PHYSICAL REVIEW B VOLUME 30, NUMBER 4 15 AUGUST 1984

Crystal-field parameters in rare-earth compounds: Extended charge contribution

D. Garcia and M. Faucher

Laboratoire des Elĕments de Transition dans les Solides (Equipe de Recherche No. 60210 du Centre National de la Recherche Scientifique), 1 Place A. Briand, F-92190 Meudon-Bellevue, France

(Received 28 November 1983)

The Coulombic interaction between the extended charge distributions of a rare-earth $4f$ electron and its ligands' closed electronic shells is exactly calculated utilizing the development by Buehler and Hirschfelder. The results are presented in terms of crystal-field parameters acting within the rare-earth orbitals basis set. A comparison is made with respect to point-charge values. The higher the k rank of the B_q^k parameter, the more it is reduced with respect to the point-charge value, the latter being the limit attained for large internuclear distances. For usual nearest-neighbor distances, the B_0^0 value is not much changed with respect to the point-charge limit whereas the B_q^6 values are greatly reduced and may even display an opposite sign. The calculations are performed with use of analytical radial wave functions given in the literature for nine pairs of rare-earth ligands: Nd^{3+}, Eu^{3+}, Tm^{3+}/Cl^-, O^{2-}, and F^-. The values obtained are fitted with an analytical function of the distance so as to be utilized in a subsequent LCAO calculation.

I. INTRODUCTION

Two theories prevail for the description of crystal-field effects on the electronic energy levels of transition elements in weakly covalent hosts such as rare-earth compounds.

(1) The rather isolationist electrostatic model (EM) where the cloud of the rare-earth open-shell electrons interact with a network of punctualized polarizable charges. The leading interaction term in this case is the ligand point-charge interaction and probably in a decreasing order the dipolar, quadrupolar, etc., terms. Such a point-multipole model is efficient in describing experimental effects (energy splittings) provided some corrections are performed: screening by external closed shells, fittings of charges as well as of the expectation values of r^k. The revival of the EM stated in literature of the past years is mostly due to the contributions of Morrison and coworkers (Ref. 1 and quoted papers). We have also recently reported electrostatic calculations on a series of rare-earth compounds.[2,3] However satisfactory in view of their results, these manipulations reflect underlying physical effects which should naturally proceed from a more rigorous treatment of the problem.

(2) The other approach consists in a more communal description of the central ion-ligands cluster. The problem is handled in first approximation by building molecular orbitals on the basis of linear combinations of atomic orbitals (LCAO). After Jörgensen *et al.*[4] in 1963 proposed the "angular overlap model" based on pure covalency, Ellis and Newman,[5] the first in 1967, applied the complete LCAO method to the rare-earth halide $PrCl_3$.

Provided the charges are not smeared out in the cluster as it is likely to occur in strongly covalent cases, one of the leading interaction terms is, as hereabove, the Coulombic electrostatic interaction, except this time it is between the extended charge distributions of the central-ion open shell and its ligands' electrons. In 1967, Raychaudhuri and Ray[6] calculating the "Coulombic part of the overlap" in $PrCl_3$ found that it was strongly reduced with respect to the point-charge limit.

For a systematic application of the LCAO methods to lanthanide compounds, the first step therefore is the computation of this Coulombic term. Quite recently, aiming to correct point-multipolar lattice sums, Morrison[7] investigated these so called "charge penetration effects." The bipolar expansion of the interaction potential was expressed using Bessel functions. Utilizing hydrogenic wave functions for the ligand electrons, and assuming that the r coordinate of the open-shell electron is small, Morrison derived an easily computable expression likely to cover a large number of experimental cases.

