

## Finite Ligand Size and Sternheimer Antiscreening in Lanthanide Ions

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### *Abstract*

A finite ligand affects the quadrupole potential at the nucleus of a lanthanide ion in two ways: it produces a positive exchange charge in the region of overlap and it reduces the antiscreening of the point-charge interaction due to charge penetration. We estimate the magnitude of the exchange charge contribution in the system  $\text{Pr}^{3+} - \text{Cl}^-$  using a simple model based on calculating the change in the antiscreening of a point charge as it moves towards the lanthanide ion. A significant contribution is produced, which is not sensitive to the position of the exchange charge, showing that the conventional antiscreening factor  $\gamma_\infty$  cannot properly represent the effect of antiscreening on the ligand contributions to the nuclear quadrupole potential.

### **Introduction**

Previous calculations of the Sternheimer quadrupolar nuclear antiscreening factor  $\gamma_\infty$  for lanthanide ions have invariably been based on the assumption that the charges which generate the quadrupolar field are situated outside the electronic charge distribution which produces the screening (e.g. see Sternheimer 1966; Erdős and Kang 1972; Gupta and Sen 1973). This is consistent with regarding the crystalline environment as an array of point charges which is, of course, the usual starting point in attempts to evaluate the lattice sum of contributions to the quadrupolar field at a particular ionic site. Most published calculations for lanthanide ions find  $\gamma_\infty \approx -65$ , corresponding to an amplification of the crystalline electrostatic quadrupole potential at the nucleus by a factor of  $(1 - \gamma_\infty) \approx 66$ .

Some workers (e.g. Taylor 1968; Sawatzky and Hupkes 1970) have pointed out that the redistribution of electronic charge due to ionic overlap produces a quadrupole field at the atomic nuclei in a crystal which is very different from that obtained by simply summing ionic point charge contributions. To our knowledge, however, no previous attempts have been made to determine the changes in the screening factor which are appropriate to such a redistributed charge. This is essential if a quantitative estimate of the quadrupole field at the nucleus is to be obtained, because of the importance of the amplification factor  $(1 - \gamma_\infty)$ .

In the case of the lanthanides, we may distinguish between two types of contribution to the quadrupolar potential at the nucleus which are both generated by the interpenetration of the electronic charge distribution with that on neighbouring ions (or ligands). Similar contributions to the 4f electron crystal field have been termed 'exchange charge effects' (Bishton *et al.* 1967) and 'charge penetration effects' (Ellis and

Newman 1968), and we shall use the same terminology in the present paper. A summary of all the important ligand interaction effects relevant in lanthanide crystal field theory has been given by Newman (1971).

The exchange charge contribution arises as a result of including ligand electronic wavefunctions explicitly in the quantum mechanical formulation, rather than simply assigning all ligand electronic charge to a point charge at the ligand site. Pauli exclusion between the two (originally) spherically symmetric overlapping charge distributions produces a redistribution of the electronic charge which must be taken into account in calculating the electrostatic field. The mathematical expression for the energy due to this redistribution involves both overlap integrals, due to the non-orthogonality of the basis states, and exchange Coulomb matrix elements (see Newman 1971). To a first approximation (Bishton *et al.* 1967) it can be represented by a positive exchange charge in the region of maximum overlap, i.e. at some point on a line between the ionic nuclei.

The charge penetration contribution is purely classical, being due to the fact that the Coulomb potential between a point (electronic) charge and a finite spherically symmetric charge distribution on the ligand will differ from the simple Coulombic  $e^2/r$  value if the electron penetrates the charge cloud. The relative importance of this contribution (see Raychaudhuri and Ray 1967; Ellis and Newman 1968) is largely due to the fact that there are eight electrons in an outer ligand  $s^2p^6$  shell. Hence, in a realistic model, a single negative ionic charge will be divided between eight negative distributed charges and seven positive charges at the nucleus, the inner closed-shell charge distribution still being represented by point charges.

