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Relativistic effects in nuclear quadrupole coupling

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Abstract. Relativistic effects strongly influence the nuclear quadrupole coupling of atoms, molecules or solids. As first shown by Casimir in 1936, in the atomic or single-centre case, for the two states $j = l \pm s$, three radial electric-field-gradient (EFG) integrals, R_{++}, R_{+-}, and R_{--}, must be introduced. The relativistic correction factors, defined for operator $\hat{q}$ as

$$C = \langle \mathrm{R}|\hat{q}|\mathrm{R}\rangle / \langle \mathrm{NR}|\hat{q}|\mathrm{NR}\rangle,$$

have quite different values for the three combinations. For example, for the Bi atom ground state 6p shell at Dirac-Fock(DF) level, C_{++} and C_{+-} are 1.28 and 1.91, respectively, while $q_{-,-}$ vanishes entirely, due to $j = 1/2$. There also is a dependence on the n quantum number. In addition to these relativistic changes of the integrals (at the atomic centre), *spin-orbit tilting effects* may occur, even at light atoms, bonded to heavy ones.

We have produced DF-level, EFG integrals for the elements 1–93, investigated the hydrogen-like, n-dependent correction factors, C and used simple molecular-orbital models for estimating the spin-orbit tilting effects.

Key Words: Relativistic corrections – Nuclear quadrupole coupling – Electric field gradients – Spin-orbit coupling

1 Introduction

Relativistic effects on nuclear electric quadrupole coupling in atomic spectra were first analysed in 1936 by Casimir [1]. Using a Dirac wave function where a Coulombic inner part is fitted to a quantum-defect treatment of the outer part, he derived for the diagonal and off-diagonal radial integrals $\langle r^{-3} \rangle$ of the two states $j = l \pm s$, the diagonal and off-diagonal correction factors C_{++}, C_{+-} and C_{--} (denoted by him as R', S and R'', respectively). A numerical table of these, n-independent factors was published in 1958 by Kopfermann [2]. An alternative is to calculate these correction factors using hydrogen(H)-like, Dirac-Coulomb functions. Expressions in closed form appear in Ref. [3] for the diagonal case ('$++$' and '$-,-$'). Numerical examples have also been published for p elements [3–5] and for d, f and g elements [4,6].

The atomic one-valence-electron [7] and many-electron [8] cases were further analysed. The latter work is, in particular, applicable to cases where spin-orbit effects cause an EFG, q, for atoms with a half-filled shell (p^3, d^5, f^7), where the nonrelativistic value vanishes. The latest review on electric quadrupole coupling in atoms, including the relativistic aspects, seems to be that by Lindgren and Rosén [9]. They also give a number of radial integrals, calculated at the Dirac-Slater level. Desclaux's tables [10] list the average-of-configuration, DF diagonal integrals for the atomic ground states of the elements 1–120. Further integrals, for both p and d elements, are given by Lindgren and Rosén [9]. Data for the lanthanide [11] and actinide [12] ions also exist.

For molecules, Townes and Dailey [13] introduced a simple analysis based on one-centre contributions only and a population analysis. These integrals can be corrected using a quasirelativistic (spin-orbit-averaged) combination of Casimir's factors. The limitations of this simple model, as compared with full, all-electron treatments, were illustrated by Balakina et al. [14].

Dunlap [15,16] considered the actinide coupling in actinyl ions, under the hypothesis that it comes from the $5f$ shell, using the theory of Sandars and Beck [8]. Larsson and Pyykkö [17] proposed the possibility that the hole in the $6p\sigma$ ($6p_{\frac{3}{2}}(m_j = \frac{1}{2})$) shell suffices to explain the observed trend.

At ab initio level, a perturbative study of relativistic effects on the halogen field gradients in HCl, HBr and HI [18,19] and BrCl [20] has been published by Sadlej and coworkers. In the future it is hoped that fully relativistic all-electron data will be reported for this property. No such data exist yet.

Quasirelativistic pseudopotential and MSXα calculations on gold halide systems by Schwerdtfeger et al. [21]

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show that relativistic electronic effects at constant geometry increase the Cl nuclear quadrupole coupling constant (NQCC), presumably via the increased electronegativity of gold. The q_{Au} is made more negative at the same time. No obvious relationship exists between correction factors of the present type and these results.

Quasirelativistic band-structure calculations of solids have now reached a point where they can give, combined with experimental coupling constants, competitive values of Q. An example is the Mössbauer state of ^{57}Fe [22]. The data on the relativistic changes are more limited [23].

The present paper has several aims. Currently, the best way of determining nuclear quadrupole moments, Q, for the lighter elements is to combine experimental quadrupole coupling constants, eqQ/h, with good ab initio calculations of q for atoms or small molecules [24]. The present standard values [25] for the first 25 elements indeed come from that source. It is interesting to know how to correct these results for relativistic effects. Secondly, we would like to get a feeling for the spin-orbit tilting effects in molecules at the semiempirical level. We therefore derive an expression for the off-diagonal Dirac-Coulomb case and report both diagonal and off-diagonal DF-level integrals for the elements up to $_{93}$Np.

2 Theory

The $1/r_{ne}$ Coulomb interaction between the nuclear and electronic (and other external) charge distributions is

$$E_{ne} = \int dV_n \int dV_e \rho_n \rho_e \frac{1}{r_{ne}}. \tag{1}$$

Using the multipole expansion

$$\frac{1}{r_{ne}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{1}{2l+1} \frac{r_<^l}{r_>^{l+1}} \times Y_l^{m*}(\theta_n, \phi_n) Y_l^m(\theta_e, \phi_e), \tag{2}$$

and assuming that the nuclear radius, $r_n < r_e$, we can write [26,27] the interaction energy in Eq. (1) as

$$E_{ne} = \sum_{l,m} A_l^{m*} B_l^m, \tag{3}$$

where

$$A_l^m = \left[\frac{4\pi}{2l+1}\right]^{1/2} \int \rho_n r_n^l Y_l^m dV_n, \tag{4}$$

$$B_l^m = \left[\frac{4\pi}{2l+1}\right]^{1/2} \int \rho_e r_e^{-l-1} Y_l^m dV_e. \tag{5}$$

The external charge distribution can be regarded as space-fixed for molecules and solids. Its $l = 2, m = 0$ part will directly correspond to the EFG, q:

$$2B_2^0 = \langle r^{-3} 2P_2^0(\cos\theta_e)\rangle = \langle (3z^2 - r^2)/r^5 \rangle = q_{zz} \equiv q. \tag{6}$$

The nuclear quadrupole moment is defined for a nuclear spin I as

$$Q = \langle II \mid 3z^2 - r^2 \mid II \rangle. \tag{7}$$

The final nuclear quadrupole Hamiltonian becomes [26]

$$H_Q = \frac{eqQ}{4I(2I-1)}[3I_z^2 - I(I+1) + \frac{1}{2}\eta(I_+^2 + I_-^2)], \tag{8}$$

where the *asymmetry parameter* is defined as

$$\eta = (q_{xx} - q_{yy})/q_{zz}, \tag{9}$$

each component corresponding to Eq. (6), in the principal axis system of the tensor $\mathbf{q}$. This derivation is valid for relativistic or nonrelativistic external charge densities, ρ_e.

For the latest compilation of nuclear quadrupole moments, see Ref. [25].

In the atomic or one-centre case, the atomic orbitals at the nucleus considered will be of the type $j = l \pm \frac{1}{2}$. It was already noted by Casimir [1] that one will then need three different radial integrals for $l > 1$ (for p electrons, the q_{--} disappears):

$$q_{++} = \langle l + \frac{1}{2} \mid q \mid l + \frac{1}{2} \rangle \tag{10}$$

$$q_{+-} = \langle l + \frac{1}{2} \mid q \mid l - \frac{1}{2} \rangle \tag{11}$$

$$q_{--} = \langle l - \frac{1}{2} \mid q \mid l - \frac{1}{2} \rangle. \tag{12}$$

Sandars and Beck [8] considered the same problem for atoms in SLJ coupling and Dunlap [15] adopted their theory for transition-metal compounds, where J is well defined. Then the effective Hamiltonian is written as a scalar product of a nuclear and electronic irreducible tensor,

$$H_Q^{\mathrm{eff}} = \mathbf{T}_n^2 \cdot \mathbf{T}_e^2, \tag{13}$$

where the $l = 2$ electronic tensor operator can be vector coupled from the (SL)J combinations (02)2, (13)2 and (11)2. The latter two contributions reduce to zero at the nonrelativistic limit. The first one also corresponds to the quasirelativistic correction factor

$$C(l,Z) = \frac{(l+2)(2l-1)R_{++} + (l-1)(2l+3)R_{--} + 6R_{+-}}{(2l+1)^2 R_{\mathrm{NR}}}. \tag{14}$$

Here the radial integrals

$$R_{ab} = \int_0^{\infty} (g_a^* g_b + f_a^* f_b) r^{-3} (r^2 dr), \tag{15}$$

where the indices a, b carry both n, l and j. For a given combination n_a, l_a, n_b, l_b, the j-values are given by the combinations R_{++}, R_{+-}, R_{-+} and R_{--}. Here the lower indices give the sign of $j = l \pm \frac{1}{2}$ for the bra and ket vectors, a and b, respectively, analogously with Eqs. (10–12).

We find the same result for a quasirelativistic treatment of one-centre contributions of a molecule.