Presently, in a somewhat different approach, we calculate without approximation the bipolar expansion of the interaction potential with use of the development by Buehler and Hirschfelder.[8,9] The computations are extended (a) to a series of interatomic distances covering the range of possible nearest-neighbor distances (2—4 Å), (b) to nine pairs of metal ligands, the lanthanides being Nd^{3+}, Eu^{3+}, and Tm^{3+}, respectively, and the ligands Cl^-, O^{2-}, and F^- closed shells, respectively. Analytical Slater-type orbitals from the literature are utilized in the computations. The calculated values are fitted in each case as analytical functions of the metal-ligand distance so as to be utilized subsequently in a LCAO-type calculation. At short distances, the spherical part of the Coulombic interaction is not very different from point-charge values, whereas the multipolar contributions are much smaller. In terms of crystal-field parameters of a Hamiltonian acting on the rare-earth basis, this means that the extended charge and point charge B_0^0 and B_q^2 are nearly the same whereas the extended charge B_q^4 and especially B_q^6 are much reduced and may even change their sign. At large distances, the differences with the point-charge contributions become negligible.

In the first part we shall give the physicomathematical references, and in the second part the numerical values of the parameters in an analytical expression fitting the discrete values of the computed Coulombic interaction.

II. CALCULATION OF THE "EXTENDED CHARGE" CRYSTAL-FIELD PARAMETERS

The conventional crystal-field Hamiltonian acting within the lanthanide $4f$ (or actinide $5f$) (L,M) set is written as

$$H_{\mathrm{cf}}=\sum_k B^{(k)}C^{(k)}(\hat{r}_i)\ , \tag{1}$$

where $C^{(k)}(\hat{r}_i)$ is a tensor operator of rank k depending on the angular coordinates of the ith electron.

If $\rho(\vec{r}_j)$ is the charge density throughout the lattice, the electrostatic interaction between an (L,M) central-ion electron and the lattice is given by

$$W=-e\int\int P_{4f}^2(r_i)Y_L^{M*}(\hat{r}_i)Y_L^M(\hat{r}_i)\frac{\rho(\vec{r}_j)}{r_{ij}}\,d^3r_i d^3r_j\ , \tag{2}$$

so that

$$H_{\mathrm{cf}}=-e\int\int P_{4f}^2(r_i)\frac{\rho(\vec{r}_j)}{r_{ij}}\,dr_i d^3r_j\ . \tag{3}$$

More specifically, we now consider the rare-earth $4f$ electron interaction with a single ligand formed by a point charge $(+q_N)$ including the nucleus and the tight internal closed shells ($1s^2$ in the case of O^{2-}), surrounded by one or several outer closed shells $nl^{2(2l+1)}$ ($2s^2$ and $2p^6$ for O^{2-}, for instance) displaying an extended charge distribution. As allowed by the superposition theorem, both interactions will be added together. $\vec{r}_1$ and $\vec{r}_2$ refer to the rare-earth and ligand electron positions with respect to their nucleus (Fig. 1).

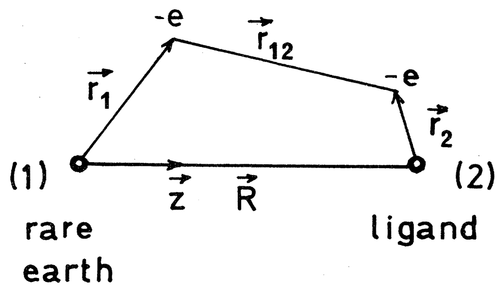

FIG. 1. Interaction between a $4f$ and a ligand electron.

Following Buehler and Hirschfelder,[8,9] the inverse distance between electrons (1) and (2) is

$$\frac{1}{r_{12}}=\sum_{k,K,\mu} b_{kK}^{\mu}(r_1,r_2,R)C_{\mu}^{k}(\hat{r}_1)C_{\mu}^{K*}(\hat{r}_2)\ , \tag{4}$$

where b_{kK}^{μ} is a function of r_1, r_2, and R. We now write the charge density $\rho(\vec{r}_2)$ of the ligand in (2),

$$\rho(\vec{r}_2)=q_N\delta(\vec{r}_2)-e\sum_{n,l}\frac{2(2l+1)}{4\pi}P_{nl}^2(r_2)\times\sum_m C_l^{m*}(\hat{r}_2)C_l^m(\hat{r}_2)\ , \tag{5}$$

where δ is the Dirac function [if $\vec{r}_2=\vec{0}$, then $\delta(\vec{r}_2)=1$, otherwise $\delta(\vec{r}_2)=0$].