### Model Calculation for $\text{Pr}^{3+}$

We now seek to avoid some of the computational problems in carrying out an exact calculation of the two processes described above by considering a model in which we calculate the nuclear screening for a 'sample' point charge which penetrates the lanthanide ion charge distribution. Arguments are given below to relate the results of this calculation to the real charge distribution for the overlapping ligand-lanthanide pair.

A point charge at distance  $R$  from the nucleus of the lanthanide ion produces a quadrupolar potential of the form  $(r^2/R^3)P_2(\theta)$  at a point  $r = (r, \theta, \phi)$  with  $r < R$ , the principal axis defining the spherical polar coordinates being taken in the direction of the charge. If we have  $r > R$  the expression changes to  $(R^2/r^3)P_2(\theta)$ . It follows, therefore, that the usual procedure of assuming the perturbing potential to be proportional to  $r^2 P_2(\theta)$  is based on the implicit assumption that the sources of the electrostatic field are outside the lanthanide ion. Our model calculation is based on replacing the radial integrals over  $r^2/R^3$  used in the standard screening calculation (see e.g. Ahmad and Newman 1978) by the correct expression for a point charge at *any* distance  $R$ , that is,

$$r^2/R^3 \quad \text{for} \quad r < R, \quad R^2/r^3 \quad \text{for} \quad r > R.$$

In carrying out the calculation we shall be primarily interested in the effect of this change on the  $5p \rightarrow n'p$  excitations which dominate all other mechanisms in their contribution to  $\gamma_\infty$ . We need calculate only the second-order perturbation contributions explicitly, as all the important higher order contributions involve the same matrix elements and will be modified approximately in proportion. These second-order

contributions take the general form (Ahmad and Newman 1978)

$$\gamma_{\infty} = -\frac{4}{5} \sum_{\substack{nl \\ n'l'}} [l, l'] \begin{pmatrix} l' & 2 & l \\ 0 & 0 & 0 \end{pmatrix}^2 \frac{\langle nl | r^{-3} | n'l' \rangle \langle n'l' | q | nl \rangle}{\Delta E(nl \rightarrow n'l')}, \quad (1)$$

where

$$\begin{aligned} q &= r^2 & \text{for } r < R, \\ &= R^5/r^3 & \text{for } r > R. \end{aligned}$$

We have calculated the contributions to  $\gamma_{\infty}$  for  $\text{Pr}^{3+}$  corresponding to  $l = l' = 1$ ,  $n = 5$  and  $6 \leq n' \leq 30$ .

The calculation was carried out for several values of  $R$  in the range 1.4–5.4 atomic units. Results are given graphically in Fig. 1, which shows a pronounced decrease in the magnitude of  $\gamma_{\infty}$  for  $R$  in the range 3–1.5 a.u. This demonstrates that the potential due to charges which penetrate the lanthanide 5p shell is subject to considerably less antiscreening (or amplification) than that due to the externally generated fields.

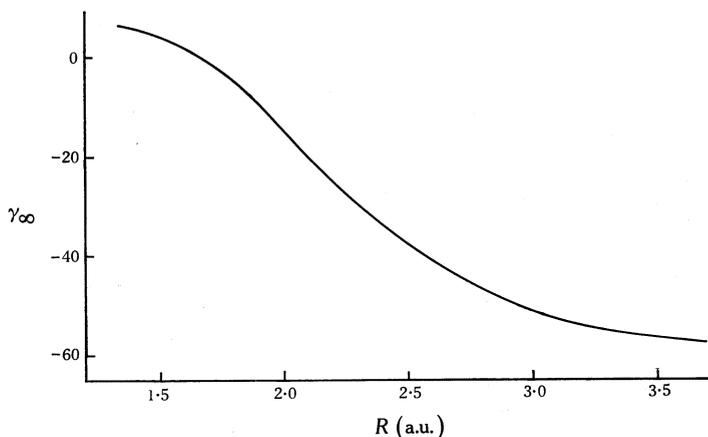


Fig. 1. Sum over  $n'$  of the  $5p \rightarrow n'p$  contributions to  $\gamma_{\infty}$  (see equation 1) for  $\text{Pr}^{3+}$  plotted against the position  $R$  of the point charge generating the potential.