In a simple, one-centre treatment of q in molecules, using the orbital

$$|\psi_{n,l,m_l}\rangle|\chi_{\frac{1}{2},m_s}\rangle = a_{l+\frac{1}{2}}|\phi_{n,l+\frac{1}{2},m_l+m_s}\rangle + a_{l-\frac{1}{2}}|\phi_{n,l-\frac{1}{2},m_l+m_s}\rangle \tag{16}$$

there will also be a mixed term denoted as R_{+-}.

It is of interest to see what effect, if any, these off-diagonal terms have. In the absence of spin-orbit splitting [hereafter called the quasirelativistic (QR) limit] the coefficients $a_{l+\frac{1}{2}}$ and $a_{l-\frac{1}{2}}$ can be determined very easily. If spin-orbit coupling is included both the coefficients and the radial $\langle r^{-3}\rangle$ integrals, R, will deviate from their QR averages. We call these changes of q, *spin-orbit tilting*.

First, treating the quasirelativistic case, the matrix elements over the angular portion of the $\hat{q}$ operator are calculated and combined with the r-dependent part calculated by one of the methods described in Sect. 3. Once this is carried out for both the relativistic and nonrelativistic case and the ratio taken, a series of formulae depending on l and m_j are derived. Consider, for instance, a $p_\pi(1/2)$ orbital. At the quasirelativistic limit we have

$$|\psi_{n,l=1,m_l=1,m_j=\frac{1}{2}}\rangle = \sqrt{\frac{2}{3}}|p_{\frac{1}{2}}(\frac{1}{2})\rangle + \sqrt{\frac{1}{3}}|p_{\frac{3}{2}}(\frac{1}{2})\rangle. \tag{17}$$

We then express the expectation value q as a sum of radial integrals, R_{ab}, each multiplied by an angular integral A_{ab}. The appropriate angular coefficients for Eq. (17) are $A_{--} = 0$, $A_{+-} = -\frac{2\sqrt{2}}{5}$ and $A_{++} = \frac{2}{5}$. The A values are calculated using the appropriate coefficients from Eq. (17) and integrals over the angular portion of q. The total answer for Eq. (17) becomes

$$q_{\pi_{\frac{1}{2}}} = -\frac{8}{15}R_{+-} + \frac{2}{15}R_{++}. \tag{18}$$

Combining Eq. (18) with the appropriate nonrelativistic value i.e.

$$q_{\mathrm{NR},\pi} = -\frac{2}{5}R_{\mathrm{NR}} \tag{19}$$

a correction factor is obtained. Two methods for obtaining the radial integrals, R, are described in Sect. 3. Examination of Eq. (18) reveals that for p orbitals the off-diagonal contribution in quasirelativistic $\langle r^{-3}\rangle$ expectation values is more important than the diagonal contribution. Averaging the two $m_l, m_l \pm \frac{1}{2}$ values revealed that R is independent of m_l. The ratios derived for $l = 1, 2, 3$ were in agreement with those calculated by the formula of Sandars and Beck [8], see Eq. (14). One further point of interest was found while deriving these formulae. *The f_δ orbital contributes nothing to the EFG at the nucleus owing to its octahedral symmetry.* However, as soon as the population in the $f\delta_{\frac{5}{2}}$ and $f\delta_{\frac{7}{2}}$ orbitals becomes different from the nonrelativistic limit an EFG is created.

3 Atomic matrix elements

3.1 Dirac-Coulomb case

Perhaps the simplest way to obtain relativistic corrections for EFGs is to calculate the expectation values of r^{-3} with the solution of the one-electron Dirac equation and the solution of the one-electron Schrödinger equation and then take the ratio of these two results. The algebraic expression for the diagonal values of $\langle r^{-3}\rangle_{\mathrm{NR}}$ is [29]

$$\langle r^{-3}\rangle_{nl} = \frac{Z^3}{n^3 l(l+1)(l+\frac{1}{2})}. \tag{20}$$

The more general, off-diagonal expression has recently been published [30], and agrees with our results, provided that in their Eq. (3) the expression $n_1^{l_2+1}n_2^{l_1+1}$ is replaced by $n_1^{l_2+1+k}n_2^{l_1+1+k}$. To our knowledge, no such expression exists for solutions of the Dirac equation, though the diagonal solution was first worked out in 1939 [31]. The starting point for the more general expression is the form of the H-like, Darwin-Gordon solution of the Dirac equation, as given by Davis [31] and Hill and Landshoff [32]; see these references for the notation used.

$$f_s(r) = isC(1 - s\epsilon)^{\frac{1}{2}}e^{-\lambda r}(2\lambda)^\gamma r^{\gamma-1}(v_{1,s} - v_{2,s}), \tag{21}$$

$$G_s(r) = C(1 + s\epsilon)^{\frac{1}{2}}e^{-\lambda r}(2\lambda)^\gamma r^{\gamma-1}(v_{1,s} + v_{2,s}), \tag{22}$$

where

$$C = \lambda(n'!)^{\frac{1}{2}}[2Z\epsilon\Gamma(2\gamma + n' + 1)]^{\frac{1}{2}} \tag{23}$$

$$\epsilon = E\alpha^2 = [1 + Z^2\alpha^2/(n' + \gamma)^2]^{-\frac{1}{2}} \tag{24}$$

$$\lambda = (1/\alpha)(1 - \epsilon^2)^{\frac{1}{2}} \tag{25}$$

$$\gamma = [\kappa^2 - Z^2\alpha^2]^{\frac{1}{2}} \tag{26}$$

$$n' = n - J - \frac{1}{2} \tag{27}$$

$$v_{1,s} = (2\gamma + n')[\gamma + n' - \kappa\epsilon]^{-\frac{1}{2}}\epsilon L_{n'-1}^{2\gamma}(2\lambda r) \tag{28}$$

$$v_{2,s} = -s[\gamma + n' - \kappa\epsilon]^{-\frac{1}{2}}L_{n'}^{2\gamma}(2\lambda r). \tag{29}$$

Here s is the negative of the sign of κ. $L_a^b(z)$ is the generalized Laguerre polynomial. Atomic units are used throughout. When $s = +1$ f_s corresponds to the small component and G_s to the large one. When $s = -1$ the situation is reversed.

We are interested in the totally general situation, i.e.

$$\langle r^k\rangle_{ab} = \int_0^\infty (G_a^* G_b + f_a^* f_b) r^{k+2} dr \tag{30}$$

Note that here the states a and b may have differing n and l. Considering the definitions in Eqs. (21–29), they correspond to the case $s_1 = s_2$. This is the case that we shall treat here. In the case where $s_1 = -s_2$ the argument is the same but a few signs are changed. The generalized Laguerre polynomial is written according to its definition,

$$L_n^\gamma(r) = \sum_{i=0}^{n}(-1)^i\binom{n+\gamma}{n-i}\frac{(2\lambda r)^i}{i!}. \tag{31}$$

Once this is done, all that is required is the use of the integral

$$\int_0^\infty r^{v-1}e^{-\mu r}dr = \frac{1}{\mu^v}\Gamma(v) \tag{32}$$

and some algebra to arrive at the final equation

$$\begin{aligned}
\langle r^k\rangle_{ab} &= C_aC_b2^{(\gamma_a+\gamma_b)}(\lambda_a)^{\gamma_a}(\lambda_b)^{\gamma_b} \\
&\times \Big[\Big(s_as_b(1-s_a\epsilon_a)^{\frac{1}{2}}(1-s_b\epsilon_b)^{\frac{1}{2}} + (1+s_a\epsilon_a)^{\frac{1}{2}}(1+s_b\epsilon_b)^{\frac{1}{2}}\Big) \\
&\times (2\gamma_a+n'_a)(2\gamma_b+n'_b)(\gamma_a+n'_a-\kappa_a\epsilon_a)^{-\frac{1}{2}} \\
&\times (\gamma_b+n'_b-\kappa_b\epsilon_b)^{-\frac{1}{2}}\epsilon_a\epsilon_b \\
&\times \sum_{i=0}^{n'_a-1}\sum_{j=0}^{n'_b-1}\frac{(-1)^{i+j}}{i!j!}\lambda_a^i\lambda_b^j\binom{n'_a+2\gamma_a-1}{n'_a-i-1}\binom{n'_b+2\gamma_b-1}{n'_b-j-1} \\
&\frac{\Gamma(\gamma_a+\gamma_b+k+i+j+1)}{(\lambda_a+\lambda_b)^{(\gamma_a+\gamma_b+k+i+j+1)}} + \Big(s_a(1-s_a\epsilon_a)^{\frac{1}{2}}(1-s_b\epsilon_b)^{\frac{1}{2}} \\
&-s_b(1+s_a\epsilon_a)^{\frac{1}{2}}(1+s_b\epsilon_b)^{\frac{1}{2}}\Big) \\
&\times (2\gamma_a+n'_a)(\gamma_a+n'_a-\kappa_a\epsilon_a)^{-\frac{1}{2}} \times (\gamma_b+n'_b-\kappa_b\epsilon_b)^{\frac{1}{2}}\epsilon_a \\
&\times \sum_{i=0}^{n'_a-1}\sum_{j=0}^{n'_b}\frac{(-1)^{i+j}}{i!j!}\lambda_a^i\lambda_b^j\binom{n'_a+2\gamma_a-1}{n'_a-i-1}\binom{n'_b+2\gamma_b}{n'_b-j} \\
&\frac{\Gamma(\gamma_a+\gamma_b+k+i+j+1)}{(\lambda_a+\lambda_b)^{(\gamma_a+\gamma_b+k+i+j+1)}} + \Big(s_b(1-s_a\epsilon_a)^{\frac{1}{2}}(1-s_b\epsilon_b)^{\frac{1}{2}} \\
&- s_a(1+s_a\epsilon_a)^{\frac{1}{2}}(1+s_b\epsilon_b)^{\frac{1}{2}}\Big) \times (2\gamma_b+n'_b)(\gamma_a+n'_a-\kappa_a\epsilon_a)^{\frac{1}{2}} \\
&(\gamma_b+n'_b-\kappa_b\epsilon_b)^{-\frac{1}{2}}\epsilon_b \times \sum_{i=0}^{n'_a}\sum_{j=0}^{n'_b-1}\frac{(-1)^{i+j}}{i!j!}\lambda_a^i\lambda_b^j \\
&\binom{n'_a+2\gamma_a}{n'_a-i}\binom{n'_b+2\gamma_b-1}{n'_b-j-1}\frac{\Gamma(\gamma_a+\gamma_b+k+i+j+1)}{(\lambda_a+\lambda_b)^{(\gamma_a+\gamma_b+k+i+j+1)}} \\
&+ \Big((1-s_a\epsilon_a)^{\frac{1}{2}}(1-s_b\epsilon_b)^{\frac{1}{2}} + s_as_b(1+s_a\epsilon_a)^{\frac{1}{2}}(1+s_b\epsilon_b)^{\frac{1}{2}}\Big) \\
&\times (\gamma_a+n'_a-\kappa_a\epsilon_a)^{\frac{1}{2}}(\gamma_b+n'_b-\kappa_b\epsilon_b)^{\frac{1}{2}} \\
&\times \sum_{i=0}^{n'_a}\sum_{j=0}^{n'_b}\frac{(-1)^{i+j}}{i!j!}\lambda_a^i\lambda_b^j\binom{n'_a+2\gamma_a}{n'_a-i}\binom{n'_b+2\gamma_b}{n'_b-j} \\
&\frac{\Gamma(\gamma_a+\gamma_b+k+i+j+1)}{(\lambda_a+\lambda_b)^{(\gamma_a+\gamma_b+k+i+j+1)}}\Big].
\end{aligned} \tag{33}$$

