right] u_0(nl) = 0\,, \tag{45}$$

which gives

$$V_0 - E_0 = \frac{1}{u_0}\frac{\mathrm{d}^2 u_0}{\mathrm{d}r^2} - \frac{l(l+1)}{r^2}\,. \tag{46}$$

Thus the sum of the last 3 terms in the l. h. s. of (9) becomes

$$\frac{l'(l'+1)}{r^2} + V_0(r) - E_0 = \frac{1}{u_0}\frac{\mathrm{d}^2 u_0}{\mathrm{d}r^2} + \frac{l'(l'+1) - l(l+1)}{r^2}\,. \tag{47}$$

Equation (47) determines the effective potential pertaining to u_0, and since the difference $V_0(r) - E_0$ in the l. h. s. does not involve E_0 separately, it is not necessary to determine directly the energy eigenvalue E_0 pertaining to the particular function $u_0(r)$ used in the calculations by a solution of (45). Equation (46) has been called the local field or local potential approximation and has been widely used in a wide variety of problems of perturbation theory since 1952 when I first introduced it. The results obtained from the combination of (9), (10), and (47) have been called the Sternheimer approximation particularly by Sandars in his calculations of the effect of a time-reversal violating electric dipole moment of the electron (usually the valence ns electron of the alkali-metal atoms) [44], and also in his calculations of the atomic effects arising from the weak neutral currents of the electroweak theory. The results given above ((45) to (47)) elaborate on the previous discussion pertaining to (15).

I shall now return to the actual calculations of γ_∞ from the $u_0(nl)$ and $u_1(nl \to l')$, and I shall also discuss the basic function $\gamma(r)$ which arises in the calculation of both γ_∞ and R.

If $Q_{\mathrm{ind}}(r)$ is the induced quadrupole moment density at a point r, then we find that the potential energy due to the induced moment effects at a radius r are proportional to $\gamma(r)/r^3$, where $\gamma(r)$ is defined as

$$\gamma(r) \equiv \frac{1}{Q}\int_0^r Q_{\mathrm{ind}}(r')\,\mathrm{d}r' + r^5 \int_r^\infty Q_{\mathrm{ind}}(r')\,r'^{-5}\,\mathrm{d}r'\,. \tag{48}$$

Thus the atomic shielding or antishielding factor R_{nl} is given by

$$R_{nl} = \frac{\langle \gamma r^{-3}\rangle}{\langle r^{-3}\rangle}\,, \tag{49}$$

where the brackets $\langle\,\rangle$ indicate an average over the radial valence wave function $v(nl)$. Thus

$$\langle \gamma r^{-3}\rangle = \int_0^\infty \gamma(r)\,r^{-3}[v(nl)]^2\,\mathrm{d}r\,, \tag{50}$$

and similarly

$$\langle r^{-3}\rangle = \int_0^\infty [v(nl)]^2 r^{-3}\,\mathrm{d}r \tag{51}$$

with the normalization

$$\int_0^\infty [v(nl)]^2\,\mathrm{d}r = 1\,. \tag{52}$$

On the other hand γ_∞ is simply given by

$$\gamma_\infty = \gamma(r \to \infty)\,. \tag{53}$$

The function $\gamma(r)$ was first calculated by myself in connection with my original calculations using the TF model [1] and the slightly later calculations using accurate solutions of (9), [3]. These functions for 4 representative ions (Cl^-, Cu^+, Rb^+ and Cs^+) were calculated and published by Foley et al. [6]. Revised and more accurate values of $\gamma(r)$ and γ_∞ were calculated by myself [25].

Some of the values of γ_∞ which I obtained in the period from 1950 to 1967 have been more recently re-evaluated by Feiock and Johnson [45]. These results, which were calculated relativistically, show that γ_∞ is generally not sensitive to the modifications brought about by making relativistic calculations. Thus the difference $|\gamma_\infty^{\mathrm{N\,Rel}} - \gamma_\infty^{\mathrm{Rel}}|$ is generally $\leqq 10\%$ of γ_∞, which is also the inherent uncertainty in γ_∞ due to the particular choice of the unperturbed core wave functions $u_0(n\,l)$ used in the calculations.

Additional calculations of γ_∞ and R have been carried out by Gupta et al. [46], and Lauer et al. [47].

The last reference [47] is actually concerned more directly with the evaluation of $\gamma(r)$ defined here in (48). Similar calculations have also been done by Sen et al. [48]; see also earlier papers by Sen [49] and by Rao and Mohapatra [50].

The function $\gamma(r)$ (which goes asymptotically to γ_∞ as $r \to \infty$) is of great importance when the lattice spacing in the crystal is relatively small, or when one of the ions has a large spatial extension, e.g. for negative ions such as F^- and O^{2-}. This aspect of the hyperfine interaction has been investigated by Beri et al. [51].