### Exchange Charge Effects

The results of the model calculation shown in Fig. 1 can be readily used to estimate the contribution of the exchange charge set up by ligand- $\text{Pr}^{3+}$  overlap. Consider any pair of overlapping (real) one-electron free ion wavefunctions  $\phi, \chi$  on the  $\text{Pr}^{3+}$  and ligand respectively. Orthogonalizing  $\phi$  with respect to  $\chi$  we obtain

$$\phi' = (1 - S^2)^{-\frac{1}{2}}(\phi - S\chi), \quad \text{where } S = \langle \chi | \phi \rangle. \quad (2)$$

The total charge density is thus given by

$$\phi'^2 + \chi^2 = \frac{\phi^2 - 2S\chi\phi + S^2\chi^2}{1 - S^2} + \chi^2 = \phi^2 + \chi^2 + \frac{S^2(\phi^2 + \chi^2)}{1 - S^2} - \frac{2S\chi\phi}{1 - S^2}.$$

This corresponds to the creation of a positive exchange charge of net magnitude  $2S^2/(1 - S^2)$  in the region of overlap, compensated by equal (negative) additions to

the net charge associated with  $\phi$  and  $\chi$ . Note that this result is independent of the orthogonalization procedure, and always gives a symmetrical redistribution. In most practical applications we have  $S^2 \ll 1$ , so that the magnitude of the exchange charge is close to  $2S^2$ . For closed shell systems this result must be doubled for each orbital to allow for the two spin directions.

As an example, consider the case of a  $\text{Cl}^-$  ion separated from the  $\text{Pr}^{3+}$  ion by a distance of 5.5812 a.u. According to Bishton *et al.* (1967) the total exchange charge in this case is

$$\begin{aligned} \lambda &= 4(\langle 5s | 3s \rangle^2 + \langle 5s | 3p\sigma \rangle^2 + \langle 5p\sigma | 3s \rangle^2 + \langle 5p\sigma | 3p\sigma \rangle^2 + 2\langle 5p\pi | 3p\pi \rangle^2) \\ &= 0.1264 \text{ a.u.}, \end{aligned} \quad (3)$$

that is, an appreciable fraction of an electronic charge. A more recent calculation by the present authors using the program reported by Copland *et al.* (1978) gives  $\lambda = 0.0938$ .

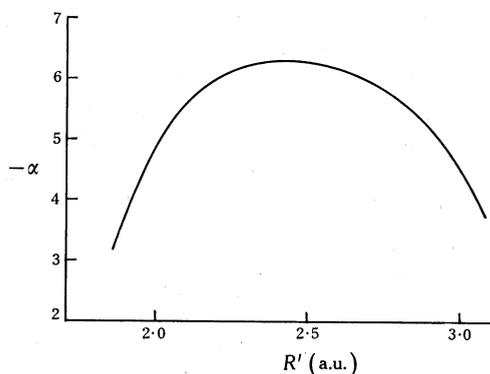


Fig. 2. Plot of the factor  $\alpha$  defined by equation (4) against the position  $R'$  of the exchange charge. This graph shows the variation of the exchange charge correction with the position of a 'point' exchange charge (supposing its magnitude to be fixed).

It is considerably more difficult to determine the mean position of the  $\text{Cl}^-$  exchange charge than to estimate its magnitude. Bishton *et al.* (1967) calculate its distance from the lanthanide ion centre as being 2.511 a.u., while a comparison of tabulated ionic radii (Weast 1975) suggests that 2 a.u. is more realistic. A glance at Fig. 1 suggests that discrepancies of this magnitude will be very important in obtaining a realistic estimate of the effect. It turns out, however, that the strong  $R$  dependence shown in Fig. 1 is, to a large extent, compensated by the  $R^{-3}$  dependence of the quadrupolar potential.