The integral Eq. (33) is non-singular if γ is real and $\gamma_a+\gamma_b+k+1$ is positive. The first condition requires that $Z \leq |\kappa|\alpha^{-1}$. To satisfy the second condition in the most singular case of $|\kappa_a| = 1, |\kappa_b| = 2$, for a point nucleus and $k = -3$, this implies that the nuclear charge $Z \leq 132$.

If we have $a = b$, i.e. the diagonal integral, then the equation reduces to that given by Davis [31].

Using Eq. (33) and the equation for the nonrelativistic expectation value of r^{-3}, relativistic corrections for a nonrelativistic expectation value can be determined. These corrections can be compared with those obtained from Dirac-Fock (DF) and Hartree-Fock (HF) values in the next section. Of special interest in the dependence of the correction on the quantum number *n*.

3.2 Dirac-Fock case

The DF procedure provides a more realistic method for calculating $\langle r^{-3}\rangle$ expectation values than the simple one-electron Dirac equation. Using the program of Desclaux [33] the relevant matrix elements were obtained for the valence shells of the elements with Z 1,3–93. Nonrelativistic results were obtained by setting *c* to a very large number. A finite, homogeneously charged nuclear model was used in the calculation but no other provision was taken for nuclear-size effects. For a discussion on this point, see Fedorov et al. [34]. The results are given in Tables 1–4

3.3 Periodic trends

The dependence of the quasirelativistic correction factor, $C_{\mathrm{QR}}(\mathrm{DF})$ for *p* electrons on the nuclear charge, *Z*, is shown in Fig. 1. It follows the structureless Casimir correction but local maxima occur at the coinage metals, $Z = 29$, 47 and 79, as noted earlier for other properties [10,35].

3.4 Dependence on n

The dependence of the individual correction factors C_{++} and C_{+-} on the principal quantum number, *n*, for the *p* shells of Bi is illustrated in Fig. 2. Both DF-, H-like and Casimir corrections are given. The DF- and H-like trends are found to be qualitatively similar. It is not obvious, why the innermost shell should have the smallest *C*, as already found before for C_{++}, and for the analogous magnetic hyperfine correction factor [3].

3.5 Effects of atomic state and ionicity

All the corrections in Sect. 3.2 are calculated for a particular state. The question still remains, how trans-

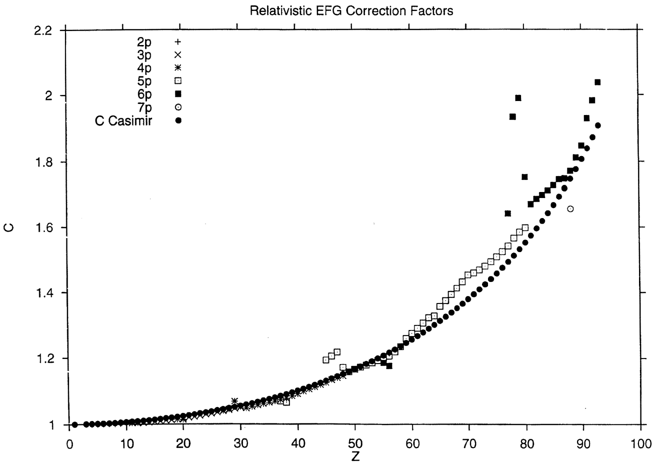

Fig. 1. Dirac-Fock quasirelativistic correction factors for the valence *np* shells as function of the (full) nuclear charge, *Z*. The *n*-independent Casimir correction is included

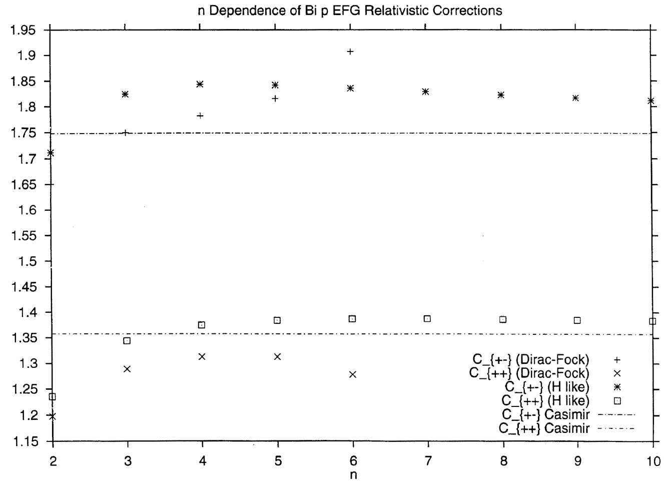

Fig. 2. Dirac-Fock, Dirac-Coulomb ($Z = 83$) and Casimir relativistic correction factors, C, for the np states of Bi

ferable are these correction factors to other atomic states or ionicities? If these corrections are to be used in a molecular context, then which atomic state should be chosen? Some examples are given in Table 5 and suggest that, within the limits of the approach, the atomic state hardly matters at all for C_{QR}. The quantity $C_{++} - 1$ is close to 0 and can therefore show large percental changes for Ne and S.

3.6 Previous atomic calculations

Sundholm and Olsen [36–43] have made calculations of the EFG at the nucleus of several elements. Taking their EFG and experimental NQCCs they determined accurate values for the nuclear quadrupole moments of the elements in question. As an application of our EFG relativistic correction factors, the earlier calculations can be re-examined and perhaps improved upon.

Although the corrections are numerically small, their qualitative properties are interesting. The cases of B, Na, Al and K($4p^1$) derive most of their EFG from a single $np_{3/2}$ electron. Similarly, Ne($2p^5 3s$), S$^-$, Cl and K($3p^5 3d^1 4s^1$) have a single $p_{3/2}$ hole. In these cases we recommend the C_{++}(DF) correction factor in Table 1. For Ne, Na and Al the original authors however used various, substantially larger correction factors. Here it should be emphasized that K($3p^5 3d 4s$; $^4F_{\frac{9}{2}}$) has only the jj-coupled configuration at single-configuration level

$$| JM\rangle = | \frac{9}{2} M\rangle = | 3d_{\frac{5}{2}}\rangle \, | 3p_{\frac{3}{2}}\rangle \, | 4s_{\frac{1}{2}}\rangle . \tag{34}$$

Hence the EFG of this state is dominated by the $3p_{\frac{3}{2}}$ hole and is well described already at the HF-level. For the $3p$ AO of this state, the $C_{++}(\mathrm{DF}) = 1.006$, close to the value of 1.0054, applied in the original work [43]. The C_{QR}(DF) of the $3p$ shell is 1.0146 and would reduce Q(K) by 1% .

The other atomic configurations require a more careful analysis, given in Table 6.

The present recommendations are compared with previously used C in Table 7. The case of Na deserves special mention because of the existing discrepancy of the muonic, atomic and molecular $Q(^{23}\mathrm{Na})$ of 100.6(2.0), 107.1(2.1) and 104.2(1.0) mb, respectively [51]. The latest atomic value is 105.6 mb [59]. No relativistic corrections were applied in the molecular work. If the quasirelativistic, H-like Na $3p$ correction factor, 1.00745, would be used to multiply the entire calculated q, the molecular Q value would decrease to 103.4 mb. Sundholm and Olsen's correlated, QR atomic $C - 1$ [40] is twice as large as the $C_{++}(\mathrm{DF}) - 1$ and also somewhat larger than $C_{\mathrm{QR}}(\mathrm{DF}) - 1$. The correlation contribution to q_{Na} is also large. A definitive conclusion can therefore not be drawn.

