

Ab initio calculation of the contribution from anion dipole polarization and dynamic correlation to $4f$ - $5d$ excitations of Ce^{3+} in ionic compounds

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(Received 12 April 2005; published 19 July 2005)

In this study basic effects are investigated of ion-host interactions on $4f$ - $5d$ excitations of Ce^{3+} ions in wideband ionic host compounds. Particularly the shift of the average $4f$ - $5d$ transition energy compared to that of the free ion, the centroid shift, is of interest. The self-induced dipole effect where the $4f$ or $5d$ electron dynamically polarizes the neighboring ions is analyzed in detail. Taking into account the overlap of the $5d$ orbital of Ce^{3+} with the neighbor anions, the standard classical expression was modified, and the result is that this not only drastically reduces the value of the polarization contribution to the centroid shift but also the steep dependence on the distance to the anions almost vanishes. This polarization effect and the additional contributions such as covalency and dynamic correlation should be included in a configuration interaction (CI) calculation applied on a cluster of ions around the Ce^{3+} ion. Calculations with Hartree-Fock Møller-Plesset perturbation theory corrected to second order for perturbation effects and coupled-cluster theory with single, double, and triple excitations were conducted with various basis sets and cluster sizes and it turned out that the results do not include the polarization effect and so this contribution had to be calculated separately and was added to the CI results. Good agreement at the 0.15 eV level is obtained between theory and experiment for Ce^{3+} in BaF_2 , $LaAlO_3$, and $LaCl_3$.

DOI: 10.1103/PhysRevB.72.045129

PACS number(s): 76.30.Kg, 74.25.Jb, 71.23.-k

I. INTRODUCTION

For many decades the spectra of lanthanide ions have been studied in great detail and a wealth of experimental data of these ions is available today both as free ions and as dopants in a large variety of crystals. The theory of $4f^N$ spectra was formulated and based on that methods were developed for calculating spectral results. The most widely used approach for $4f^N$ configurations is crystal-field theory based on a semiempirical model Hamiltonian.¹ This method can be applied also to $4f^N \leftrightarrow 4f^{N-1}5d$ transitions,² which are of interest for this paper. *Ab initio methods* based on density functional theory (DFT) or the Hartree-Fock (HF) formalism with configuration interaction (CI) are rarely used because of the complexity of the systems.

There is, however, a growing interest in calculating *ab initio* properties of the lanthanide ion and its compounds using the CI method as is evident from the work of Cao and Dolg³ on ionization potentials and that of Seijo *et al.*⁴ on $4f$ - $5d$ transitions of Ce^{3+} in elpasolites. Only a single important reference is chosen from the extensive studies of the two groups because it is not the purpose of this work to give a review on the matter.

One of the most important conclusions of the study on ionization potentials was that the absolute value of $4f$ - $5d$ transition energies is very hard to calculate *ab initio* because of the poor convergence in the CI expansion, where i functions ($\ell=6$) still give sizable contributions. This is the reason why the property of interest for this paper was chosen to be the centroid or barycenter shift of the $4f$ - $5d$ transitions of Ce^{3+} through the interaction with the neighboring anions. It is defined as the $4f$ - $5d$ transition energy averaged over the $5d$ levels compared to the corresponding quantity of the free

ion. This shift is very important for explaining laser action and scintillation behavior in many application crystals.

The centroid shift was found to result from complicated physical effects in which the polarization of the anions by the $4f$ or $5d$ valence electron and dynamical correlation with the valence electrons of the anions contribute to the shift. These effects turned out to be hard to calculate *ab initio* and this paper actually is an explorative study where the effects have been calculated at various levels of theory. Starting with crystal-field modeling using the polarizable anion model, Møller-Plesset perturbation theory corrected to second order for correlation effects (HF-MP2) as well as coupled-cluster theory with single, double, and triple excitations [CCSD(T) level] were applied using various basis sets.

The splitting of the $5d$ level also important for applications appears to be much easier to calculate because polarization and the dynamic correlation effects are much less important and useful results are already obtained at the HF level.

The Ce^{3+} ion was chosen because it has the simplest $4f^N$ configuration ($N=1$) and the $4f$ - $5d$ transitions are typical for the other lanthanide ions because the $5d$ orbitals of the $4f^{N-1}5d$ levels of all triply ionized lanthanide ions are very similar. Particularly this can be seen from the binding energy of the $5d$ electron,⁵ which is almost constant along the series.

Recently in a series of papers Dorenbos showed that using a simple model for the centroid shift a useful trend was found for Ce^{3+} in a large variety of crystals containing fluorides,⁶ oxides,^{7,8} chlorides, bromides, and iodides.⁹ The model is the self-induced dipole contribution to the crystal field originally proposed by Morrison *et al.*¹⁰ for $4f^N$ spectra and reformulated for $4f$ - $5d$ transitions of Ce^{3+} in a CeF_6 complex by Aull and Jenssen.¹¹ The model uses the fact that

the $4f$ and $5d$ electrons dynamically polarize the surrounding anions and the centroid shift can be calculated just using a value for the anionic polarizability, which for fluorides is close to the value for the host material. The model actually describes classically the dynamic polarization mentioned above but ignores quantum mechanical effects like covalency, overlap, and contributions from dynamic correlation. Therefore this study was started to investigate these effects in detail.

The structure of the approach is as follows. First the simple classical point dipole model is considered and account is taken of the fact that the $5d$ orbital has a substantial overlap with the surrounding anions. The charge penetration and the exclusion principle will reduce the polarization of the anions. This is implemented as a modification of the simple model and results are calculated for Ce^{3+} in BaF_2 , LaAlO_3 and LaCl_3 in order to compare three typical classes of compounds.

Subsequently, configuration interaction at the HF-MP2, MP4, CCSD, and CCSD(T) levels was applied to a cluster of ions containing the Ce^{3+} ion and its nearest anions, embedded in an array of nearest cations and point charges for the larger distances. In theory one expects that the polarization effect is included in the CI expansion but the perturbation expansion was found to be inadequate for this and an estimate of the polarization contribution has to be added to that of the CI expansion. This work is part of the continuing effort taken in our group^{12–15} for describing energy levels of Ce^{3+} in solids. A preliminary version of this study was published earlier.¹⁶

One may wonder why the calculations were not done using the density functional formalism so successful in other areas of electronic structure calculations. In that approach there is no need for the demanding CI calculations. However, it was found that the $4f$ - $5d$ energy differences of Ce^{3+} calculated using DFT band structure codes come out much too small and they do not show useful centroid shifts. For instance, using the DFT codes VASP (Ref. 17) as well as WIEN (Ref. 18) it was found that the average $4f$ - $5d$ energy difference of Ce^{3+} in LaF_3 is smaller than that in LaAlO_3 . Experiment⁶ shows, however, that the latter compound gives a very large centroid shift that is around 1 eV larger than in fluoride compounds and so the $4f$ - $5d$ energy difference should be much smaller. This discrepancy may be due to the fact that the $5d$ levels in DFT are all in the conduction band and so they are broadened to a wide band and do not show a proper crystal-field splitting.