$P_{nl}(r_2)$ is r_2 times the radial part of the nl shell wave function. Accordingly, we have

$$\begin{aligned}H_{\mathrm{cf}}&=-e\int\int P_{4f}^2(r_1)\frac{\rho(\vec{r}_2)}{r_{12}}dr_1 d^3r_2\\&=-eq_N\int\frac{P_{4f}^2(r_1)}{|\vec{r}_1-\vec{R}|}dr_1+e^2\sum_{n,l}\frac{2(2l+1)}{4\pi}\int\int P_{nl}^2(r_2)P_{4f}^2(r_1)\frac{1}{r_{12}}\sum_m C_m^{l*}(\hat{r}_2)C_m^l(\hat{r}_2)dr_1\,d^3r_2\ ,\end{aligned} \tag{6}$$

$$H_{\mathrm{cf}}=H_N+H_E\ . \tag{7}$$

H_N may be developed on a basis of spherical tensors:

$$H_N=-eq_N\sum_k\int P_{4f}^2(r_1)\frac{r_<^k}{r_>^{k+1}}C^{(k)}(\hat{r}_1)C^{(k)}(\hat{R})dr_1\ , \tag{8}$$

and since the z axis is along the internuclear axis R,

$$H_N=-eq_N\sum_k\int P_{4f}^2(r_1)\frac{r_<^k}{r_>^{k+1}}C_0^k(\hat{r}_1)dr_1\ , \tag{9}$$

where $r_<$ and $r_>$ stand for the smallest and largest distance of the set (r_1,R), respectively. Equation (4) in (6) yields

$$H_E=e^2\int\int\sum_{\substack{n,l,m\\k,K,\mu}} b_{kK}^{\mu}(r_1,r_2,R)\frac{2(2l+1)}{4\pi}P_{nl}^2(r_2)P_{4f}^2(r_1)C_{\mu}^k(\hat{r}_1)C_{\mu}^{K*}(\hat{r}_2)C_m^{l*}(\hat{r}_2)C_m^l(\hat{r}_2)dr_1 d^3r_2\ . \tag{10}$$

The integration of the product of the three spherical tensor functions of $\hat{r}_2$ leaves

$$4\pi\sum_{m}(-1)^m\begin{bmatrix}K & l & l\\ \mu & -m & m\end{bmatrix}\begin{bmatrix}K & l & l\\ 0 & 0 & 0\end{bmatrix}=4\pi\delta(K,0)\delta(\mu,0)$$

so that H_E reduces to the simpler form

$$H_E=e^2\int\int\sum_{n,l,k}2(2l+1)b_{k0}^{0}(r_1,r_2,R)P_{nl}^2(r_2)P_{4f}^2(r_1)C_0^k(\hat{r}_1)dr_1dr_2\ , \tag{11}$$

Eqs. (1), (7), (9), and (11) finally yield

$$B_0^k=-eq_N\int P_{4f}^2(r_1)\frac{r_<^k}{r_>^{k+1}}dr_1+e^2\int\int\sum_{n,l}2(2l+1)b_{k0}^0(r_1,r_2,R)P_{4f}^2(r_1)P_{nl}^2(r_2)dr_1dr_2\ . \tag{12}$$

The expressions of b_{k0}^0 as functions of r_1, r_2, and R are given in Refs. 8 and 9:
for $R>|\vec{r}_1+\vec{r}_2|$, $b_{k0}^0=r_1^k/R^{k+1}$;
for $r_1>|\vec{R}+\vec{r}_2|$, $b_{k0}^0=R^k/r_1^{k+1}$;
for $|\vec{r}_1-\vec{r}_2|<R<|\vec{r}_1+\vec{r}_2|$ the expression is more complicated:

$$b_{k0}^0(r_1,r_2,R)=\sum_{i,j=0}^{2(k+1)}A(k,i,j)r_1^{i-k-1}r_2^{j-1}R^{k-i-j+1}\ . \tag{13}$$

Reference 9 gives the summation allowing for the computation of the $A(k,i,j)$.