Similarly, for K($4p^1$), the correlation contribution to q is large and Sundholm and Olsen's [43] C_{QR}(QR) is comparable with the C_{++}(DF). The C_{++}(H) is larger, 1.0160 [3]. The C for the pure $3p$ contribution could approach 1.02, see Table 1 and Table 5.

For the s^1p^1 $^3P_2$ states of Be and Mg, Table 6 recommends C_{++}. For Mg, a $^3P_1$ measurement is also available. It is of lower accuracy and would require C_{QR}. For the Ca s^1d^1 $^1D_2$ case, C_{QR} is recommended, as well. With Dirac-Coulomb and DF integrals, its value is 1.0084 and 0.9490, respectively. The correlated, quasirelativistic value given by Sundholm and Olsen [43] is 1.0029.

The ground states of C and O have two $2p$ electrons and two $2p$ holes, respectively. They are close to LS coupling and a closer analysis leads to the C in Table 6 for the $^3P_2$ term. Note that it is even larger than C_{+-}!

For the lighter elements no changes of Q follow. For Ne, Na, Mg and Al, a very slight increase from the literature values of 101.55, 104.2, 199.4 and 140.3 mb would be obtained, if the "Rec." correction factors are used for the total q, (see Table 7).

3.7 Previous molecular calculations

The quasirelativistic correlated results for diatomic halides [18,20] are compared with the present C_{QR}(DF) in Table 8 and are found to be of the same order of magnitude. The best agreement is obtained for the heaviest molecule, HI. Note that the Cl in BrCl has a heavier neighbour.

It is interesting to note that while the $C_{\mathrm{QR}}(\mathrm{Cd}, 5p)$ is 1.17, Hemmingsen and Ryde [60] only obtain a relativistic increase of about 1.03 for $\mathrm{CdF_2Cl_2^{2-}}$, a natural consequence of the ionicity and the predominant $5s$ character of the bonds of Cd in the compound.

3.8 Previous solid-state calculations

We also include the available solid-state data in Table 8. Qualitative agreement is again found for the p component of Zr and Hf. For the d components, the atomic C(DF) are < 1 while the solid-state results are close to the H-like or Casimir ones. By this criterion, the d shells of the metals contract.

Returning to Eq. (14), for p electrons with quasirelativistic weights, the ratio of the "$+,-$" q contributions to "$+,+$" ones becomes $2R_{+-}/R_{++}$, approaching 2 at

Table 1. Relativistic correction factors for EFGs due to valence *p* electrons. g stands for ground state. The integrals *R* are defined previously. The *C*s are the correction factors to be applied to the corresponding NR *R*. C_{QR} is the correction factor to be applied to a non-relativistic orbital, assuming quasirelativistic weights for the *jj*-coupled basis states. DF stands for using DF expectation values, H is for using H-like expectation values calculated using Eq. (33) and Cas denotes using Casimir's *n*-independent formulae [1]

Atom	Conf	AO	R_{+-}(DF)	R_{++}	C_{+-}	C_{++}	C_{QR}(DF)	C_{QR}(H)	C_{QR}(Cas)
H	$2p^1$	2p	0.0416693	0.0416679	1.00006	1.00003	1.00005	1.00005	1.00006
Li	$2p^1$		0.0585757	0.0585698	1.00007	0.99997	1.00004	1.00047	1.00052
Be	$2s^12p^1$		0.2717683	0.2716826	1.00015	0.999837	1.00005	1.00083	1.00093
B	g		0.7758502	0.7753598	1.00034	0.999708	1.00013	1.00130	1.00145
C	g		1.6632687	1.6614371	1.00086	0.999758	1.00050	1.00187	1.00209
N	g		3.0250399	3.0198740	1.00150	0.999789	1.00093	1.00254	1.00285
O	g		4.9602880	4.9480997	1.00226	0.999802	1.00144	1.00332	1.00372
F	g		7.5689497	7.5435751	1.00316	0.999797	1.00204	1.00421	1.00472
Ne	g		10.951873	10.903722	1.00419	0.999773	1.00272	1.00520	1.00583
Na	g		17.094061	17.009389	1.00525	1.00027	1.00359	1.00630	1.00706
Mg	g		25.080753	24.938260	1.00645	1.00073	1.00454	1.00751	1.00841
Na	$3p^1$	3p	0.1700175	0.1695890	1.00451	1.00198	1.00367	1.00745	1.00706
Mg	$3s^13p^1$		0.5036400	0.5015960	1.00474	1.00066	1.00338	1.00887	1.00841
Al	g		1.0945415	1.0887925	1.00570	1.00042	1.00394	1.01042	1.00988
Si	g		2.0437851	2.0301115	1.00802	1.00127	1.00577	1.01211	1.01148
P	g		3.2998634	3.2730157	1.01016	1.00194	1.00742	1.01392	1.01320
S	g		4.8960471	4.8488783	1.01233	1.00258	1.00908	1.01587	1.01504
Cl	g		6.8674938	6.7905423	1.01459	1.00323	1.01080	1.01794	1.01701
Ar	g		9.1271096	9.0087387	1.01698	1.00379	1.01258	1.02015	1.01910
K	g		13.204898	13.025013	1.01922	1.00533	1.01459	1.0225	1.02132
Ca	g		18.124220	17.859375	1.02162	1.00670	1.01665	1.02498	1.02367
Sc	g		22.974063	22.604084	1.02511	1.00860	1.01961	1.02760	1.02615
Ti	g		28.386945	27.883838	1.02854	1.01031	1.02246	1.03037	1.02877
V	g		34.451156	33.781229	1.03208	1.01201	1.02539	1.03327	1.03152
Cr	g		40.435930	39.564914	1.03656	1.01423	1.02911	1.03632	1.0344
Mn	g		48.776912	47.646406	1.03963	1.01554	1.0316	1.03951	1.03743
Fe	g		57.148505	55.709420	1.04367	1.01739	1.03491	1.04286	1.04059
Co	g		66.397970	64.586865	1.0479	1.01932	1.03837	1.04635	1.04389
Ni	g		76.580175	74.323884	1.05232	1.02132	1.04199	1.05000	1.04734
Cu	g		86.564833	83.786129	1.05770	1.02375	1.04638	1.05380	1.05093
Zn	g		99.967933	96.558267	1.06177	1.02556	1.04970	1.05776	1.05468
K	$4p^1$	4p	0.2514489	0.2489178	1.01752	1.00727	1.01410	1.02322	1.02132
Ca	$4s^14p^1$		0.6597136	0.6513837	1.01799	1.00514	1.01371	1.02578	1.02367
Co	$4s^14p^1$		1.4195843	1.3803264	1.04959	1.02057	1.03992	1.04784	1.04389
Ni	$4s^14p^1$		1.5163924	1.4707297	1.05438	1.02263	1.04379	1.05160	1.04730
Cu	$4p^1$		0.7941934	0.7697782	1.07997	1.04677	1.06890	1.05553	1.05093
Zn	$4s^14p^1$		1.7050008	1.6448526	1.06453	1.02697	1.05201	1.05962	1.05468
Ga	g		3.0670392	2.9512144	1.06096	1.02090	1.0476	1.06388	1.05857
Ge	g		5.0522677	4.8440573	1.06739	1.02341	1.05273	1.06831	1.06262
As	g		7.3525537	7.0257524	1.07271	1.02503	1.05682	1.07291	1.06683
Se	g		9.9940951	9.5184130	1.07793	1.02662	1.06082	1.07769	1.07120
Br	g		12.998923	12.339528	1.08326	1.02831	1.06494	1.08265	1.07573
Kr	g		16.210825	15.330472	1.08895	1.02981	1.06923	1.08779	1.08043
Rb	g		21.972716	20.788114	1.09333	1.03438	1.07368	1.09312	1.08530
Sr	g		28.436958	26.876267	1.09816	1.03789	1.07807	1.09865	1.09034
Y	g		34.834270	32.847982	1.10619	1.04311	1.08516	1.10437	1.09556
Zr	g		41.607637	39.130549	1.11369	1.04739	1.09159	1.11029	1.10096
Nb	g		48.082349	45.066704	1.12321	1.05277	1.09973	1.11642	1.10655
Mo	g		55.804265	52.141876	1.13071	1.05651	1.10598	1.12276	1.11233
Tc	g		64.144940	59.739770	1.13843	1.06025	1.11237	1.12932	1.11831
Ru	g		73.147871	67.893185	1.14639	1.06404	1.11894	1.13610	1.12448
Rh	g		82.856345	76.632794	1.15461	1.06788	1.12570	1.14311	1.13086
Pd	g		92.303407	85.011450	1.16443	1.07244	1.13377	1.15036	1.13745
Ag	g		104.56010	95.988671	1.17187	1.07580	1.13985	1.15784	1.14426
Cd	g		118.23050	108.18564	1.1792	1.07902	1.14581	1.16558	1.15129
Rb	$5p^1$	5p	0.4897922	0.4691272	1.08438	1.03863	1.06913	1.09354	1.08530
Sr	$5s^15p^1$		1.1947847	1.1365862	1.08285	1.03010	1.06527	1.09909	1.09034
Rh	$4d^85p^1$		1.5522867	1.4137708	1.2305	1.12070	1.19390	1.14375	1.13086
Pd	$4d^95p^1$		1.6086950	1.4568486	1.24505	1.12753	1.20588	1.15102	1.13745
Ag	$5p^1$		1.6590100	1.4938540	1.25992	1.13449	1.21811	1.15854	1.14426

Table 2. Relativistic correction factors for *p* electrons (continued). Symbols as in Table 1