II. THEORETICAL MODELS FOR THE CENTROID SHIFT

A. Crystal-field theory

1. Polarizable anion model

First the simple classical point dipole model is briefly described. It is considered first for historical reasons. The expression for the centroid shift is reproduced here for reasons of completeness. The basic physical mechanism is taken from Ref. 11: an electron belonging to the lanthanide ion at distance R from a ligand ion causes an electric field of mag-

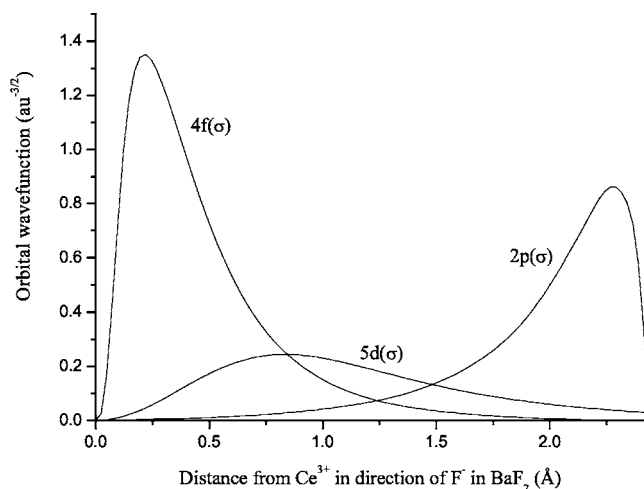


FIG. 1. $4f$ and $5d$ wave functions of the ECP basis set Cebasf1 of Ce^{3+} overlapping (σ) the $2p$ wave function of the basis set Fbas of F^- in BaF_2 . The distance $\text{Ce}-\text{F}$ was taken to be 2.43 Å, estimated from a relaxation study.

nitude e/R^2 at the ligand center. For large R the polarization energy is given by

$$E = -0.5\alpha e^2/R^4 \quad (1)$$

with α the dipole polarizability of the ligand ion and e the electronic charge. The radius vector R is expressed in terms of the distance r from the lanthanide center and the resulting expression is expanded as a function of r/R_0 , with R_0 the distance between the atomic centers. For the centroid shift only spherical terms are retained and the series is truncated after r^2/R_0^2 . The result is

$$E = -0.5\alpha e^2(1/R_0^4 + 2r^2/R_0^6). \quad (2)$$

For calculating the centroid shift Δ this expression has to be averaged over the $4f$ and $5d$ orbitals and the following form is readily obtained:

$$\Delta = -\alpha e^2(\langle r^2 \rangle_{5d} - \langle r^2 \rangle_{4f})/R_0^6. \quad (3)$$

2. Overlap modification of ligand polarization

In Fig. 1 a picture is drawn of typical $4f$ and $5d$ orbital wave functions of Ce^{3+} overlapping (σ type) the valence $2p$ wave functions of a fluorine ion. The distance between Ce^{3+} and F^- is 2.43 Å, the assumed value for Ce^{3+} in BaF_2 as explained further on. The $5d$ orbital is nodeless because $4f$ and $5d$ are part of a large-core effective-core-potential-(ECP-) type valence basis set¹⁹ of Ce^{3+} . The $2p$ wave function of the F^- ion is from the tables of Huzinaga.²⁰

It is obvious that the $5d$ orbital overlaps considerably the fluorine $2p$ orbital and the point dipole model is not applicable. Account is taken of overlap in the following simple way. Equation (1) is retained with the modification that α is considered to be a function of R , the distance of the point charge to the anion center. Further, the $4f$ and $5d$ orbitals are orthogonalized to the ligand p orbitals by the following simple substitutions:

$$|4f_m\rangle \rightarrow N_{fm} \left(|4f_m\rangle - \sum_i S_i^{fm} |p_i\rangle \right), \quad (4a)$$

$$|5d_n\rangle \rightarrow N_{dn} \left(|5d_n\rangle - \sum_i S_i^{dn} |p_i\rangle \right). \quad (4b)$$

S_i^{fm} and S_i^{dn} are the overlap integrals of the $4f_m$ and $5d_n$ orbitals with the anion valence shells, the N_{fm} and N_{dn} are normalization factors, and the index i runs over all the neighboring anion p orbitals.

The resulting expression for the modified centroid shift for orbital $5d_n$ becomes

$$\begin{aligned} \Delta'_n = & -0.5e^2 \left(\langle 5d_n | \alpha_R / R^4 | 5d_n \rangle - \langle 4f_m | \alpha_R / R^4 | 4f_m \rangle \right. \\ & \left. - 2 \sum_i (S_i^{dn} \langle p_i | \alpha_R / R^4 | 5d_n \rangle - S_i^{fm} \langle p_i | \alpha_R / R^4 | 4f_m \rangle) \right). \end{aligned} \quad (5)$$

This expression has to be averaged over the $5d_n$ orbitals and orbital $4f_m$ is the one of lowest energy. Because the normalization factors N in Eqs. (4a) and (4b) are close to unity they are not shown. Equation (5) is the expression for the centroid shift that takes account of overlap.

It would be more accurate to use molecular orbitals from a HF calculation instead of the expressions of Eqs. (4a) and (4b). However, the idea was to derive a simple expression like Eq. (5), in which the main effect of overlap is accounted for. It will be obvious that the main trend of this study is to obtain the centroid shift from a CI calculation and not much effort is spend on the classical model.

B. Quantum chemical approach

The most satisfying approach for calculating the centroid shift is using configuration interaction in many-electron theory. In this work various levels of this theory were applied. At the HF-MP2 level a relation could be established between a certain term in the perturbation expansion and the polarization effect. Calculations were conducted at this and higher levels such as CCSD in order to see if the polarization effect is part of the CI results.

The centroid shift is obtained from the difference in total energy of a molecular fragment containing Ce^{3+} in the state $4f_m$ and the average $5d$ state, compared with the isolated Ce^{3+} ion, calculated at the same level of theory, using the same basis sets and embedding procedure.

1. HF-MP2 model

It can be shown that an expression similar to Eq. (1) can be obtained as part of the HF solution of a Ce^{3+} -anion system corrected to second order for correlation effects (MP2). Only correlation between the Ce^{3+} valence $4f$ or $5d$ electron and the valence shell of the anions is considered. For a $4f_m$ state of the Ce^{3+} ion this part of the MP2 energy can be formulated as follows:

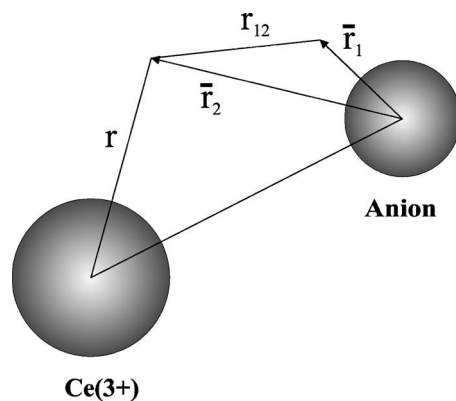


FIG. 2. The coordinate system used for the derivation of the dipole polarization contribution to the centroid shift from configuration interaction at the MP2 level.

$$E_2(4f_m) = \sum_{k,l,i} \frac{|\langle 4f_m(1) p_i(2) | 1/r_{12} | k(1) l(2) \rangle|^2}{\varepsilon_{4f_m} + \varepsilon_{p_i} - \varepsilon_k - \varepsilon_l}. \quad (6)$$

For the $5d$ states a similar expression can be formulated. The p_i label p -type valence shells of the anion excited to states l and $4f_m$ is excited to states k . The ε variables in the denominator label the HF orbital energies. For the subsequent discussion it is important to include also one-electron excitations with ε_k equal to ε_{4f} , which are included in the HF solution. The exchange part of Eq. (6) is neglected.