Taking into account the integration limits, the "extended charge" crystal-field parameter due to an axial ligand is written as

$$\begin{aligned}B_0^k=-eq_N\int_0^\infty P_{4f}^2(r_1)\frac{r_<^k}{r_>^{k+1}}dr_1+e^2\sum_{n,l}2(2l+1)\Bigg[&\int_0^\infty P_{4f}^2(r_1)dr_1\frac{r_<^k}{r_>^{k+1}}\int_0^{|R-r_1|}P_{nl}^2(r_2)dr_2\\ &+\sum_{i,j=0}^{2(k+1)}A(k,i,j)R^{k-i-j+1}\int_0^\infty P_{4f}^2(r_1)r_1^{i-k-1}dr_1\\ &\times\int_{|R-r_1|}^{R+r_1}P_{nl}^2(r_2)r_2^{j-1}dr_2\Bigg]\ .\end{aligned} \tag{14}$$

Calling Z_{00} the nuclear charge times $-e$ and Z_{nl} the total charge of the nl shell times $-e$, (13) may be expressed in an even more condensed final form:

$$\begin{aligned}B_0^k=\sum_{n,l}Z_{nl}\Bigg[&\int_0^\infty P_{4f}^2(r_1)\frac{r_<^k}{r_>^{k+1}}dr_1\int_0^{|R-r_1|}P_{nl}^2(r_2)dr_2\\ &+\sum_{i,j=0}^{2k+2}A(k,i,j)R^{k-i-j+1}\int_0^\infty P_{4f}^2(r_1)r_1^{i-k-1}dr_1\int_{|R-r_1|}^{R+r_1}P_{nl}^2(r_2)r_2^{j-1}dr_2\Bigg]\ .\end{aligned} \tag{15}$$

The crystal-field parameter produced by a no-longer axial ligand with coordinates R,θ,φ with respect to the rare-earth axes is

$$B_q^k=B_0^kC_q^{k*}(\theta,\varphi)\ , \tag{16}$$

and the total crystal-field Hamiltonian due to this ligand is given by (1).

III. RESULTS AND DISCUSSION

Values of B_0^k were computed for a series of internuclear distances and for nine couples of trivalent rare-earth ligands; namely, Nd^{3+}, Eu^{3+}, and Tm^{3+} on one hand, and O^{2-}, Cl^-, and F^- on the other. The wave functions utilized in the calculations were those of Ref. 10 for Nd^{3+}, of Ref. 11 for Eu^{3+} and Tm^{3+}, of Ref. 12 for O^- and F^-, and Ref. 13 for Cl^-.

The discrete values of B_0^k were fitted to the analytical formula

$$\beta_k=B_0^k(\text{extended charge})/B_0^k(\text{PCEM})=1-ae^{-bR^d}\ , \tag{17}$$

$$B_0^k(\text{PCEM})=-e\left[\frac{4\pi}{2k+1}\right]^{1/2}\times\frac{\langle r^k\rangle}{R^{k+1}}\left[q_N-2e\sum_{nl}(2l+1)\right]\ .$$

B_0^k (PCEM) is the corresponding point-charge electrostatic model value. The three parameters a, b, and d are listed in Table I with the range of internuclear distances for $k=2$, 4, and 6.

It is noteworthy that the B_0^0 (extended-charge values) are very close to the PCEM values. The lowest β_0 obtained in the computations was 0.9504 for the couple Tm^{3+}-Cl^- at 2.6 Å. At a standard nearest-neighbor distance (2.4 Å), for the couples Nd^{3+},Eu^{3+}/O^{2-},F^-, β_0 ranges between 0.9974 and 0.9988. Therefore, we did not

TABLE I. Parameters fitting the expression $\beta_k = B_0^k(\text{extended charge})/B_0^k(\text{PCEM}) = 1 - ae^{-bR^d}$. The distances are in Å.