Atom	Conf	AO	R_{+-}(DF)	R_{++}	C_{+-}	C_{++}	C_{QR}(DF)	C_{QR}(H)	C_{QR}(Cas)
Cd	$5s^1 5p^1$	5p	3.2321387	2.8968145	1.21334	1.08746	1.17138	1.16630	1.15129
In	g		5.3470653	4.7873331	1.19964	1.07406	1.15778	1.17433	1.15855
Sn	g		8.1606316	7.2743856	1.20963	1.07826	1.16584	1.18261	1.16604
Sb	g		11.241814	9.9771496	1.21773	1.08074	1.17207	1.19117	1.17377
Te	g		14.632777	12.929641	1.22594	1.08325	1.17838	1.20001	1.18175
I	g		18.361428	16.151641	1.23463	1.08604	1.18510	1.20913	1.18999
Xe	g		22.180169	19.399076	1.24424	1.08823	1.19224	1.21855	1.19849
Cs	g		29.074352	25.494971	1.25028	1.09636	1.19897	1.22828	1.20727
Ba	g		36.548516	32.028916	1.25744	1.10195	1.20561	1.23833	1.21632
La	g		43.620316	38.108438	1.27187	1.11115	1.21830	1.24871	1.22567
Ce	g		47.055785	40.853505	1.29076	1.12062	1.23405	1.25942	1.23532
Pr	g		46.727762	40.179838	1.32049	1.13545	1.25881	1.27049	1.24528
Nd	g		50.125780	42.808424	1.33945	1.14392	1.27427	1.28192	1.25555
Pm	g		53.616823	45.468413	1.35871	1.15222	1.28988	1.29373	1.26617
Sm	g		57.223172	48.175821	1.37842	1.16048	1.30577	1.30593	1.27712
Eu	g		60.965630	50.943331	1.39876	1.16881	1.32211	1.31853	1.28844
Gd	g		69.695495	58.030653	1.40595	1.17064	1.32751	1.33156	1.30012
Tb	g		68.918339	56.693977	1.44154	1.18585	1.35631	1.34502	1.31219
Dy	g		73.157970	59.691760	1.46412	1.19462	1.37429	1.35895	1.32466
Ho	g		77.593716	62.779893	1.48761	1.2036	1.39294	1.37334	1.33754
Er	g		82.239668	65.964198	1.51205	1.21281	1.41231	1.38823	1.35086
Tm	g		87.109997	69.250466	1.53748	1.22226	1.43241	1.40364	1.36463
Yb	g		92.220572	72.644666	1.56397	1.23198	1.45331	1.41958	1.37886
Lu	g		104.37438	81.927899	1.5721	1.23400	1.45940	1.43608	1.39359
Hf	g		117.45320	91.762232	1.58415	1.23765	1.46865	1.45317	1.40883
Ta	g		131.56815	102.23186	1.59919	1.24261	1.48033	1.47087	1.42460
W	g		146.75487	113.35078	1.61636	1.24845	1.49372	1.48922	1.44093
Re	g		163.06072	125.13330	1.63526	1.25491	1.50848	1.50823	1.45784
Os	g		180.53776	137.59736	1.65564	1.26185	1.52437	1.52795	1.47537
Ir	g		199.25832	150.76445	1.67743	1.26919	1.54135	1.54842	1.49354
Pt	g		216.93767	162.73136	1.70765	1.28096	1.56542	1.56965	1.51238
Au	g		238.16571	177.23843	1.73180	1.28877	1.58412	1.59171	1.53193
Hg	g		263.57151	194.73288	1.75020	1.29309	1.59783	1.61462	1.55222
Cs	$6p^1$	6p	0.7640284	0.6853768	1.22763	1.10125	1.18551	1.22752	1.20727
Ba	$6s^1 6p^1$		1.7896053	1.5874625	1.22174	1.08374	1.17574	1.23753	1.21632
Ir	$6s^1 6p^1$		7.6757975	5.4731816	1.81421	1.29361	1.64068	1.54613	1.51238
Pt	$6p^1$		5.2422454	3.6095642	2.15694	1.48517	1.93301	1.56725	1.53193
Au	$6p^1$		5.5148385	3.7225656	2.23098	1.50593	1.98930	1.58918	1.53193
Hg	$6s^1 6p^1$		9.2805756	6.2405709	1.96703	1.3227	1.75226	1.61197	1.55222
Tl	g		14.136952	9.5458466	1.87166	1.26382	1.66906	1.63565	1.57330
Pb	g		20.775574	13.995243	1.89084	1.27374	1.68514	1.66028	1.59520
Bi	g		27.785598	18.621763	1.90686	1.27797	1.69723	1.68591	1.61797
Po	g		35.320485	23.518398	1.92568	1.28223	1.71121	1.71260	1.64167
At	g		43.463609	28.727556	1.94763	1.28730	1.72752	1.74042	1.66633
Rn	g		51.638634	33.746810	1.97331	1.28960	1.74541	1.76942	1.69203
Fr	g		66.152497	43.668858	1.97109	1.30116	1.74778	1.79968	1.71882
Ra	g		81.544171	53.855762	1.99727	1.31909	1.77121	1.83128	1.74677
Ac	g		96.683904	63.559428	2.04455	1.34407	1.81105	1.86432	1.77595
Th	g		112.33382	73.324099	2.08819	1.36304	1.84647	1.89887	1.80645
Pa	g		117.59720	75.143162	2.19206	1.40070	1.92828	1.93505	1.83836
U	g		128.12390	80.608955	2.2617	1.42294	1.98211	1.97297	1.87175
Np	g		138.98650	86.023437	2.33282	1.44386	2.03650	2.01274	1.90676
Fr	$7p^1$	7p	1.8220838	1.2895277	1.9029	1.34672	1.71751	1.79429	1.71882
Ra	$7s^1 7p^1$		4.0610252	2.7837348	1.84841	1.26704	1.65464	1.82563	1.74677

the nonrelativistic (NR) limit. The integrals in Table 2 would give 2.55, 2.56, 2.61 and 2.62 for Lu, Hf, Re and Os, respectively. A full Dirac calculation on the metals [61] gives a ratio of 2.25, 2.25, 2.36–2.38 and 2.6, respectively.

4 Simple molecular models

4.1 Effects of hybridization

4.1.1 pσ and pπ MOs

In Fig. 3 we illustrate the effect of the hybridization between p^* and p orbitals, assuming that the radial

Table 3. Relativistic correction factors for EFGs due to valence *d* electrons in the atomic ground state. Symbols are as for Table 1

Atom	AO	R_{--}(DF)	R_{+-}	R_{++}	C_{--}	C_{+-}	C_{++}	C_{QR}(DF)	C_{QR}(H)	C_{QR}(Cas)
Sc	3d	1.4146461	1.4054375	1.4014424	0.98966	0.98322	0.98043	0.98369	1.01214	1.01263
Ti		1.9632135	1.9483127	1.9419411	0.99398	0.98644	0.98321	0.98700	1.01334	1.01387
V		2.5809984	2.5584220	2.5488254	0.99697	0.98825	0.98454	0.98891	1.01460	1.01518
Cr		2.8389762	2.8076318	2.7923752	0.99999	0.98895	0.98358	0.98946	1.01591	1.01655
Mn		4.0669089	4.0209342	4.0013748	1.00176	0.99044	0.98562	0.99130	1.01729	1.01797
Fe		4.9502757	4.8873644	4.8604993	1.00399	0.99123	0.98578	0.99219	1.01872	1.01946
Co		5.9362597	5.8519772	5.8158103	1.00621	0.99192	0.98579	0.99298	1.02021	1.02101
Ni		7.0313683	6.9204565	6.8725968	1.00847	0.99257	0.98570	0.99373	1.02177	1.02263
Cu		7.5999011	7.4540592	7.3828893	1.01275	0.99331	0.98383	0.99420	1.02338	1.0243
Zn		9.5749734	9.3912227	9.3109623	1.01322	0.99378	0.98528	0.99514	1.02506	1.02604
Y	4d	1.6778162	1.6198831	1.6004486	0.98017	0.94632	0.93497	0.95035	1.05271	1.04465
Zr		2.3998290	2.3108652	2.2814018	1.00101	0.96391	0.95162	0.96840	1.05556	1.04705
Nb		2.7752643	2.6591763	2.6169743	1.01641	0.97389	0.95844	0.97838	1.05850	1.04953
Mo		3.5692452	3.4107095	3.3539893	1.02568	0.98013	0.96383	0.98506	1.06153	1.05207
Tc		4.4312172	4.2226703	4.1491312	1.03326	0.98463	0.96748	0.99002	1.06464	1.05469
Ru		5.3681046	5.1008933	5.0078967	1.03993	0.98816	0.97015	0.99401	1.06784	1.05738
Rh		6.3855634	6.0499157	5.9344907	1.04608	0.99110	0.97219	0.99742	1.07113	1.06015
Pd		6.8865543	6.4780584	6.3220573	1.05841	0.99562	0.97165	1.00169	1.07452	1.06298
Ag		8.6068077	8.1037279	7.9336804	1.05771	0.99588	0.97499	1.00316	1.07799	1.06589
Cd		10.494951	9.8742299	9.6822686	1.05965	0.99698	0.97760	1.00523	1.08155	1.06889
La	5d	2.3592101	2.1548951	2.1009653	1.01577	0.92780	0.90458	0.94129	1.12688	1.09935
Ce		2.5012290	2.2745777	2.2143264	1.02385	0.93107	0.90641	0.94521	1.13181	1.10315
Gd		3.1464787	2.7811384	2.6808562	1.04244	0.92140	0.88818	0.93935	1.16394	1.12787
Lu		3.5643885	3.0337208	2.8852979	1.02755	0.87457	0.83178	0.89687	1.20750	1.16110
Hf		5.0108167	4.2426863	4.0314048	1.09658	0.92848	0.88225	0.95336	1.21430	1.16627
Ta		6.4379917	5.4233849	5.1489994	1.13447	0.95568	0.90733	0.98254	1.22126	1.17155
W		7.9136768	6.6322021	6.2911693	1.16123	0.97319	0.92315	1.00182	1.22837	1.17693
Re		9.4638192	7.8897004	7.4770648	1.18263	0.98592	0.93436	1.01625	1.23565	1.18244
Os		11.102649	9.2062866	8.7161760	1.20106	0.99591	0.94289	1.02790	1.24308	1.18806
Ir		12.839792	10.588383	10.014264	1.21768	1.00416	0.94971	1.03781	1.25069	1.1938
Pt		13.886130	11.315482	10.622105	1.24836	1.01726	0.95493	1.05205	1.25847	1.19966
Au		15.696720	12.715750	11.920751	1.26335	1.02343	0.95944	1.05989	1.26642	1.20563
Hg		18.571663	15.049049	14.179195	1.26280	1.02328	0.96413	1.06196	1.27455	1.21174
Ac	6d	3.4267189	2.6422355	2.4795558	1.04798	0.80806	0.75831	0.85136	1.36821	1.27278
Th		4.7731643	3.6483070	3.4136300	1.14813	0.87756	0.82111	0.92622	1.37871	1.28029
Pa		4.2228737	3.1980146	2.9805967	1.13145	0.85686	0.79860	0.90578	1.38947	1.28795
U		4.5242227	3.3953530	3.1537644	1.15149	0.86418	0.80269	0.91511	1.40046	1.29578
Np		4.7898001	3.5619659	3.2972096	1.16559	0.86680	0.80237	0.91953	1.41170	1.30378