For obtaining the contribution of dipole polarization of the anion the term $1/r_{12}$ is expanded in the standard way and only the first degree multipole is retained:

$$1/r_{12} \rightarrow \sum_q -1^q C_q^1(\omega_1) C_{-q}^1(\omega_2) r_1 / r_2^2, \quad r_2 \geq r_1. \quad (7)$$

As shown in Fig. 2 the expansion is done with respect to the anion center and the vectors r_1 and r_2 have coordinates r_1, ω_1 and r_2, ω_2 , respectively.

Following the derivation of crystal-field components by Faulkner and Richardson²¹ two assumptions can be made to reformulate Eq. (6). First the energy differences $\varepsilon_{4f} - \varepsilon_k$ are neglected compared to $\varepsilon_p - \varepsilon_l$ and second closure is applied to the part $|k\rangle\langle k|$ contained in Eq. (6). This is only a realistic assumption if k equal to $4f_m$ is included. The resulting expression for the dipole part $E_2^{(1)}(4f_m)$ is

$$\begin{aligned} E_2^{(1)}(4f_m) = & -1/2 \alpha \langle 4f_m(r) | 1/r_2^4 \\ & \times \sum_q -1^q C_q^1(\omega_2) C_{-q}^1(\omega_2) | 4f_m(r) \rangle, \end{aligned} \quad (8)$$

with α the dipole polarizability of the anion defined by

$$\alpha = -2 \sum_{i,l} \frac{|\langle p_i | r_1 C_q^1(\omega_1) | l \rangle|^2}{\varepsilon_{p_i} - \varepsilon_l}. \quad (9)$$

The summation over q in Eq. (8) gives unity and Eq. (1), averaged over $4f_m$, is obtained. This derivation is put forward in its most simple form. Actually the expression of Eq. (9) for the polarizability is too simple and the assumptions mentioned above are not satisfied in the usual practice of

HF-MP2 calculations where the actual excitation energies of the Ce^{3+} ion are not all small compared to those of the anions. Also the basis sets are not chosen in such a way that they satisfy the required closure property.

The derivation indicates that a HF-MP2 calculation would approximately include the polarization effect and additionally take into account contributions from overlap, covalency, and dynamic correlation. It is expected that higher-order CI terms such as MP4 and CCSD will add sizable contributions.

A special note is in order concerning dynamic correlation. It is important to note that Eq. (6) is also the expression for dynamic correlation up to second order. So in this expression two physically distinct effects are present. The dynamic correlation can only be described by two-electron excitations from the HF state in contrast to the polarization effect, which also can be described (using closure) by single excitations. It is clear, however, that the HF-MP2 practice as expressed by Eq. (6) cannot distinguish between these two effects and there is no guarantee that the basis set is adequate for calculating the two contributions together. By varying the basis sets of the Ce^{3+} ion and the anions, information about this may be found.

The calculations were done for a cluster of ions around the Ce^{3+} ion embedded in an array of point charges adjusted to give the correct Madelung potential at the cluster sites. The ions of the cluster have to be chosen carefully. Using only the nearest anions can give exaggerated correlation and polarization in the anions. At least the second-neighbor cations are required; for oxygen compounds also this type of cluster is inadequate and all cation neighbors of the oxygen anions must be part of the cluster.

This is in accordance with the findings of Dorenbos⁸ in his studies of oxide compounds, where good evidence was found that binding with second-neighbor cations substantially decreases the centroid shift.

2. CCSD model

Coupled cluster theory using single and double excitations is the standard improvement of the preceding model. These excitations from the HF ground state are taken to all orders and limitations in the MP2 expansion are corrected. Particularly the rather poor description of excitation energies by HF orbital energies is improved and the conditions mentioned above in linking part of MP2 with the polarization contribution should be better satisfied. Where appropriate the triples correction to CCSD, improving the fourth-order contribution in the CI expansion, has also been investigated.

It is important to point out that these calculations are extremely demanding with respect to computer resources, with sometimes over 500 basis functions needed for some of the cluster calculations. Therefore CCSD calculations could only be done for the smaller basis sets. More details will be given below.

III. DETAILS OF THE CALCULATIONS

For studying the centroid shift in different compounds, specimens were chosen from three major classes of ionic compounds, fluorides, oxides, and chlorides, because the po-

larization of the anions is expected to be rather different in these compounds. As the fluoride, the compound BaF_2 doped with cerium was chosen, a well-known scintillation crystal. Second, the crystal $\text{LaAlO}_3:\text{Ce}^{3+}$ was sorted out as an interesting oxide compound because the centroid shift is very large and the $5d$ levels are enough separated from the virtual level structure of the HF calculation to obtain useful $5d$ level occupations. This point is crucial because in many oxide compounds it was found that $5d$ levels are partly in the virtual region and it is very hard to occupy these states because of orbital mixing. All $5d$ levels have to be occupied for the calculation of the centroid shift because one has to average over all $5d$ levels.

$\text{LaCl}_3:\text{Ce}^{3+}$ was chosen as a representative of chloride compounds. The large polarizability of the Cl^- ion and also the degree of covalency, which is expected to be the largest of the three cases, make it interesting. Also for this crystal the crystal-field splitting is so small that the $5d$ levels are well below the virtual level structure.

For our calculations, particularly the CCSD calculations, a robust molecular computer code was required and the Gaussian²² G98 code served our purpose.

A. Basis sets

The calculations were done with various basis sets in order to study their influence on the centroid shift. For the cations Ce^{3+} , Ba^{2+} , La^{3+} , and Al^{3+} the calculations were done with effective core potentials. For the anions fluorine and oxygen all electron basis sets were used and for chlorine also an ECP type basis was chosen. From the literature a large number of basis sets is available for describing the anions. The choice was made as a compromise between computer resources and the capability to describe polarization effects.

1. The cations Ce^{3+} , Ba^{2+} , La^{3+} , and Al^{3+}

In the study of Merenga¹² on $4f$ - $5d$ energy differences of Ce^{3+} ions in solids, the Dirac-Hartree-Fock formalism was used for the description of the ion. Spin-orbit effects and other relativistic effects are included in a consistent way. For a free Ce^{3+} ion the $4f_{5/2}$ - $5d_{3/2}$ energy difference expressed in eV was found to be 5.488 and the spin-orbit splitting for $4f$ and $5d$ was 0.256 and 0.269, respectively, in the same units. The experimental values²³ are 6.167, 0.279, and 0.308 for these quantities.

From these data it is found that the *ab initio* Dirac-HF value of the spin-averaged $4f$ - $5d$ energy difference is too small by 0.690 eV and configuration interaction should bridge this gap.

The Dirac-HF formalism with the four-component basis sets is not useful for complex solids and it is usual practice to work with spinless single-component wave functions and a number of core electrons is replaced by an effective core potential. The valence basis sets published in the literature mostly are formed in such a way that properties of the HF ground state are in close agreement with those of numerical all-electron HF calculation. There is no guarantee, however, that also the CI results will be similar. Considering the problems with the CI expansion found by Cao and Dolg³ one can

TABLE I. Spin-averaged $5d-4f$ energy differences for free Ce^{3+} calculated with the HF and HF-MP2 models using various ECP basis sets. The experimental value is 6.192 eV (Ref. 23). The DHF values are results of numerical all-electron Dirac-HF calculations.

Basis set	HF (eV)	HF-MP2 (eV)
Cebasf1	6.357	6.592
Cebasf1x	6.336	6.398
Cebasf2	5.513	4.287
Cebasfg	5.579	5.621
DHF	5.503	

safely assume that it is prohibitively complex to calculate *ab initio* absolute $4f-5d$ energy differences for Ce^{3+} in solids.

