

Finite Ligand Size and the Sternheimer Antishielding Factor γ_∞

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Abstract

Two distinct processes, one classical and the other quantum mechanical, have to be considered in allowing for the effect of the finite size of atoms on the shielding of the coupling between crystal and nuclear electric quadrupole moments. The effect of the quantum mechanical process has already been calculated; in this paper we employ a simple numerical technique for evaluating multicentre integrals to calculate the effect of charge penetration. This effect is found to be significant and it suggests that a new approach is necessary in the parameterization of the crystal-nuclear-quadrupole interaction.

Introduction

Ahmad and Newman (1978) described two distinct processes by which the finite size of a neighbouring ion (or ligand) reduces the effective Sternheimer shielding γ_∞ for a metal ion. In brief, these are:

- (1) the production of a positive exchange charge in the metal-ligand overlap region, due to the (quantum mechanical) effect of Pauli exclusion. This results in a reduction of the net electrostatic field at the metal ion nucleus;
- (2) the penetration of the ligand charge cloud into the metal electron orbitals which are involved in the production of the antishielding. This, as we shall see, also produces a reduction of the electrostatic field at the metal ion nucleus.

Ahmad and Newman (1978) calculated the effect of (1) for the Pr^{3+} ion with Cl^- ligands, using an approximate technique which involved replacing the exchange charge by a point charge of similar magnitude. In the present paper we calculate the process (2) for the same system. In order to avoid calculating two-centre Coulomb integrals we expand the Cl^- outer shell wavefunctions in terms of a set of states generated for Pr^{3+} in a spherical box of radius 11.621 a.u. The calculations were carried out for three $\text{Pr}^{3+}-\text{Cl}^-$ distances, namely $R = 5.5812$ a.u. and $R \pm 5\%$. Details of the physical implications of this method will be found in the paper by Ahmad and Newman (1979a), while an account of our numerical methods is given by Ahmad and Newman (1979b). For ease of comparison with previous work we have employed the same Cl^- wavefunctions as in earlier calculations of finite ligand effects (see e.g. Table II of Ellis and Newman 1967).

Effect of Charge Penetration on Nuclear Quadrupole Shielding

Charge-penetration effects on shielding parameters are analogous to the effect of charge penetration on the electrostatic contributions to the crystal field (Raychaudhuri and Ray 1967; Ellis and Newman 1968). In both cases the calculation is carried out simply by replacing the point-charge approximation of the ligands by a more accurate representation of the charge distribution. The point-charge representation of Cl^- consists of a single negative electronic charge at the nucleus. In the present calculation this is replaced by seven positive nuclear charges and eight negative electronic charges distributed in the $3s^2p^6$ outer orbitals. The charge penetration correction may then be ascribed to the interaction of the neutral system consisting of eight positive nuclear charges and eight negative electronic charges on the outer 3s and 3p orbitals.

The lowest order contribution from configuration interaction to the charge-penetration correction arises from the dominant $5p \rightarrow np$ excitations and may be written

$$\Delta\gamma_\infty = -\frac{2^4}{2^5} R^3 \sum_{n\chi} \{\Delta E(5p \rightarrow np)\}^{-1} \langle np | r^{-3} | 5p \rangle \langle \chi 5p | (r_-^2/r_+^3) C_0^{(2)} | \chi np \rangle + 8\gamma_\infty^{(1)}(5p \rightarrow p).$$

Here χ represents the outer $3s^2p^6$ orbitals of a Cl^- ion lying on the z axis and $\gamma_\infty^{(1)}(5p \rightarrow np)$ denotes the corresponding point-charge contribution calculated by Ahmad and Newman (1979a); R is the distance between the metal and ligand nuclei, and the operator $C_0^{(2)}$ acts on the angular variables describing the χ orbitals.

The two-centre integral is easily evaluated by expanding the χ wavefunctions in terms of the set of states $|nlm\rangle$ generated using the Pr^{3+} Hartree-Fock-Slater potential centred in a spherical well of radius 11.621 a.u. We have given the details of this procedure in another paper (Ahmad and Newman 1979b), where the problems of obtaining convergence are discussed in some detail. In that paper we also reported a recalculation of the *crystal field* contribution of charge penetration, which had already been determined by Raychaudhuri and Ray (1967) and Ellis and Newman (1968) using more conventional techniques for evaluating the two-centre integrals. The comparison given in Table 6 of Ahmad and Newman (1979b) shows that very similar results are obtained in all the calculations.

In the present work we have carried out a simple check on convergence by comparing the corrections to γ_∞ calculated for two sets of excited states, one limited by having orbital angular momenta $l \leq 9$, the other with $l \leq 12$. This check was made to test the sensitivity of our results to the accuracy of the expansion of the ligand functions in terms of Pr^{3+} excited states.