Table 4. Relativistic correction factors for EFGs due to valence *f* electrons in the atomic ground state. Symbols are as for Table 1

Atom	AO	R_{--}(DF)	R_{+-}	R_{++}	C_{--}	C_{+-}	C_{++}	C_{QR}(DF)	C_{QR}(H)	C_{QR}(Cas)
Ce	4f	4.4348469	4.3639694	4.3286546	0.92075	0.90604	0.89871	0.90771	1.03225	1.04766
Pr		4.4779477	4.3939017	4.3478175	0.91603	0.89883	0.88941	0.90034	1.0334	1.04938
Nd		5.0984464	4.9975157	4.9427009	0.92605	0.90772	0.89776	0.90937	1.03458	1.05113
Pm		5.7362929	5.6163742	5.5516328	0.93365	0.91413	0.90359	0.91592	1.03578	1.05291
Sm		6.3967877	6.2555378	6.1795436	0.93976	0.91901	0.90785	0.92094	1.03700	1.05472
Eu		7.0834459	6.9182743	6.8295571	0.94490	0.92287	0.91104	0.92493	1.03824	1.05657
Gd		8.3595833	8.1702236	8.0764834	0.95298	0.93140	0.92071	0.93387	1.03951	1.05845
Tb		8.5451611	8.3233193	8.2041142	0.95338	0.92863	0.91533	0.93094	1.04080	1.06037
Dy		9.3241049	9.0689431	8.9316216	0.95703	0.93084	0.91675	0.93327	1.04211	1.06233
Ho		10.137282	9.8450619	9.6874493	0.96043	0.93275	0.91782	0.93530	1.04344	1.06432
Er		10.986190	10.652835	10.472544	0.96364	0.93440	0.91859	0.93708	1.04480	1.06634
Tm		11.872242	11.493308	11.287715	0.96672	0.93586	0.91912	0.93865	1.04618	1.0684
Yb		12.796802	12.367450	12.133679	0.96969	0.93716	0.91944	0.94007	1.04759	1.07049
Lu		14.398800	13.932292	13.695315	0.97244	0.94093	0.92493	0.94434	1.04902	1.07263
Pa	5f	4.9064633	4.6029063	4.4755050	0.82389	0.77292	0.75153	0.78073	1.10585	1.12329
U		5.7088706	5.3496348	5.2027738	0.85247	0.79883	0.77690	0.80734	1.10838	1.12625
Np		6.5099835	6.0914825	5.9236853	0.87367	0.81751	0.79499	0.82665	1.11095	1.12926

Table 5. Correction factor as a function of state/ionicity. g stands for ground state

System	State	AO	R_{+-}	R_{++}	C_{+-}	C_{++}	C_{QR}(DF)
Ne	g	2p	10.951873	10.903722	1.00419	0.99977	1.00272
Ne	$2p^5 3s^1$		12.500306	12.451743	1.00412	1.00022	1.00282
S	g	3p	4.8960471	4.8488783	1.01233	1.00258	1.00908
S^-	g		4.0739840	4.0262490	1.01270	1.00083	1.00874
K	g		13.204898	13.025013	1.01922	1.00533	1.01459
K	$3p^5 4s^2$		14.696568	14.508362	1.01903	1.00598	1.01468
K	$4p^1$		13.256353	13.076826	1.01927	1.00547	1.01467
Ca	g		18.124220	17.859375	1.02162	1.00670	1.01665
Ca	$3p^5 4s^2 4p^1$		19.964067	19.687063	1.02155	1.00738	1.01683
Ca	$4s^1 4p^1$		18.186163	17.921598	1.02168	1.00681	1.01672
Cu	g		86.564833	83.786129	1.05770	1.02375	1.04638
Cu	$4p^1$		86.494915	83.720806	1.05761	1.02369	1.04630
Zn	g		99.967933	96.558267	1.06177	1.02556	1.04970
Zn	$4s^1 4p^1$		99.971216	96.565017	1.06172	1.02555	1.04967
Ca	$3p^5 4s^2 4p^1$	4p	1.1250398	1.1103262	1.01813	1.00481	1.01369
Ca	$4s^1 4p^1$		0.6597136	0.6513837	1.01799	1.00514	1.01371
Ag	g		104.56010	95.988671	1.17187	1.07580	1.13985
Ag	$5p^1$		104.54448	95.987474	1.17176	1.07585	1.13979
Cd	g		118.23050	108.18564	1.17920	1.07902	1.14581
Cd	$5s^1 5p^1$		118.29751	108.26378	1.17918	1.07916	1.14584
Au	g	5p	238.16571	177.23843	1.73180	1.28877	1.58412
Au	$6p^1$		238.20863	188.39043	1.73191	1.3697	1.61117

Table 6. The *jj*-coupled parentage of various LS-coupled atomic terms at the NR limit and the relativistic corrections, *C*, recommended for their NQCC for light elements. The symbols $l*$ and l stand for $j = l - \frac{1}{2}$ and $j = l + \frac{1}{2}$, respectively. The C_{QR} corrections correspond to Eq. (14)

Conf	J	Term	Parentage	C
$s^1 p^1$	0	$^3P_0$	$sp*$	–
	1	$^1P_1$	$\sqrt{\frac{1}{3}}sp * + \sqrt{\frac{2}{3}}sp$	$C_{\mathrm{QR}} = \frac{1}{3}C_{++} + \frac{2}{3}C_{+-}$
		$^3P_1$	$-\sqrt{\frac{2}{3}}sp * + \sqrt{\frac{1}{3}}sp$	$-\frac{1}{3}C_{++} + \frac{4}{3}C_{+-}$
	2	$^3P_2$	sp	C_{++}
$s^1 d^1$	1	$^3D_1$	$sd*$	C_{--}
	2	$^1D_2(M = 2)$	$\sqrt{\frac{2}{5}}s\alpha d * (\frac{3}{2})$	$C_{\mathrm{QR}} =$
			$+\sqrt{\frac{1}{10}}s\alpha d(\frac{3}{2}) - \sqrt{\frac{1}{2}}s\beta d(\frac{5}{2})$	$\frac{12}{25}C_{++} + \frac{6}{25}C_{+-} + \frac{7}{25}C_{--}$
		$^3D_2(M = 2)$	$\sqrt{\frac{3}{5}}s\alpha d * (\frac{3}{2})$	$\frac{16}{25}C_{++} - \frac{12}{25}C_{+-} + \frac{21}{25}C_{--}$
			$-\sqrt{\frac{1}{15}}s\alpha d(\frac{3}{2}) + \sqrt{\frac{1}{3}}s\beta d(\frac{5}{2})$	
	3	$^3D_3(M = 2)$	$\sqrt{\frac{1}{6}}s\alpha d(\frac{3}{2}) - \sqrt{\frac{5}{6}}s\beta d(\frac{5}{2})$	C_{++}
p^2	0	$^3P_0$	$\sqrt{\frac{2}{3}}(p*)^2 - \sqrt{\frac{1}{3}}p^2$	–
		$^1S_0$	$\sqrt{\frac{1}{3}}(p*)^2 + \sqrt{\frac{2}{3}}p^2$	–
	1	$^3P_1$	$p * p$	C_{++}
	2	$^3P_2$	$\sqrt{\frac{1}{3}}p * p + \sqrt{\frac{2}{3}}p^2$	$-\frac{1}{3}C_{++} + \frac{4}{3}C_{+-}$
		$^1D_2$	$-\sqrt{\frac{2}{3}}p * p + \sqrt{\frac{1}{3}}p^2$	$C_{\mathrm{QR}} = \frac{1}{3}C_{++} + \frac{2}{3}C_{+-}$

integrals R_{+-} and R_{++} have their relativistic or non-relativistic HF values for Bi.