The centroid shift, however, is very likely not influenced by the slow convergence in the CI expansion of the isolated Ce^{3+} ion. It is assumed that this slow convergence is related to the interior electronic structure of the ion and that the exterior part of the ion, which interacts with the anions, is not affected. By choosing basis sets with different numbers of core electrons this assumption may be verified.

For this study two published basis sets were chosen. The first one is the large-core ECP valence basis set of Cundari and Stevens¹⁹ already referenced above. The core contains all *s*, *p*, and *d* shells up to $n=4$ and has 46 electrons. The valence set describing $5s$, $5p$, and $4f/5d$ is a $[5s5p3d7f]$ set contracted to $[3s3p2d1f]$. In the following it is denoted by Cebasf1. In the calculations also a modification of this basis was used where the *f* function was split in to two components and diffuse components of *f* and *p* type were added (exponent 0.15). This basis set is called Cebasf1x.

The second one is a small-core ECP valence basis used in the work of Cao and Dolg referenced earlier. The core contains all shells up to $3d$ and has 28 electrons. The valence set is an uncontracted $[12s13p10d8f6g]$ basis. For the work of this paper the diffuse *s* components can be left out and from the remaining set two modifications were constructed. The first basis consisted of all uncontracted basis components up to *f* functions and is called Cebasf2. The second one, also contained the *g* functions, is called Cebasfg. The use of uncontracted sets is necessary because the basis set was optimized for the neutral cerium atom.

For comparing results obtained with these basis sets spin-averaged $5d-4f$ energy differences for free Ce^{3+} calculated in the HF and MP2 models are listed in Table I. The experimental value is 6.192 eV. Note that the HF values of the first two basis sets occasionally are close to experiment and that the HF values of the last two basis sets are close to the value 5.503 eV of the all-electron Dirac-HF calculations mentioned above, and it is concluded that these sets are almost *ab initio* at the HF level. They require, however, much greater computer resources than the first two basis sets. It will be interesting to see what the differences are in the centroid shift using these very different basis sets for Ce^{3+} .

From Table I it clear that the addition of *g* functions for small-core basis sets drastically changes the MP2 contribution showing the slow convergence in the CI expansion. It was found that the addition of *g* functions has only a small

effect for the large-core basis sets and this confirms the assumption that the large difference in the CI expansion for the large- and small-core basis sets is only related to the inner region of the ion because it is in this region that the ECP potentials are very different.

For barium,²⁴ lanthanum,²⁵ and aluminum²⁶ large-core ECP basis sets were used from the basis sets library of the G98 program package.

2. The anions fluorine, oxygen, and chlorine

In the calculations, two basis sets per anion were used: a compact set including only one *d*-type polarization function for studying the higher-order CI expansions such as CCSD and an extended set optimized for studies of the dipole polarizability for studies at the HF-MP2 level.

For fluorine and oxygen the compact sets were taken from Huzinaga²⁰ and are $[7s6p]$ sets contracted to $[3s3p]$ extended with a *d*-type polarization function with exponent 0.24. These sets are referenced by Fbas and Obas, respectively.

For chlorine the compact set was chosen to be a $[4s4p]$ ECP basis from the G98 basis set library extended with one polarization function with exponent 0.3, denoted by Clbas.

The extended sets Fbasx and Obasx for fluorine and oxygen were those used in polarization studies by Fowler and Madden.^{27,28} For fluorine the $[15s10p5d1f]$ set contracted to $[12s8p5d1f]$ was modified by omitting the *f* function and all components with exponents smaller than 0.10. For oxygen the set was a modification of the $[14s9p5d]$ uncontracted set, with all diffuse components omitted.

For chlorine the extended basis Clbasx consisted of the compact ECP $[4s4p]$ basis extended with the three *d*-type polarization functions used in Ref. 27 with the exponents 0.852 284, 0.239 705, and 0.079 901 6.

3. Basis sets centered at interstitial sites

As was mentioned earlier the calculation of the polarization contribution to the centroid shift may require extra functions because of the fact that dynamic correlation uses the same excitations in the CI expansion. Therefore the regular basis was extended with so-called bond functions centered at the sites halfway between the Ce^{3+} ion and the neighboring anions. These functions may be better suited for describing the polarization effect. The basis consisted of one *s*-type, one *p*-type, and one *d*-type function of which the exponential coefficients were obtained by optimizing at the HF-MP2 level. For BaF_2 and $LaAlO_3$ the exponents were 0.3, 0.4, and 0.4 for *s*, *p*, and *d*, respectively. For $LaCl_3$ the three exponents were all 0.3.

They are referenced by Fbas_bond, Obas_bond, and Clbas_bond, because the compact basis sets were used for the centered anion basis sets.

B. Calculation of the polarization contribution

The actual evaluation of Eq. (5) requires knowledge of the polarizability of the anions also in the region inside the anionic charge cloud. This was estimated by running standard

HF calculations of the anion, surrounded by its cation neighbors, in the field of a unit point charge placed at a range of distances up to the center of the anion. In this way an approximate value of α_R was obtained by using the resulting dipole moment D of the anion charge distribution in the expression $D = \alpha_R F(R)$ with $F(R)$ the electric field at the center of the anion caused by the polarizing charge at distance R . The polarization was evaluated on a molecular fragment containing the specific anion and all of its cation neighbors. More details will be given below.

The basis sets used in these HF calculations were the Fbasx, Obasx, and Clbasx sets mentioned in the preceding section. It is important to point out that the in-crystal polarization considered in the work of Fowler and Madden is different from the polarization required by Eq. (5). The in-crystal polarization is a response to a homogeneous electric field in the crystal whereas for α_R short-range effects of a point charge next to the anion are of interest.

The estimate of α_R clearly is not accurate but is useful because the largest error occurs near the anion nucleus and this region has been found to be not important for the centroid shift.

For BaF_2 the fragment consisted of a fluorine ion surrounded by four Ba^{2+} ions in the BaF_2 lattice. The basis set of these Ba^{2+} ions was chosen in such a way that the contribution to the dipole moment was negligible. The polarizing charge was put at distances ranging from $R=0$ to 2.5 Å in a direction between two Ba^{2+} ions. In this region α_R approaches the in-crystal polarizability. This was verified by a coupled Hartree-Fock (CPHF) calculation applied to the fragment. The choice of a direction between two Ba^{2+} ions is a practical choice because one must avoid the charge being near the nucleus of one of these ions.

The O^{2-} ion in LaAlO_3 has to be surrounded by the two nearest Al^{3+} ions and the four nearest La^{3+} ions. It is assumed that in this way realistic values for α_R can be obtained. It is important to realize that α_R is not isotropic because of the site symmetry (D_{4h}) and therefore the polarizing charge was put on a line perpendicular to the O—Al direction between two La^{3+} ions because Ce^{3+} replaces a La^{3+} ion. Also for this fragment CPHF calculations served to verify the limiting value of α_R . More details will be given below.

The estimate of α_R for Cl^- in LaCl_3 was done using a Cl^- ion surrounded by its three nearest-neighbor La^{3+} ions. The polarizing charge was put on a line pointing between two of the La^{3+} cations. The anisotropy in α_R is small enough to be neglected.

C. HF-MP2 and CCSD cluster calculations

The most extensive calculations were done for Ce^{3+} in BaF_2 because of the relatively small number of anions in a cluster with high symmetry (O_h). A complication is that in the BaF_2 crystal the Ce^{3+} ion replaces a Ba^{2+} ion that has a somewhat larger radius. So the neighboring eight fluorine ions will relax inward. Also there will be a nearby charge-compensating fluorine ion in the [111] direction. The influence of the latter defect was neglected because of the long distance to the Ce^{3+} ion.