An unscreened electronic charge at distance  $R$  produces a quadrupolar field at the lanthanide nucleus of magnitude  $A/R^3$  (where  $A$  is a constant). With antiscreening this becomes

$$(1 - \gamma_\infty)A/R^3 \quad (\text{with } -\gamma_\infty \gg 1).$$

A point exchange charge  $\lambda$  situated at  $R'$  ( $< R$ ) similarly produces a quadrupolar potential contribution

$$\lambda(1 - \gamma'_\infty)A/R'^3,$$

where  $\gamma'_\infty$  is our calculated antiscreening factor for a point charge at  $R'$ . It follows that the overall effect of the exchange charge with its compensating charge at the

ligand is to modify the calculated screening factor  $(1 - \gamma_\infty)$  by the additional factor  $(1 + \alpha\lambda)$ , where

$$\alpha = \frac{1}{2} - \{(1 - \gamma'_\infty)/(1 - \gamma_\infty)\}R^3/R'^3. \quad (4)$$

Fig. 2 gives the variation of  $\alpha$  which has been calculated using the results of Fig. 1 and  $R = 5.5812$  a.u. A surprising aspect of this figure is the nearly constant value of  $\alpha$  over the range of distances  $R'$  of physical interest. Hence the position of the exchange charge and its finite distribution are not, in fact, crucial.

Taking a mean value of  $\alpha \approx -6$  along with the magnitude of the exchange charge estimated above (equation 3), we find that the uncorrected quadrupolar potential due to an external point-charge ligand interaction is reduced by a factor  $(1 + \alpha\lambda) = 0.24$  if we take  $\lambda = 0.1264$  a.u. or  $0.44$  if  $\lambda = 0.0938$  a.u. This will make an important difference to point-charge lattice sum estimates of the quadrupole field, as well as making it more difficult to set up direct comparisons of the nuclear and electronic crystal field potentials (see e.g. Newman and Price 1975).

Previous workers (e.g. Sawatzky and Hupkes 1970; Sengupta *et al.* 1971) have assumed that the nuclear screening of an exchange charge can be approximated by the factor  $(1 - R)$  appropriate for the ionic states that are involved in producing the exchange charge. Values of  $R$  have apparently never been calculated for the 5p and 5s states of  $\text{Pr}^{3+}$ , but Sternheimer (1967) obtained the (antiscreening) value  $R = -0.384$  for the 5d state of Pr. This is in accord with the order of magnitude found in many calculations, namely  $|R| < 1$ . Such antiscreening factors are considerably less than we have obtained for the penetrating point charge, showing that approximations for the effect of an exchange charge based on  $R$  are likely to be very inaccurate compared with the results of the present work.

## Conclusions

We have shown in the previous section that the production of exchange charges in the region of lanthanide–ligand overlap results in a considerable reduction of the ‘effective’ antiscreening effect on a ligand ‘point charge’. A second reduction of the antiscreening effect must also result from charge penetration, for it is clear from Fig. 1 that the potential arising from penetrating electrons will not be subject to such strong antiscreening. Unfortunately, it is considerably more difficult to make quantitative estimates of this effect based on the simple model developed in this paper. Nevertheless, a definite qualitative conclusion has emerged: the electrostatic antiscreening factor  $\gamma_\infty$  cannot be applied to that part of the crystal potential generated by the ligands, for finite-size effects provide radical changes in ligand contributions to the nuclear quadrupole field. This undermines the whole concept of expressing the crystal–nuclear interaction as a product of a lattice sum times an antiscreening factor, and shows that future attempts to relate experimental and theoretical results must be based on a more sophisticated model in which the ligands are treated separately from other sources of the electrostatic potential in the crystal.

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