For a QR ratio of the two coefficients, the same Relativistic/NR ratio is obtained for σ as for the average of the two π orbitals, $1.69723 = (2.1164908 + 1.27797)/2$.

For pure p orbitals ($C(p_{1/2}) = 0$), a smaller ratio is obtained. It is identical with that for the $\pi(m_j = 3/2)$ one. The q contribution vanishes for π orbitals if $C(p_{1/2})$ is 0.23057 or $\frac{3}{9}$, for relativistic and NR-radial integrals, respectively.

The curves with NR-integrals in Fig. 3 can be used for understanding spin-orbit tilting effects on a light element.

4.1.2 d AOs

In Fig. 4 we show the coefficient dependence of *d* AO contributions assuming the three relativistic or non-relativistic DF 5*d* integrals for Au. As seen from Table 3, the C_{QR}(DF) equals 1.060 for the atomic ground state. The same value is obtained in Fig. 4 as the ratio of the

Table 7. Some previously used relativistic correction factors. g stands for the ground state, Exp. and Calc. are the experimental and theoretical references, respectively. Orig. is the relativistic correction factor originally applied and Rec. the one recommended in Table 6. Q in mb = 10^{-31}m^2

System	State	Exp.	Shell	Orig.	Calc.	Rec.	Conclusion
Be	$2s^1 2p^1\ (^3P_2)$	[44]	2p	1.0005^a	[36]	0.999837^b	PRVU^i
B	g $(^2P_{\frac{3}{2}})$	[45]	2p	1.0001^c	[37]	0.999708^b	PRVU
C	g $(^3P_2)$	[46]	2p	1.0010^a	[38]	1.00123^h	PUVR^j
N^+	$2p3p\ ^1P_1$	[47]	2p	1.0018^d	[39]	1.00254^g	PRVR^k
O	g $(^3P_2)$	[48]	2p	1.0020^d	[38]	1.00308^h	PUVR^k
Ne	$2p^5 3s^1\ (^3P_2)$	[49]	2p	1.0028^d	[38]	1.00022^e	PUVU^l, $Q = 101.8$
Na	$3p^1\ (^2P_{\frac{3}{2}})$	[50]	3p	1.0046^d	[40]	1.00198^b	PUVU^l
NaF,	$X\ ^1\Sigma$		3p	1.	[51]	1.00745^g	$Q = 103.4$
NaCl	”						
Mg	$3s^1 3p^1\ (^3P_2)$	[52]	3p	1.0044^d	[41]	1.00066^b	PUVU^l, $Q = 200.1$
Al	g $(^2P_{\frac{3}{2}})$	[53]	3p	1.0049^d	[40]	1.00042^b	PUVU^l, $Q = 140.9$
S^-	g $(^2P_{\frac{3}{2}})$	[54]	3p	1.00083^f	[42]	–	PRVR^k
Cl	g $(^2P_{\frac{3}{2}})$	[55]	3p	1.00323^b	[43]	–	PRVR^k
K	$4p^1\ (^2P_{\frac{3}{2}})$	[56]	4p	1.0065^d	[43]	1.00727^b	PUVR^j
K	$3p^5 3d^1 4s^1\ (^4F_{\frac{9}{2}})$	[57]	3p	1.0054^b	[43]	–	PRVR^k
Ca	$4s^1 3d^1\ (^1D_2)$	[58]	3d	1.0029^d	[43]		PRVR^k

[a] The C_{++}(H) of [3]
[b] The C_{++}(DF) of Table 1
[c] Scaled from Li
[d] Author's own correlated C_{QR} for the system in question
[e] The C_{++}(DF) for this state of Ne. Note that the ground state value is < 1
[f] DF for $3p_{3/2}$ of S^-
[g] C_{QR}(H)
[h] $C(^3P_2)$(DF)
[i] Principle Reasonable, Value Unreasonable
[j] Principle Unreasonable, Value Reasonable
[k] Principle Reasonable, Value Reasonable
[l] Principle Unreasonable, Value Unreasonable.

Table 8. Some previous results for relativistic correction factors in molecules and solids. Core p factors given for Zr and Hf

System	State	Shell	Orig.	Ref.	C_{QR}(DF)	C_{QR}(H)	C_{QR}(Cas)
HCl	$X\ ^1\Sigma$	3p	1.022	[18]	1.0108	1.018	1.017
BrCl	$X\ ^1\Sigma$	3p(Cl)	1.035	[20]	”	”	”
HBr	$X\ ^1\Sigma$	4p	1.100	[18]	1.0649	1.083	1.076
BrCl	$X\ ^1\Sigma$	4p(Br)	1.106	[20]	”	”	”
HI	$X\ ^1\Sigma$	5p	1.212	[18]	1.1851	1.209	1.190
Zr	hcp	5p	1.252	[23]	1.0916	1.110	1.101
		4d	1.048	”	0.968	1.056	1.047
Hf	hcp	6p	1.300	[23]	1.469	1.453	1.409
		5d	1.221	”	0.953	1.214	1.166

two σ curves for the QR coefficients. It also is obtained as the average of the two $5d\pi$ ratios or the two $5d\delta$ ratios.

4.1.3 f AOs

In Fig. 5 we show the coefficient dependence of the $5f$ q assuming the DF integrals for U. Note in this case the zero contribution from the $f\delta$ orbital for NR integrals and (QR or NR) coefficients.

4.2 The Townes-Dailey model

In this model [13], only one-centre contributions, from the nucleus in question are considered, and the NQCC is expressed in terms of a one-electron radial integral and a combination of the occupation numbers. For p-electrons,

$$q_{\text{mol}} = U_p < p \mid \hat{q} \mid p >, \tag{35}$$

$$U_p = n_z - \frac{n_x + n_y}{2}. \tag{36}$$

Obviously, the U_p can be multiplied by the corresponding quasirelativistic correction factor. The proposed [13] Casimir corrections [1] are still a good choice.

The Townes-Dailey model can easily be extended to jj or intermediate coupling. Consider the EFG at the nucleus of a main group element in a simple valence-electrons-only, one-centre model. In a molecular environment the relevant orbitals can be represented by

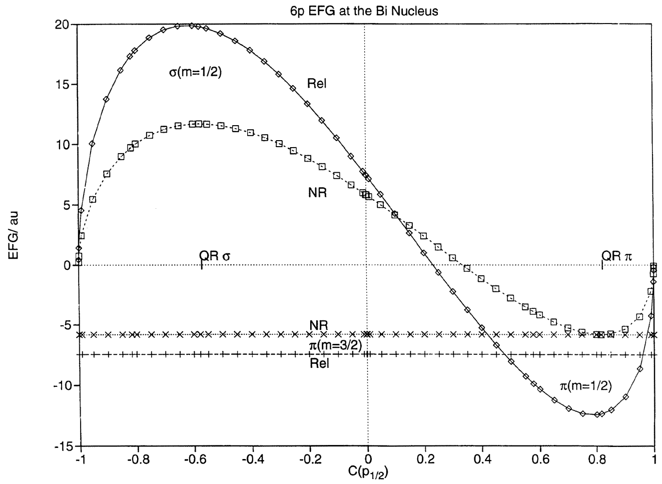

Fig. 3. The dependence of the q at a Bi nucleus from the hybridization between $6p^*$ and $6p$ atomic orbitals ($j=\frac{1}{2}$ and $\frac{3}{2}$, respectively, for the three cases of σ, $\pi(1/2)$ and $\pi(3/2)$.

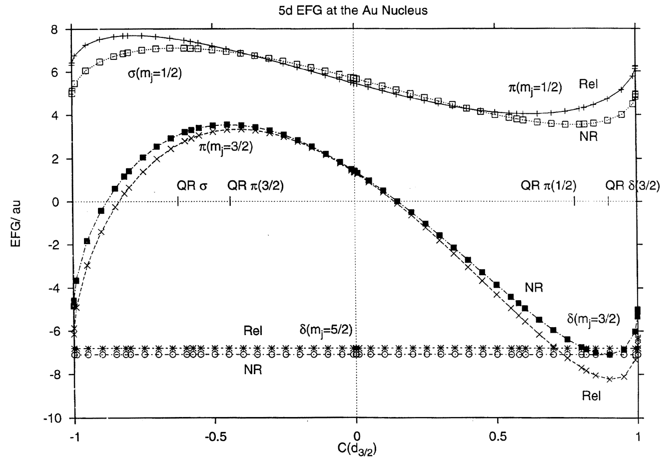

Fig. 4. Coefficient dependence of individual hybridized contributions to the $5d$ q of Au