The relaxation was estimated by a relaxation study using the VASP DFT code¹⁷ by which it was found that the fluorine- Ce^{3+} distance changed from the value in the bulk (2.663 Å) to 2.438 Å. This distance was used in the ionic cluster calculation. This introduces some uncertainty in the results but fortunately the centroid shift has only a weak dependence on distance.

Configuration interaction up to the CCSD(T) level was done for a CeF_8 fragment embedded in point charges and could only be done using the basis set Cebasf1 for Ce^{3+} and Fbas for the fluorine ion. Similar calculations using bond functions were done on a Ce^{3+}F_8 cluster where bq stands for the center of the bond function.

The extended sets of Ce^{3+} Cebasf1x, Cebasf2, and Cebasfg in combination with the extended basis Fbasx were used in HF-MP2 calculations for investigating the presence of a polarization contribution to the resulting centroid shift. The cluster was also chosen to be a CeF_8 fragment because it was found that the results of calculations on a $\text{CeF}_8\text{Ba}_{12}$ fragment were hardly different, a result of the strong ionic character of the fluorine ions.

Here and for the other compounds the calculations were done for the 4*f* and 5*d* states of interest. The centroid shift was calculated from the difference in the 5*d*-averaged 5*d*-4*f* energy difference of the cluster calculation and that of a counterpoise calculation where all fluorine nuclei were removed. In this way the basis set superposition error (BSSE) is minimized.

The crystal structure of LaAlO_3 is a distorted perovskite, spacegroup $R-3c$.²⁹ In this work the structure was simplified to the pure perovskite structure with lattice constant 3.829 Å. The Ce^{3+} ion at a La^{3+} site has 12 O^{2-} ions as nearest neighbors at a distance of 2.707 Å.

The high-level CI cluster calculations were done for a $\text{CeO}_{12}\text{Al}_8$ fragment and a $\text{CeO}_{12}\text{bq}_{12}\text{Al}_8$ ionic cluster for the calculations with bond functions using the basis Cebasf1 for Ce^{3+} and Obas_bond for O^{2-} . The cluster was too large to conduct CCSD(T) calculations for the bond functions. Therefore for these calculations the higher-level CI was approximated by MP4(SDQT) with single, double, triple, and quadruple substitutions. The extended oxygen basis sets Obasx in combination with Cebasf1x and Cebasfg were used in HF-MP2 calculations using a $\text{CeO}_{12}\text{Al}_8\text{La}_{18}$ fragment.

The calculations on Ce^{3+} in LaCl_3 are similar in complexity to BaF_2 . The crystal structure is $P63/M$ (Ref. 30) and the Ce^{3+} ion has nine chlorine neighbors, six at 2.951 Å and three at 2.953 Å.

The high-level CI cluster calculations were done for a CeCl_9 fragment embedded in point charges with the basis Cebasf1 for Ce^{3+} and the compact Clbas for Cl^- . The bond function calculation could be done up to the HF-MP4(SDQT) level. The extended sets Cebasf1x and Cebasfg combined with Clbasx were used in HF-MP2 calculations applied on a CeCl_9La_8 fragment for investigating possible polarization effects because such a set should show a large polarization contribution.

IV. RESULTS AND DISCUSSION

The results are presented and discussed in the same order as the different contributions were discussed in the preceding

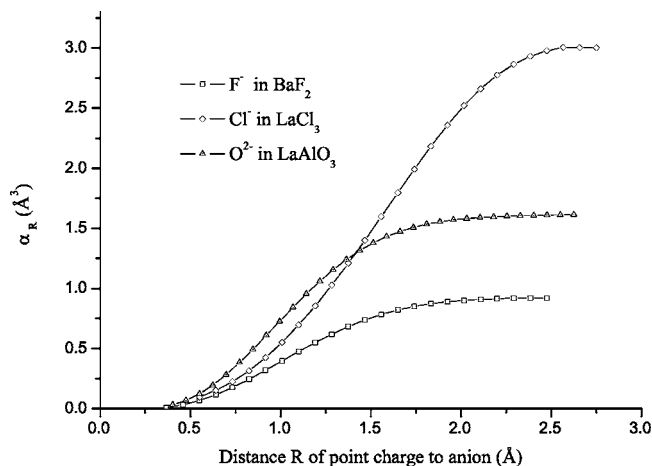


FIG. 3. Curves of the short-range polarizability α_R as a function of the distance R to the polarizing charge for F^- in BaF_2 , O^{2-} in $LaAlO_3$, and Cl^- in $LaCl_3$. At around 2.5 Å the values were scaled to match the in-crystal polarizability.

section. First the focus is on the polarization contribution, which is assumed to be not part of the dynamic correlation energy found from the CI cluster calculations and is presented together with the HF contribution and additional data of the crystal-field splitting. Subsequently the CI results are described.

A. Polarization and HF contributions

For the calculation of the polarization contribution the most difficult part is the calculation of the short-range polar-

izability α_R . The method was described above and in Fig. 3, for each compound, the curves are drawn of α_R as a function of the distance R . The values had to be scaled in order to match the in-crystal polarizability from the literature. This is because in this work the polarizability α_R was determined by the HF model and results for $\alpha(\infty)$ are somewhat smaller than those determined by the CPHF-MP2 calculations used by Fowler and Madden. For F^- and Cl^- the scaling was to $\alpha(\infty)=0.93$ and 2.9 \AA^3 , respectively.²⁷

For O^{2-} in $LaAlO_3$ the short-distance polarization α_R is more complicated because it is anisotropic. Using CPHF-MP2 applied to an OAl_2La_4 fragment two values were found for the in-crystal polarization. For the Al—O direction [nearest-neighbor (NN) distance 1.88 Å] the calculations gave a value of 2.20 \AA^3 and for the other two directions (NN distance 2.66 Å) 1.61 \AA^3 . Fowler²⁵ reports a value of 1.82 \AA^3 for O^{2-} in MgO (NN distance 2.1 Å), also calculated with the CPHF-MP2 approach, compared with the experimental value of 1.68 \AA^3 . Considering the position of the cerium ion the value 1.61 was taken as the best estimate for $\alpha(\infty)$. The curves show the drastic reduction of the polarizability inside the anions. It is obvious that the results are increasingly inaccurate with smaller distances to the anion nuclei but this is not serious because these regions hardly contribute to the centroid shift.

With Eqs. (3) and (5) the values of the polarization contribution to the centroid shift were calculated. The in-crystal polarizability α occurring in Eq. (3) is identified with the limiting value of α_R for larger distances. The resulting values are shown in the ΔE_{pol} columns of Table II. They are also shown graphically in the histogram of Fig. 5 below. For BaF_2 the value of the centroid shift calculated with the classical

TABLE II. The contributions of polarization $\Delta E_{pol}(5d-4f)$ to the centroid shift of $4f-5d$ transitions of Ce^{3+} calculated classically and with overlap correction. $E_{HF}(5d-4f)_{av}$ are the average $5d-4f$ energy differences calculated for the ionic cluster of the compound and for isolated Ce^{3+} (same cluster but anion orbitals unoccupied) called bsse. Values are in eV.