The results of the present calculation for the lowest order contributions to γ_∞ are summarized in Table 1. This table gives the shielding factors appropriate to electrons distributed in Cl^- 3s states and to the electrons in the spherically symmetric 3p charge distribution (p^* results in column 5). We see that the anti-shielding factor is slightly smaller in magnitude for distributed electronic charges than it is for a point charge at the ligand nucleus. Nevertheless, the overall effect on the field at the nucleus is quite large, for the Cl^- ion has a total of eight electrons in its outer 3s and 3p shells and we are comparing our result with the screening of the

field due to a single point charge at the Cl^- nucleus. In order to obtain the total effect of the $3s^2p^6$ charge distribution as a correction to the electrostatic field we have summed the corrections to obtain the $\Delta\gamma_\infty$ results shown in the last column of Table 1. These may be regarded as 'effective' contributions to γ_∞ due to charge penetration. A calculation of the corresponding correction to the higher order 'self-consistency' contributions to γ_∞ has also been carried out. It shows that the reduction of these contributions is similar in relative magnitude to that shown in Table 1.

It is hard to estimate the accuracy of this type of calculation because of the difficulty of making direct comparisons between calculated atomic wavefunctions and experimental data. Nevertheless, the method of calculation used in this work produces results which agree to within 15% with previous results using similar wavefunctions (Table 6 of Ahmad and Newman 1979b). We expect the *relative* magnitude of the distributed and point-charge contributions to γ_∞ to be more accurate than this.

Table 1. First-order $5p \rightarrow np$ charge penetration corrections to γ_∞ in Pr^{3+}

The values listed are calculated for a $\text{Pr}^{3+}-\text{Cl}^-$ system, allowing for the finite distribution of the Cl^- 3s and 3p states. The Cl^- states are expanded in terms of Pr^{3+} excited states up to $l = 12$ and $n = 20$. An external point charge gives contributions to γ_∞ for these processes which sum to -60.06 (independent of the ligand distance). The values given here have all been renormalized to correspond to a single electronic charge. The results in parentheses are obtained if the Cl^- state expansions are restricted to $l \leq 9$

(1) $\text{Pr}^{3+}-\text{Cl}^-$ distance (a.u.)	(2) γ_∞ contributions s	(3) p_σ	(4) p_π	(5) p^*	(6) Correction ^B $\Delta\gamma_\infty$
5.3021	-58.7 (-57.9)	-68.6 (-66.2)	-45.9 (-40.4)	-53.5 (-50.6)	+42.3 (+46.7)
5.5812	-59.2 (-58.2)	-70.5 (-67.5)	-47.3 (-40.5)	-55.0 (-51.4)	+31.7 (+37.6)
5.8603	-59.6 (-58.2)	-71.7 (-68.1)	-48.3 (-40.4)	-56.1 (-51.9)	+24.8 (+31.4)

^A The entries for p^* show the effect of an electronic charge in an approximate spherical distribution obtained by averaging the renormalized p_σ and p_π contributions.

^B Total charge penetration correction to the point-charge value of γ_∞ corresponding to the redistribution of eight charges from the nucleus to the 3s and 3p orbitals. It is calculated from $\Delta\gamma_\infty = 2 \times s + 6 \times p^* - 8 \times (-60.06)$.

Conclusions

In previous calculations of contributions to the coupling between crystal and nuclear electric quadrupole moments it has been convenient to factorize the result as a 'bare' interaction times a shielding factor $(1 - \gamma_\infty)$. This factorization depends on being able to separate the interaction into a crystal field acting on the ion containing the nucleus in question, and the (anti)shielding effect due to the electronic excitations of that ion. It is clear from the discussion given above that finite ligand effects cannot be factorized in this way, as the electrostatic field is not produced by a source outside the Pr^{3+} ion and the magnitude of antishielding effects depends on its position. As a consequence it becomes very artificial to express our results in terms

of a shielding factor at all, as this is no longer independent of the crystalline environment.

In these circumstances it is more convenient to introduce a parameter directly proportional to the interaction energy of the nucleus with a single neighbouring ion (expressed as a function of distance). The total quadrupole interaction energy can then be built up of single-ion contributions using the superposition model (see e.g. Newman 1978). This purpose is served if we define the parameter

$$\bar{\xi}(R) = \{1 - \gamma_{\infty}(R)\}/R^3,$$

where we have written $\gamma_{\infty}(R)$ rather than γ_{∞} to emphasize the fact that $\bar{\xi}$ has a complicated dependence on the interionic distance R .

Table 2. Contributions to quadrupolar interaction factor $\bar{\xi}$ for $\text{Pr}^{3+}-\text{Cl}^{-}$

The factor $\bar{\xi}$ is defined as $(1 - \gamma_{\infty})/R^3$

R (a.u.)	Point charge	Exchange charge ^A	Charge penetration	Net contribution
5.3021	0.5340	-0.4424	-0.3893	-0.2977
5.5812	0.4578	-0.2401	-0.2450	-0.0273
5.8603	0.3955	-0.1491	-0.1655	0.0809
7.0000	0.2321	—	—	0.2321

^A These results are obtained from a slight extension of the calculation reported by Ahmad and Newman (1978).

The results obtained for $\bar{\xi}$ from this work, together with our previous results (Ahmad and Newman 1978, 1979a), are summarized in Table 2.* It appears that the nearest neighbour ions may, in fact, make a relatively small contribution to the nuclear quadrupole splitting. This is in strong contrast with the crystal field, where the coordinated ions normally provide the dominant contributions (Newman 1978).

Finally, we wish to point out that finite ligand size effects will be of similar relative importance in calculating γ_{∞} for *any* system.

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* Note that this table contains a correction factor $\frac{1}{2}$ to the self-consistency (correlation) contributions quoted by Ahmad and Newman (1978, 1979a).