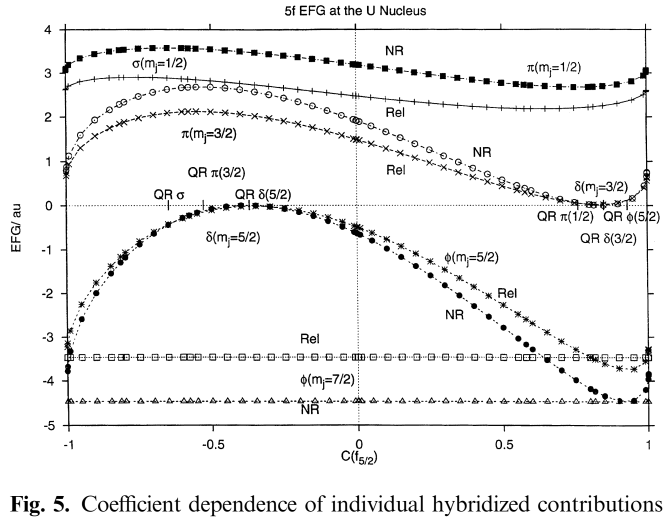

Fig. 5. Coefficient dependence of individual hybridized contributions to the $5f$ q of U

$$
\begin{aligned}
\phi_i = {} & C_{s,\frac{1}{2}} \mid s_{\frac{1}{2}}\rangle + C_{s,-\frac{1}{2}} \mid s_{-\frac{1}{2}}\rangle \\
& + C_{p,\frac{1}{2}\frac{1}{2}} \mid p_{\frac{1}{2}\frac{1}{2}}\rangle + C_{p,\frac{1}{2},-\frac{1}{2}} \mid p_{\frac{1}{2},-\frac{1}{2}}\rangle \\
& + C_{p,\frac{3}{2}\frac{1}{2}} \mid p_{\frac{3}{2}\frac{1}{2}}\rangle + C_{p,\frac{3}{2},-\frac{1}{2}} \mid p_{\frac{3}{2},-\frac{1}{2}}\rangle \\
& + C_{p,\frac{3}{2}\frac{3}{2}} \mid p_{\frac{3}{2}\frac{3}{2}}\rangle + C_{p,\frac{3}{2},-\frac{3}{2}} \mid p_{\frac{3}{2},-\frac{3}{2}}\rangle,
\end{aligned}
\tag{37}
$$

resulting in an EFG at the nucleus due to orbital i of

$$
\begin{aligned}
\langle \phi_i \mid q \mid \phi_i \rangle = {} & A_{+-}R_{+-} + A_{++}R_{++} \\
= {} & \left(C_{i,p,\frac{1}{2},-\frac{1}{2}} C_{i,p,\frac{3}{2},-\frac{1}{2}} - C_{i,p,\frac{1}{2}\frac{1}{2}} C_{i,p,\frac{3}{2}\frac{1}{2}} \right) \\
& \frac{4\sqrt{2}}{5} R_{+-} + \left[\left(C^2_{i,p,\frac{3}{2},-\frac{1}{2}} + C^2_{i,p,\frac{3}{2}\frac{1}{2}} \right) \right. \\
& \left. - \left(C^2_{i,p,\frac{3}{2},-\frac{3}{2}} + C^2_{i,p,\frac{3}{2}\frac{3}{2}} \right) \right] \frac{2}{5} R_{++}.
\end{aligned}
\tag{38}
$$

Summing over occupied orbitals gives the EFG at the nucleus.

$$
q_{\text{mol}} = \sum_i^{occ} \langle \phi_i \mid q \mid \phi_i \rangle \tag{39}
$$

In the nonrelativistic case Townes and Dailey [13] or Cotton and Harris [62] approximate the two-centre contributions as being proportional to the overlap integrals. Here we simply neglect this part.

To illustrate the method just described and some of the properties mentioned in this paper a few calculations will be presented. In particular, the EFG at the heavy element in the molecules HCl, HBr, HI and HAt illustrates the transition from a molecule where the situation is nonrelativistic to where a relativistic treatment is required.

4.3 HX and X_2

To calculate the EFG using the formulae in Sect. 4.2, AO coefficients from an LCAO expansion are required. One possible method to calculate these coefficients in a basis of eigenfunctions of the j and m_j operators is to use relativistic extended Hückel (REX) and nonrelativistic extended Hückel (EHT) calculations (for a review of the method, see [63]). Non-iterative calculations with the default parameters, or their QR averages, were used. These coefficients were combined with Eq. (39) and the appropriate integrals in Tables 1–2 to produce the EFGs of HX and X_2 in Table 9.

Here and elsewhere the sign convention is such that an electron in a σ orbital of the nucleus in question produces a negative EFG. Experimental bond lengths [64] were used for both relativistic and nonrelativistic calculations.

Results were calculated at five levels:

1) With relativistic orbitals and integrals i.e. using the integrals as given in Table 1, with the AO coefficients taken from the REX output.

2) With quasirelativistic orbitals and relativistic integrals: A quasirelativistic orbital is achieved by keeping the total $p_{\frac{1}{2}} + p_{\frac{3}{2}}$ population from REX the same but altering the $p_{\frac{1}{2}} : p_{\frac{3}{2}}$ ratio to the quasirelativistic limit.

Table 9. Some calculated molecular EFGs in Au. R denotes both relativistic orbitals and integrals used in the calculations. R/QR denotes relativistic AO coefficients but QR integrals. QR/R is QR AO coefficients. QR/QR is QR AO coefficients and integrals. NR indicates a non-relativistic calculation. NQCC is the nuclear quadrupole coupling constant (in MHz) calculated using the R, EFG and Q from Ref [66]. The experimental values are from [65]

Molec	Nucl	R	R/QR	QR/R	QR/QR	NR	NQCC	
							Calc	Exp
HCl[a]	^{35}Cl	4.058	4.059	4.050	4.051	3.991	−77.71	−67.6
HCl[b]		4.058	4.057	4.068	4.068	4.010		
HBr[a]	^{79}Br	9.372	9.377	9.173	9.176	8.670	728.9	530.6
HBr[b]		9.017	8.988	9.275	9.275	8.734		
HI[a]	^{127}I	15.617	15.663	14.741	14.768	12.881	−2895	−1823
HI[b]		13.898	13.722	15.121	15.121	12.907		
HAt[a]	At	37.155	38.418	22.327	23.696	21.087		
I_2[a]	^{127}I	17.083	17.165	16.724	16.741	14.464	−3167	−2452
At_2[a]	At	31.646	33.653	32.192	32.600	21.717		

[a] Model A [b] Model B

3) With relativistic orbitals as taken from the REX output and the quasirelativistic integrals from Tables 1–2. A quasirelativistic integral is defined as the integral calculated using R_{+-} and R_{++}, assuming quasirelativistic orbitals as already defined and Eq. (38). The integrals for $\sigma_{\frac{1}{2}}$, $\pi_{\frac{1}{2}}$ or $\pi_{\frac{3}{2}}$ orbitals are assumed to be equal to what is calculated using QR σ coefficients.

4) With both integrals and orbitals quasirelativistic.

5) Nonrelativistic integrals, i.e. calculated from Table 1 and AO coefficients from an extended Hückel calculation.

Two different models were actually used. In model A the REX or EHT C_i were used as such in Eq. (38). In model B, for the HX molecules, the REX C_i were used for the bonding σ MO, thus introducing both the σ hole and spin-orbit tilting. The $\pi(\frac{1}{2})$ MO was taken as a pure *np* orbital, orthogonalized against the σ. The $\pi(\frac{3}{2})$ was a pure $p(\frac{3}{2})$ AO.

The results are shown in Table 9. The models A and B show spin-orbit tilting effects of comparable magnitude but of opposite sign. Preliminary ab initio data [67] suggest that the latter one is correct. An inspection of Table 9 shows that the spin-orbit effect occurs when the *coefficients* change from QR to R. A further inspection shows that the changes of the contributions from the three MOs, σ, $\pi(\frac{1}{2})$ and $\pi(\frac{3}{2})$, would cancel for a filled *np* shell at the halogen. As there is a partial hole in the $np\sigma$ orbital, due to the chemical bond, causing the entire q in the Townes-Dailey model, and as that contribution reaches a maximum with the QR coefficients, as seen from Fig. 3, the spin-orbit tilting will lead to a decrease of that, positive q.

Both models A and B suggest a somewhat unusual, Z^3 behaviour for the tilting effect. In the latter case the ratio q_{QR}/q_R is 1.0025, 1.0286 and 1.088 for HCl, HBr and HI, respectively. Thus this effect is expected to be relevant in q calculations for compounds of the heavier halogens, such as the quasirelativistic calculations of Kellö and Sadlej [18,19] for HX molecules or of Blaha and Schwarz [68] for solid X_2.

The scalar relativistic effects (represented by the difference between the QR/QR and NR results) are larger than spin-orbit effects up to row 5 ($X = I$). At the end of row 6 ($X = At$), the two effects are comparable. The scalar effects come from two sources, the increase in the $\langle r^{-3}\rangle$ integrals and the shift in electron density. Except in the case of HAt, the difference between the NR and QR/QR result is almost completely due to the first source. Another possible relativistic effect is the change in EFG caused by a bond-length change. This effect is of course zero in the case of the molecules considered in this section as all calculations were at the experimental bond length.

4.4 Hole theory of Q(An) in actinyl ions

Considering the $6p_{\frac{3}{2}}(m_j = \frac{1}{2})$ semicore shell of the actinyl ions, $OAnO^{n+}$, we now find

$$q = \frac{2}{5}R_{++}(6p). \tag{40}$$

In Ref. [17], $\frac{3}{5}$ was erroneously given.

5 Conclusion

Our final conclusions concerning relativistic correction factors for EFG calculations are:

a) If the system is a molecule or solid, close to LS coupling, then the C_{QR} in Tables 1–4 should be taken. No major differences occur between the DF-, H-like or Casimir ones.

b) For atoms whose EFG arises from a single, *jj*-coupled electron or hole, the C for it should be used.

c) For the various J levels of various terms and electron configurations of light atoms with more than one valence electron (or hole), great care must be exercized in choosing the right combination of the coefficients $C_{-,-}$, C_{+-} and C_{++}, see Table 6.

d) Furthermore, our results suggest that *spin-orbit tilting* effects could change the q at iodine in HI by several percent. These effects increase with Z as Z^3, as contrasted with Z^2 for the QR terms.

e) DF-level $\langle r^{-3}\rangle$ integrals are reported here for the elements up to $_{93}$Np. These data may be useful for calibration purposes or in future empirical work.

All these qualitative suggestions should be controlled by fully relativistic all-electron calculations in the future.

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