Compound	Basis sets		$\Delta E_{pol}(5d-4f)$		$E_{HF}(5d-4f)_{av}$		$\Delta E(5d-4f)$ Expt.
	Ce^{3+}	Anions	Classical	Overlap	Cluster	Ce^{3+} bsse	
BaF_2	Cebasf1	Fbas			6.311	6.303	0.80 ^a
	Cebasf1x	Fbasx	0.81	0.34	6.275	6.264	
	Cebasf1	Fbas_bond			6.202	6.263	
	Cebasf2	Fbasx			5.366	5.419	
	Cebasfg	Fbas			5.535	5.484	
$LaAlO_3$	Cebasf1	Obas			6.042	6.342	1.85 ^b
	Cebasf1	Obasx	1.21	0.69	5.932	6.351	
	Cebasf1	Obas_bond			6.020	6.268	
	Cebasfg	Obasx			5.330	5.558	
$LaCl_3$	Cebasf1	Clbas			5.841	6.363	1.60 ^c
	Cebasf1x	Clbasx	0.84	0.26	5.764	6.336	
	Cebasf1	Clbas_bond			5.798	6.328	
	Cebasfg	Clbasx			5.045	5.582	

^aReference 6.

^bReference 8.

^cReference 9.

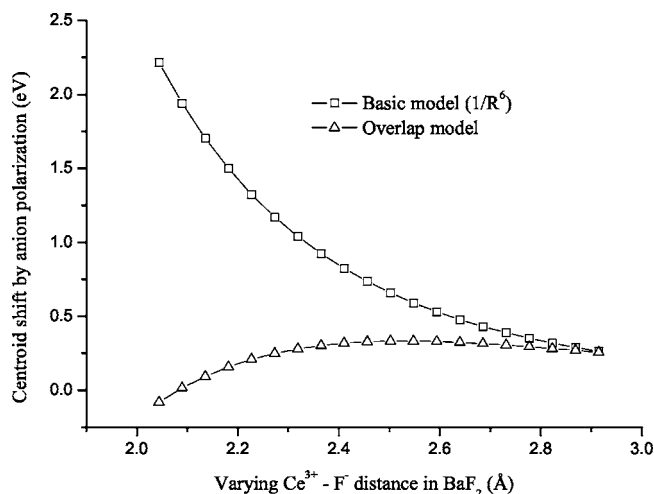


FIG. 4. Curves showing the distance dependence of the centroid shift calculated with the classical model that predicts an R^{-6} dependence and calculated with the overlap modification. The case $\text{BaF}_2:\text{Ce}$ was taken as an example.

model accidentally agrees with experiment (last column). Note that the inclusion of overlap reduces the polarization contribution so much that the resulting values are small in comparison with experiment.

In order to see how the dependence of the centroid shift on the distance to the anions was modified by overlap, a set of calculations was conducted, for the case BaF_2 , with varying $\text{Ce}^{3+}-\text{F}^-$ distance. The results are shown in Fig. 4 along with the dependence following from the basic model. It is clear that the strong decrease with distance of the overlap contribution compensates the decrease of the basic model, resulting in a weak distance dependence of the polarization contribution to the centroid shift, in strong contrast with the predictions of the Morrison model.

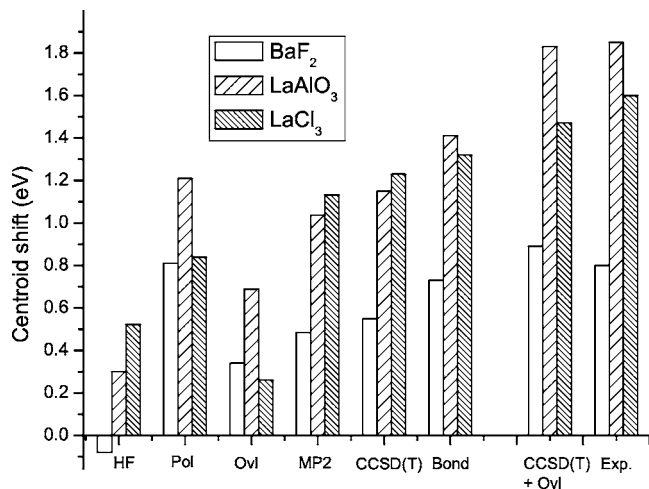


FIG. 5. Graphical presentation of the various contributions to the centroid shift of Ce^{3+} in BaF_2 , LaAlO_3 , and LaCl_3 compared to experiment (Exp). The classical polarization contribution is denoted by Pol and the overlap modification by Ovl. Note the drastic reduction of the polarization contribution when overlap is included. The label "bond" is used for the CCSD(T) results using bond functions.

In Table II are also listed the values of the shift in the average $5d-4f$ energy difference calculated with the HF method applied to a cluster of ions. The interesting point of these calculations is to see if sizable shifts are found at this level of theory. Earlier studies³¹ on Ga^+ , In^+ , and Tl^+ in KCl have shown that large centroid shifts in the $ns-np$ transition are already found at the HF level. In particular covalency should give a sizable shift and one may expect influence of the size of the basis set. Additionally a contribution due to polarization coming from the first term at the right side of Eq. (2) is expected. Due to overlap the shift in the energy of the $5d$ orbital by static polarization may not be equal to that of the $4f$ orbital.

There is a good reason for listing the polarization contribution together with the HF results. This is because the second term in the expression in Eq. (2) can be seen as a one-particle excitation (remember the closure property discussed above) from the reference HF wave function and so does not contain correlated motions.

The centroid shift is obtained by taking the difference between the results of the cluster calculations and those of the isolated Ce^{3+} ion (anion orbitals unoccupied) using the counterpoise method for minimizing basis set superposition errors. Therefore the average $5d-4f$ energy difference is also calculated for a cluster of ions where the anion nuclei are absent. In the tables this type of calculation will be labeled by bsse. The resulting values of the centroid shift are tabulated in Table V below.

The HF results tabulated in Tables II and V clearly show an increase in the covalency contribution along the series BaF_2 , LaAlO_3 , and LaCl_3 as expected. It is absent in BaF_2 and more than 0.5 eV in LaCl_3 . These results are visualized in Fig. 5. Notice the fact that apparently the BSSE is rather small because the bsse results for the $5d-4f$ energy differences do not change much in the calculations. As one may expect the extended basis sets show a somewhat larger BSSE effect because the $4f-5d$ energy differences come out somewhat smaller than for the compact sets, particularly for BaF_2 and LaCl_3 .

For LaCl_3 where the NN distance is the largest, the bsse value of $E_{\text{HF}}(5d-4f)_{\text{av}}$ for the Ce^{3+} basis set Cebasf1 is equal to that calculated for a free Ce^{3+} ion (6.36 eV) using the same basis set.¹⁶ As noted above, this value is not far from the experimental (spin-averaged) value of 6.192 eV, but far from the *ab initio* Dirac-HF value of 5.503 eV. It must be a result of the procedure used in generating the basis set, which for the $5d$ state used a Ce^{2+} ion.¹⁹

The basis sets Cebasf2 and Cebasfg represent almost *ab initio* basis sets and the results show how much *ab initio* HF values of the $5d-4f$ energy differences deviate from experiment. Presumably CI taken to high order and using additional wave functions of high angular momentum would bridge the gap with experiment, as for the free ion. The bsse values are close to the Dirac-HF values for the free ion.

The calculations with bond functions show a slight improvement in the HF contribution to the centroid shift for Ce^{3+} in BaF_2 . Finally the extended basis sets for the anions with much better polarization functions do not show larger centroid shifts at this level of theory.