These results [51] for the nuclear quadrupole coupling at the Fe nucleus in a crystal of α-Fe_2O_3 utilize my $u_1(n\,l \to l')$ perturbations (both radial $l' = l$ and angular $l' = l + 2$) for the Fe^{3+} ion, which I had previously calculated (1973). The problem which is most directly discussed in [51] is the first-principles theory of the Sternheimer shielding and antishielding effects of the nuclear quadrupole interactions (NQI) at the $^{57\mathrm{m}}$Fe nucleus in a Fe_2O_3 crystal. It is shown that the antishielding factor γ_∞ should be used directly only for the EFG produced by *distant electric charges*. For the external charges which are closer to the $^{57\mathrm{m}}$Fe nucleus, an intermediate value of the effective antishielding factor, γ_{eff}, must be used. In fact one of the main results of this paper is that the γ_{eff} value varies with the type of source (local, nonlocal and distant) and has the values -0.2, -0.7, -3.8, and -6.5, all of which are smaller in magnitude than the external $\gamma_\infty(Fe^{3+}) = -9.14$, as calculated in [28].

The paper of Beri et al. [51] is also useful, aside from its essential content, because of the extensive and rather complete list of references to work on the shielding and antishielding effects from 1950 to 1979 (see pages 2349–2351 of [51]). An earlier and somewhat different list of references was given by Sen in his PhD thesis [52]; see also [30].

The Beri et al. paper [51] also contains an essentially complete list of references to the papers of Das and coworkers on the role of consistency and correlation effects on the resulting values of γ_∞. Generally these effects change γ_∞ by corrections of the order of 10% or less, which is of the same order of magnitude as the uncertainty of γ_∞ due to the use of a particular set of core wave functions $u_0(n\,l)$, e.g. the HF wave functions, which do not include the detailed effect of electron-electron correlation arising from their repulsive interaction e^2/r_{12}. Das et al. have used the diagrammatic method in the calculations, together with the linked-cluster-many-body-perturbation theory (LCMBPT). See, in particular, the papers by Das and coworkers in [53]. It should be noted that the second paper of [48] and the two papers of [54] discuss the effect of the presence of the crystal lattice in ionic solids on the effective value of γ_∞. These calculations suggest that the presence of the neighbouring ions in the crystal lattice causes an increase in the free-ion γ_∞ for positive ions and a decrease of γ_∞ for negative ions.

In connection with these more recent papers I should mention the earlier work of Burns and Wikner [55], Sharma [56], Watson and Freeman [57], Childs and Goodman; Clieves and Steudel [58], Fischer [59], zu Putlitz [60], Ingalls [61], see also Lindgren and Morrison [62]. γ_∞ is directly involved in the proposal of Raghavan et al. [63] that the contribution to the EFG arising from the conduction electrons in a metal is directly proportional $(1 - \gamma_\infty)$. Thus the Raghavan assumption is

$$e\,q_{\mathrm{eln}} = K(1 - \gamma_\infty)\,e\,q_{\mathrm{nuclear}}\,, \tag{54}$$

where K is a constant factor of the order of 2–3.

While many metal-impurity systems fall more or less on the smooth curve predicted by (54), there were always some exceptions, and more recently the relation of (54) has been seriously challenged by the work of Hagn et al. [64]. Hagn and coworkers have measured directly the EFG's for various 5d atom impurities in Lu ($Z = 71$) and in Re ($Z = 75$) metal hosts. The two resulting curves $e\,q_{\mathrm{exp}}$ vs. Z_{imp} of the impurity atom follow similar trends, i.e., they both increase algebraically with increasing Z (from $Z = 71$ for Lu to $Z = 80$ for Hg), but the algebraic values of $e\,q_{\mathrm{expt}}$ are *positive* for Lu hosts and *negative* for the Re host lattices. In a recent paper, Watson et al. [65] have examined in extensive detail the possible reasons for this unexpected sign reversal, and we have come to the conclusion (based on the Hagn et al. and additional data) that in the basic equation

$$e\,q = e\,q_{\mathrm{intra}} + e\,q_{\mathrm{LR}} + e\,q_{\mathrm{inter}} \tag{55}$$

it is the first and the third terms which are principally responsible for the observed EFG's. Here $e\,q_{\mathrm{intra}}$ is the *intra*-atomic contribution arising from the aspherical charge distribution of the valence electron charge within the impurity cell. The second term is the long-range contribution involving a lattice sum over the host crystal. The third (and most important) term involves those *inter*-atomic contributions associated with the disturbance due to the impurity in the immediate surrounding host medium (e.g. charge transfer, charges in directional bonding, and hosts in near-neighbor nuclear positions). For details see [65]. In connection with this work, I have discovered a new scaling law for γ_∞ as a function of the volume of the ion considered. Thus for ions in the same column of the periodic table, e.g. Na^+, K^+, Rb^+ and Cs^+, γ_∞ is nearly proportional to $V^{1.5}$, where V is the ionic volume (see Appendix of [65]).