Ligand	Rare earth	β_2			β_4			β_6		
		a	b	d	a	b	d	a	b	d
Cl^-	Nd^{3+}	24.10	1.227	1.26	23.47	0.69	1.43	8.839	0.102	2.348
$2.7 < R < 3.6$	Eu^{3+}	29.96	1.370	1.207	50.47	1.101	1.213	30.33	0.511	1.531
	Tm^{3+}	27.57	1.366	1.207	55.90	1.240	1.150	99.38	1.269	1.072
O^{2-}	Nd^{3+}	38.61	2.660	1.053	12.30	1.118	1.370	3.791	0.2364	2.055
$2.2 < R < 3.3$	Eu^{3+}	24.76	2.297	1.158	10.60	0.9029	1.601	5.527	0.2618	2.280
	Tm^{3+}	54.96	3.007	1.015	27.74	1.601	1.273	14.30	0.7720	1.611
F^-	Nd^{3+}	76.79	3.006	1.051	34.84	1.606	1.215	6.832	0.3442	1.858
$2.2 < R < 3.3$	Eu^{3+}	35.29	2.314	1.249	19.28	0.986	1.660	9.885	0.2920	2.342
	Tm^{3+}	143.39	3.502	1.026	91.09	2.090	1.231	38.58	1.016	1.575

find it very useful to refine a, b, and d values for β_0.

The radial integrals for the trivalent rare earths are given in Table II. As an example Fig. 2 plots β_k as a function of the internuclear distance for Nd^{3+}-O^{2-}. For large R values, the asymptotic β_k value is equal to 1 for all k values, so that the point-charge approximation is well justified for the main part of the lattice in the electrostatic hypothesis, but the situation is very different for the rare-earth nearest neighbors. For instance, β_k equals 0.93, 0.59, and -0.10 for $k=2$, 4, and 6 for the pair Nd^{3+}/O^{2-} at $R=2.3$ Å (which is the case of the neodymium nearest-neighbor oxygen atoms in Nd_2O_3). A qualitative explanation is the following: far from the O^{2-} ion, the $4f$ electron "sees" the total charge $-2e$. The more it penetrates the O^{2-} electronic cloud, the less it sees the oxygen electrons and the more it feels the effects of the positive charge of the nucleus, $+8e$.

Consequently, the more we expand the $4f$ wave function, i.e., the more we increase the radial integrals $\langle r \rangle^k$ in order to improve tentatively the PCEM parameters, the more the PCEM hypothesis will be inadequate for the first neighbors which are the main "contributors" to the fourth- and sixth-rank parameters.

So as to establish a comparison with the results of Ref. 7, let us choose again the pair Nd^{3+}/O^{2-}. Morrison's estimate of γ for oxygen in the hydrogenic radial wave function $\rho(r) = Nr^2 e^{-\gamma r}$ is 3.86 $Å^{-1}$. At a 2.487 Å internuclear distance ($y = \gamma R = 9.6$) Morrison's results in terms of β_2, β_4, and β_6 yield 0.84, 0.484, and 0.153, respectively, while the coefficients listed Table I together with Eq. (17) lead to the values 0.963, 0.75, and 0.185, respectively. It is noteworthy that the discrepancy would subsist with another choice for γ.

TABLE II. k-even radial integrals of trivalent rare earths (atomic units).

	$\langle r^2 \rangle$	$\langle r^4 \rangle$	$\langle r^6 \rangle$
Nd^{3+} [a]	0.978	2.207	11.082
Eu^{3+} [b]	0.829	1.677	7.302
Tm^{3+} [b]	0.640	1.043	3.528

[a] With the wave function of Ref. 10.

[b] With the wave function of Ref. 11.