It is concluded that at the HF level there is no way of explaining the experimental values of the centroid shift of

TABLE III. *5d* level splitting (eV) of Ce^{3+} in different compounds calculated with various basis sets. For the cubic sites in BaF_2 and $LaAlO_3$ the value is the difference in energy between the e_{2g} and t_{2g} levels. For $LaCl_3$ the value is that between the highest and lowest *5d* levels.

Compound	Basis sets		$\Delta(5d)$	
	Cerium	Anion	HF	Expt. ^a
BaF_2	Cebasf1	Fbas	2.312	2.38
	Cebasf1	Fbasx	2.341	
	Cebasf1	Fbas_bond	2.450	
	Cebasfg	Fbas	2.272	
$LaAlO_3$	Cebasf1	Obasx	1.037 ^b	1.10
	Cebasf1	Obas	0.753	
	Cebasfg	Obasx	0.694	
$LaCl_3$	Cebasf1x	Clbasx	0.552	0.68
	Cebasf1	Clbas_bond	0.599	
	Cebasfg	Clbasx	0.543	

^aThe references are those of Table II.

^bThis value was calculated with the large cluster of ions containing NN and NNN lanthanum ions; the other two values were calculated using a cluster containing only the eight NN aluminum ions

the *4f-5d* transitions. When the overlap-corrected polarization contribution is added to the HF result, roughly 50% of the experimentally observed centroid shift is covered (see also Fig. 5).

B. Crystal-field splitting

It is interesting to investigate the splitting of the *5d* level calculated with the HF model. It gives important additional

TABLE IV. Contributions to the centroid shift of *4f-5d* transitions from configuration interaction calculated for various compounds and using different basis sets. The $E(5d-4f)_{av}$ is the energy difference between the average *5d* level and the lowest *4f* level. It is evaluated for the Ce^{3+} ionic cluster and for the isolated Ce^{3+} ion (the anion orbitals unoccupied) labeled by bsse. The difference between the two results gives the centroid shift. Values are in eV.

Compound	Basis sets		$E(5d-4f)_{av}$							
			Cluster				Ce^{3+} (bsse)			
	Ce^{3+}	Anions	MP2	MP4	CCSD	CCSD(T)	MP2	MP4	CCSD	CCSD(T)
BaF_2	Cebasf1	Fbas	6.156	5.951	5.978	5.868	6.505	6.372	6.350	6.344
	Cebasf1x	Fbasx	5.849	5.712			6.333	6.213		
	Cebasf1	Fbas_bond	5.746	5.556	5.602	5.414	6.298	6.168	6.163	6.144
	Cebasf2	Fbasx	3.819				4.212			
	Cebasfg	Fbas	5.159				5.581			
$LaAlO_3$	Cebasf1	Obas	5.724	5.568	5.637	5.448	6.498	6.347	6.358	6.328
	Cebasf1	Obasx	5.484				6.520			
	Cebasf1	Obas_bond	5.113	5.045		4.731 ^a	6.168	6.149		6.141
	Cebasfg	Obasx	4.751				5.604			
$LaCl_3$	Cebasf1	Clbas	5.620	5.472	5.484	5.366 ^a	6.588	6.444	6.427	6.411
	Cebasf1x	Clbasx	5.248				6.380			
	Cebasf1	Clbas_bond	5.206	5.018		4.915 ^a	6.336	6.256		6.235
	Cebasfg	Clbasx	4.478				5.637			

^aCCSD(T) estimate using MP4(SDQT).

information about the *4f-5d* transitions apart from the centroid shift. It has been found that the *5d* level splitting calculated by the HF method is not very much modified by CI calculations. Also the polarization of the anions has not much effect. This agrees with the experimental finding that crystal-field splitting and centroid shift are very largely independent of each other. In Table III values are given of the splitting of the *5d* level of Ce^{3+} in the three compounds calculated by the HF model and using various basis sets.

For BaF_2 there is good agreement with experiment and the dependence on the basis set is small. For $LaAlO_3$ the results show the strong dependence of the crystal-field splitting on the cluster size. The calculation with the large cluster containing NN and NNN lanthanum ions gives the best result. For $LaCl_3$ the results show a small dependence on the basis set and the disagreement with experiment is a result of the neglect of spin-orbit interaction.¹⁵

C. Dynamic correlation contributions

Subsequently the results are discussed of CI calculations at the MP2, MP4(SDQ), and CCSD(T) levels using the various basis sets of which the results are listed in Table IV. As mentioned above the centroid shift is obtained by taking the difference between the results of the averaged *5d-4f* energy differences of the cluster calculations and those of the Ce^{3+} ion using the counterpoise method for minimizing BSSE's. The values for the calculated centroid shift from the HF results of Table II and the CI results of Table IV are tabulated in Table V, and shown graphically in Fig. 5.

It is assumed that the best level for obtaining the energy differences is the CCSD(T) level, because the triples correction incorporating fourth- and fifth-order corrections to

TABLE V. The centroid shift of $4f$ - $5d$ transitions of Ce^{3+} in various compounds calculated from the difference between the results of the cluster calculations and those of the bsse calculations tabulated in Tables II and IV.

Compound	Basis sets		Centroid shift (eV)					Expt.
	Ce^{3+}	Anions	HF	MP2	MP4	CCSD	CCSD(T)	
BaF ₂	Cebasf1	Fbas	-0.008	0.349	0.421	0.372	0.476	0.80
	Cebasf1x	Fbasx	-0.011	0.484	0.501		0.556 ^a	
	Cebasf1	Fbas_bond	0.061	0.552	0.612	0.561	0.730	
	Cebasf2	Fbasx	0.053	0.393				
	Cebasfg	Fbas	-0.051	0.422				
LaAlO ₃	Cebasf1	Obas	0.300	0.774	0.779	0.721	0.880	1.85
	Cebasf1	Obasx	0.419	1.036			1.142 ^a	
	Cebasf1	Obas_bond	0.248	1.055	1.104		1.410 ^b	
	Cebasfg	Obasx	0.228	0.853				
LaCl ₃	Cebasf1	Clbas	0.522	0.968	0.972	0.943	1.045	1.60
	Cebasf1x	Clbasx	0.572	1.132			1.209 ^a	
	Cebasf1	Clbas_bond	0.530	1.130	1.238		1.320 ^b	
	Cebasfg	Clbasx	0.537	1.139				

^aExtrapolated from preceding line^bCCSD(T) estimate using MP4(SDQT).

CCSD still gives sizable contributions to the $5d$ - $4f$ energy differences as one can see from the results in Tables IV and V. However, these calculations are extremely demanding with respect to computer resources and execution time, because some of the basis sets for the ionic clusters mentioned above are rather large (more than 500 basis functions). Therefore, these calculations could only be done for small clusters and by using the smaller basis sets.

For BaF₂ the cluster was chosen to be a CeF₈ fragment embedded in point charges. The fragment for LaAlO₃ was a CeO₁₂Al₈ cluster and for LaCl₃ a CeCl₉ cluster was used. The results for these calculations are listed in Tables IV and V on the first line of every compound.

As one can see from the results in Table V, the centroid shift increases from HF-MP2 to CCSD(T) with the final values 0.47 eV for BaF₂, 0.88 eV for LaAlO₃, and 1.05 eV for LaCl₃. These values are all roughly 50% of the experimental values. The addition of the polarization contribution brings the result of BaF₂ close to experiment but for the other two compounds the disagreement with experiment is roughly 0.3 eV (see also Fig. 5).