A further application of the ionic antishielding factors arises in the analysis of certain Mössbauer-type experiments involving the rare earths. These experiments were initiated by the work of Barnes et al. [66], and from the line shift (usually expressed in units of mm/s) one obtaines directly the ratio

$$\mathscr{R} = \frac{1-\gamma_\infty}{(1-\sigma_2)(1-R_{4\mathrm{f}})}, \tag{56}$$

where $1-\gamma_\infty$ for the trivalent rare-earth ions (e.g. Pr^{3+}, Tm^{3+}) is ≈ 80 [30]. $R_{4\mathrm{f}}$ (pertaining to the 4f electrons) is 0.1 to 0.2, and σ_2 is a new shielding factor (first introduced by G. Burns) which can be easily calculated using my method of solving the pertinent inhomogeneous differential equations and performing the appropriate integration over the 4f wave function $u_{4\mathrm{f}}$. These calculations are given in two of my papers [30, 32]. The second paper in [32], by Sternheimer, Blume, and Peierls also gives values for the higher multipole (2^k) shielding factors σ_4 and σ_6. In general, in the rare-earth region σ_2 is of the order of 0.7 to 1.0, so that the presence of the factor $(1-\sigma_2)$ in the denominator of (56) is decisive for the value of $\mathscr{R}$. Good agreement with the experimental values of $\mathscr{R}$ has been generally obtained.

In connection with my original papers (1950–52) I may note that I also published a paper on the magnetic hyperfine structure, i.e. the structure connected with the hfs constant a_{nl}, in which I pointed out (at the beginning of the paper [4]) that one also expects a contribution of the electron core to a_{nl}, since the valence electron $(n\,l)$, due to its spin, will have an extra interaction with the core electrons having parallel spin, due to exchange, so that the electron density for core electrons with parallel spin will be different from the core electrons with antiparallel spin. The result is a net magnetic field at the nucleus $\boldsymbol{H}_{\mathrm{core}}(0)$ arising from the two different spin densities. This extra field $\boldsymbol{H}_{\mathrm{core}}(0)$ contributes to the observed hfs constant a_{nl}, i.e. the total field

$$\boldsymbol{H}_{\mathrm{total}}(0) = \boldsymbol{H}_{\mathrm{val}}(0) + \boldsymbol{H}_{\mathrm{core}}(0) \tag{57}$$

is effective in determining the observed a_{nl}, where $\boldsymbol{H}_{\mathrm{val}}(0)$ is the magnetic field produced by the valence electron.

For the field due to the core ns electrons, $H_{\mathrm{core,\,ns}}(0)$ is directly proportional to the difference of the charge densities at the nucleus, $\varrho_\uparrow(0) - \varrho_\downarrow(0)$. A similar effect arises from the core np, nd, etc. electrons. This is the basic mechanism for the core polarization, and it was described and calculated in a few cases in [4]. Similar calculations were performed at about the same time by Abragam, Horowitz, and Pryce [67]. It should also be noted that the suggestion of I. I. Rabi that the EFG's at the nuclei of medium and heavy atoms might not be determined solely by the EFG due to the valence electron gave the original motivation for my investigations of core effects on the nuclear quadrupole coupling in 1949.

The second comment concerns the earliest experimental verifications of γ_∞.

The verifications were found in 1953 and 1954 in two different contexts.

(i) From hfs measurements by Rabi, Kusch, and coworkers at Columbia University [68, 69], the EFG's at the halogen nucleus in alkali halides were measured, in particular for NaCl^{35}, $\mathrm{K}^{39}\mathrm{Br}^{81}$, and NaI^{127}. It was clear to Foley and myself that the measured values of the EFG's were *many* times, i.e. of the order of 10–20 times, the value $+2e/R^3$ expected for an alkali-metal point charge at a distance R (the internuclear distance of the molecule). Although these factors are less than the corresponding values of $\gamma_\infty(\mathrm{Cl})^-) = -55$, and $\gamma_\infty(\mathrm{I}^-) = -120$, they nevertheless pointed to a strong amplifying effect, which could probably be explained in terms of the calculated antishielding. In fact, it was these measurements on polar molecules which led Foley and myself to systematically calculate γ_∞ for the alkali-metal ions Na^+, K^+, Rb^+ and for the halogen ion Cl^-. The resulting paper was published in February 1954 [6].

(ii) A second confirmation of the existence and importance of the large antishielding factors γ_∞ came about 6 months later from the work of van Kranendonk [70]. Van Kranendonk found that the ultrasonic relaxation times T_1 in certain solids were too short by factors of 10^3-10^4. Since the relaxation time in these solids is of quadrupolar origin, it is proportional to $1/Q_{\text{ion}}^2$, where Q_{ion} is the total quadrupole moment of the entire ion:

$$Q_{\text{ion}} = Q(1-\gamma_\infty)\,. \tag{58}$$

We find that T_1 is proportional to $1/(1-\gamma_\infty)^2$, which can be easily of the order 10^{-2} to 10^{-4} for γ_∞ in the range of -5.1 (for Na^+) to -120 (for I^-).

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