As a conclusion, we can state the following:

(a) The $k=4$ and 6 crystal-field parameters which are already too small with respect to experimental parameters when calculated with the PCEM hypothesis are not improved when extended-charge parameters are considered since the latter are usually smaller. The contribution to sixth-order parameters due to the Coulombic interaction with O^{2-} and F^- first neighbors is negligible at standard nearest-neighbors distances (2.3—2.4 Å). In the case of Cl^- the ligand electronic cloud is so expanded that the Coulombic contribution to B_0^6 may become larger than the PCEM parameter (but with an opposite sign). However, it is still too small to match experimental values. For instance, the PCEM B_0^6 of $LaCl_3$:Nd^{3+} equals -61 cm^{-1} due to first neighbors (-49 cm^{-1}) on one hand and to the remaining part of the lattice (-12 cm^{-1}) on the other. The extended charge calculation increases slightly and changes the sign of the contribution of the first neighbors

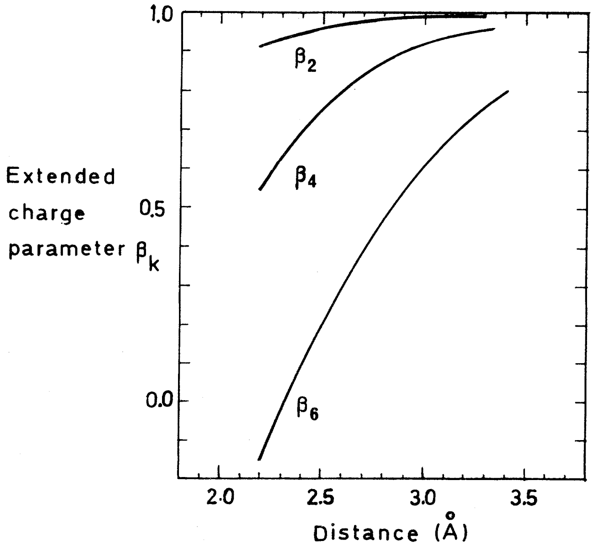

FIG. 2. "Extended charge parameter" β_k as a function of the internuclear distance for Nd^{3+}—O^{2-}.

(+ 65 cm^{-1}), which makes a new total of 53 cm^{-1} still too small to match the experimental value of -713 cm^{-1}.

(b) An attempt to increase extended-charge parameters by expanding the 4*f* wave function is unsuccessful since the B_q^2, which are already large enough, are indeed increased; the B_q^4 are not much changed whereas the small B_q^6 are further reduced.

(c) Expressions (17) together with the *a*, *b*, and *d* parameters listed Table I summarize the results of the two centers, two electron integration done once and for all. They may be useful to perform LCAO calculations on rare-earth clusters.

ACKNOWLEDGMENT

This work was done on a Cray-1 computer under the financial support of the $\mathrm{GC_2VR}$ (Groupement pour un Centre de Calcul Vectoriel pour la Recherche), Ecole Polytechnique, Palaiseau, France and thanks to the computer facilities of Laboratories de Bellevue, Centre National de la Recherche Scientifique (CNRS), 92190 Meudon.

---

[1] C. A. Morrison, Harry Diamond Laboratories Report No. HDL-SR-82-8, 1982 (unpublished).

[2] M. Faucher and D. Garcia, Phys. Rev. B **26**, 5451 (1982).

[3] D. Garcia, M. Faucher, and O. L. Malta, Phys. Rev. B **27**, 7386 (1983).

[4] C. K. Jörgensen, R. Pappalardo, and H. H. Schmidtke, J. Chem. Phys. **39**, 1422 (1963).

[5] M. M. Ellis and D. J. Newman, J. Chem. Phys. **47**, 1986 (1967).

[6] A. K. Raychaudhuri and D. K. Ray, Proc. Phys. Soc. London **90**, 839 (1967).

[7] C. A. Morrison, Harry Diamond Laboratories Report No. HDL-TR-1990, 1982 (unpublished).

[8] R. J. Buehler and J. O. Hirschfelder, Phys. Rev. **83**, 628 (1951).

[9] R. J. Buehler and J. O. Hirschfelder, Phys. Rev. **85**, 149 (1952).

[10] M. Synek and L. Corsiglia, J. Chem. Phys. **48**, 3121 (1968).

[11] O. Sovers, J. Phys. Chem. Solids, **28**, 1073 (1967).

[12] E. Clementi, C. C. Roothaan, and M. Yoshimine, Phys. Rev. **127**, 1618 (1962).

[13] E. Clementi, A. D. McLean, D. L. Raimondi, and M. Yoshimine, Phys. Rev. **133**, A1274 (1964).