The change in the shift from HF-MP2 to CCSD is comparable to the contribution of the triples correction, so this may indicate slow convergence in the CI expansion beyond second order. In all CCSD(T) calculations it is remarkable how large the triples correction to the energy actually is. This applies only to the cluster calculations. For the isolated Ce^{3+} ions (bsse) the triples correction is negligible. The separate values of the correlation energy for the $4f$ and $5d$ states of the clusters are not listed because they are dominated by the correlation energy of the anions and so are very large in comparison with the $5d$ - $4f$ energy differences.

The results of the calculations using larger basis sets are shown in Tables IV and V in the remaining lines of the three compounds. HF-MP2 calculations using the extended anion

sets F1basx, Obasx, and Clbasx were done for the complete cluster of ions as described earlier. For BaF₂ we have a CeF₈Ba₁₂ cluster, a CeO₁₂Al₈La₁₈ fragment for LaAlO₃, and a CeCl₉La₈ cluster for LaCl₃. It is assumed that the change in the results in going from HF-MP2 to CCSD(T) for the small clusters is representative of that for the larger clusters. The remarkable fact seen in Table V is that despite the much better description of polarization of the anions due to the extended sets (F1basx, Obasx, and Clbasx), the resulting centroid shift is only larger by a small amount. For BaF₂ the increase is 0.08 eV at the MP4 level, 0.26 eV for LaAlO₃ at the MP2 level, and 0.16 eV for LaCl₃ also for a HF-MP2 calculation. For LaAlO₃ the increase should be the largest because of the fact that an almost free O²⁻ ion, as used in the small-cluster calculation, has a very large polarizability compared to that bonded to all the cation neighbours in the extended basis calculation. At least a factor of 3 is expected, as found from CPHF calculations for the two fragments. From this failure it is concluded that the polarization effect is not included in the CI expansions used in this study.

The values obtained with the extended sets were corrected with estimates of the higher-order contributions. For this estimate the results were used of the small-cluster calculations. The resulting values of the centroid shift including the polarization contribution are found from Table V to be 0.89 eV for BaF₂, 1.83 eV for LaAlO₃, and 1.47 eV for LaCl₃. These values agree with experiment within 0.15 eV. The error bar in the results is mainly coming from the estimate of the polarization contribution and it is expected to be quite large if one considers the rough estimate outlined in Sec. II A. The value 0.15 eV looks like a reasonable value for this error bar.

The remaining data in Tables IV and V show results of calculations with bond functions and the impact of using the almost *ab initio* Ce^{3+} basis sets Cebasf2 and Cebasfg. The calculations with bond functions centered in between the

Ce³⁺ ion and the neighboring anions were done at the CCSD(T) level only for BaF₂ using a Cebq₈F₈ cluster where bq stands for the center of the bond function. For LaAlO₃ using a Cebq₁₂O₁₂ fragment only a MP4 calculation was feasible. This also applies to LaCl₃ where a Cebq₉Cl₉ cluster was used. The triples correction was estimated by calculating the triples correction at the MP4(SDQT) level.

The bond functions are supposed to describe the polarization effect better than the site-centered functions. The compound BaF₂ seems to confirm this, because with the small basis set, the CCSD(T) value is found to be 0.73 eV which is close to experiment (0.8 eV). However, for LaAlO₃ and LaCl₃ the success is less impressive: only 1.41 eV is obtained for the former compound and 1.32 eV for the latter, keeping some 0.3 eV disagreement with experiment. The use of bond functions may be a way to include the polarization effect in the CI expansion but the results are inconclusive so far.

The results obtained with the almost *ab initio* small-core wave functions Cebasf2 and Cebasfg for the Ce³⁺ ion do not show larger centroid shifts: the values obtained are even somewhat smaller than the values obtained with the simple bases Cebasf1 and Cebasf1x discussed above, but they require much greater computer resources and so only HF-MP2 calculations could be done. This shows that for calculating the centroid shift the former large-core ECP basis is the most useful.

An overview of all the important results for the centroid shift discussed in this section is also given in Fig. 5 in which the bars denote the results of the different levels of calculation. Actually the results of the extended basis sets, corrected for higher-order contributions, are shown together with those of the bond function calculations. The final results for the three compounds, represented by the CCSD(T)+Ov1 bars, are to be compared with experiment.

In a recent paper, Seijo and co-workers³² report a study of spectra of Ce³⁺ in elpasolites, which is somewhat related to this investigation. The subject is the change in bond length of the Ce-anion bond after excitation from the lowest 4*f* state to the 5*d* states. The authors use basis set with a large-core ECP, just like our sets Cebasf1 and Cebasf1x, but with accurate 4*f*-5*d* energy differences at the HF level, close to *ab initio* values. They claim accurate 4*f*-5*d* excitation energies in elpasolites, but from our investigation it was found that this is not possible. The basis set is not capable of describing correlation very well: from Table I it can be seen that the correlation energy, at the MP2 level, for the first two sets is much too small to cover the 0.69 eV mentioned in Sec. III A 1 for all-electron *ab initio* basis sets.

In solids, however, the small values of 5*d*-4*f* energy differences for the *ab initio* basis (see also Table I) give already at the HF level reasonable 5*d*-4*f* differences for Ce³⁺ in fluorides. If the results of the isolated Ce³⁺ ion are not taken into account, one can use this to calculate the centroid shift with CI without the need for the extra polarization contribution.

The missing part of the centroid shift (mostly on the order of 0.6 eV) is obtained from the underestimate of the 5*d*-4*f* energy differences at the HF level. This clearly is a very tricky effect but in this way one can avoid the elaborate calculations with a small-core ECP basis set and the need for wave functions of high angular momentum. The approach, however, is then no longer *ab initio*.

More interesting is that the authors discuss the polarization effect, which they label the Judd-Morrison effect. They conclude that the polarization energy sometimes has the wrong distance dependence and they claim that there must be an additional contribution partially canceling the classical effect. This seems to confirm one of the results of this study, that overlap strongly reduces the distance dependence of the classical polarization effect. Unfortunately, the authors give no further analysis of the contributions to the bond length reduction.

V. CONCLUSIONS

The *ab initio* calculation of absolute values of 4*f*-5*d* transition energies of Ce³⁺ in ionic compounds requires an almost prohibitive amount of computer resources because the CI expansion, up to the CCSD(T) level, has to include wave functions of high angular momentum. Apparently, this does not apply to the shift in the average 5*d*-4*f* energy difference with respect to that of the free ion, because the badly converging CI expansion is related to the inner region of the Ce³⁺ ion. A detailed study was done of contributions to this shift arising from polarization of the ligand anions and dynamic correlation.

At the HF level it was found there is no way of explaining the centroid shift of the 4*f*-5*d* transitions. When the polarization contribution is added to the HF results, roughly 50% of the shift is covered.

At higher levels of theory, by varying the amount of polarization of the anions, it was found that the polarization effect seems to be not included in the dynamic correlation contribution calculated with CI up to the CCSD(T) level and has to be calculated separately. It is remarkable that the triples correction to the 4*f* and 5*d* state energies for the ionic clusters is large and contributions up to 0.3 eV in the centroid shift were found. Unexpectedly this does not apply for the isolated Ce³⁺ ion in the BSSE calculations, where the triples correction is negligible.

The use of bond functions seems to indicate that a proper definition may provide a means to include the polarization contribution in the CI expansion.

ACKNOWLEDGMENTS

The Netherlands Foundation for Technical Research STW has supported this work and the computer facilities of SARA (Academic Computing Services Amsterdam) were sponsored by NCF (National Computing Facilities Foundation, The Netherlands).

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