Transferability of core potentials to f and d states of lanthanide and actinide ions

LUIS SEIJO*, ZOILA BARANDIARAN and BELEN ORDEJON

Departamento de Química, C-XIV y Instituto Universitario de Ciencia de Materiales Nicolás Cabrera, Universidad Autónoma de Madrid, 28049 Madrid, Spain

(Received 5 November 2001; accepted 14 January 2002)

An analysis is made of the transferability of frozen core potentials of neutral lanthanide and actinide elements to 4f/5f and 5d/6d states of their respective 3+ and 4+ ions. A good description of the orbital spin-orbit coupling constants \( \zeta_{5f} / \zeta_{6d} \) and \( \zeta_{5d} / \zeta_{6d} \) of the Ln\(^{3+} \) / An\(^{4+} \) ions and of the 4f \( \rightarrow \) 5d/5f \( \rightarrow \) 6d transition energies is achieved by using [Kr]/[Xe, 4f] cores. The corresponding relativistic core \textit{ab initio} model potentials (AIMPs) based on Cowan–Griffin–Wood–Boring calculations, together with optimized Gaussian valence basis sets, are produced for the lanthanide elements Ce to Lu and for the actinide elements Th to Lr. Results are given for the Ce\(^{3+} \) and Pa\(^{4+} \) free ions and in Ce\(^{3+} \)- and Pr\(^{3+} \)-doped \( \text{Cs}_2\text{NaYCl}_6 \) and Pa\(^{4+} \)- and U\(^{4+} \)-doped \( \text{Cs}_2\text{ZrCl}_6 \) materials.

1. Introduction

Relativistic effective core potentials corresponding to the \textit{ab initio} model potential method (AIMP) [1, 2] have been published for the [Kr,4d] core of the lanthanide elements and for the [Xe,4f,5d] core of the actinide elements, based on atomic Cowan–Griffin–Wood–Boring calculations [3, 4] together with optimized Gaussian valence basis sets and Wood–Boring spin–orbit operators [5]. These core sizes are known to be reasonable in quantum chemistry calculations as long as energy differences between states of configurations with different f orbital occupation are not involved, in which case the use of a small M shell core (1s–3d) for the lanthanide elements and N shell core (1s–4f) for the actinide elements is considered to be safe [6–10].

Ionic crystalline solids doped with lanthanide and actinide ions are important materials from the technological and the fundamental points of view [11], most of the interest coming from their luminescent properties associated with local states of the impurity ions. In particular, excited states with occupied 5d/6d ion orbitals are the subject of current and increasing interest [12–15]. Spin–orbit coupling is a very important effect in these materials and states [12–15]. It has been commented [16] that a correct calculation of the 6d orbital spin–orbit coupling constant, \( \zeta_{6d} \), of Pa\(^{4+} \) (6d\(^{1–2}D\)) cannot be made with a frozen [Xe,4f,5d] core taken from neutral Pa (5f\(^6\)6d\(^1\)75\(^1–6\)L), in spite of the fact that this frozen core leads to a good value of the \( \zeta_{5f} \) of Pa\(^{4+} \) (5f\(^{1–2}F\)). Fortunately, however, a frozen [Xe,4f,5d] core taken from Pa\(^{4+} \) (6d\(^{1–2}D\)) is able to lead simultaneously to good values of \( \zeta_{5f} \) and \( \zeta_{6d} \) of Pa\(^{4+} \), as well as of the 5f \( \rightarrow \) 6d transition energies of Pa\(^{4+} \)-doped \( \text{Cs}_2\text{ZrCl}_6 \) [16].

Here we find that this fortunate fact does not hold for the isoelectronic ion of the lanthanide series Ce\(^{3+} \). However, a smaller [Kr] frozen core of neutral Ce is shown to be sufficient for a good description of \( \zeta_{4d} \) and \( \zeta_{5d} \) in the respective 4f\(^{1–2}F\) and 5d\(^{1–2}D\) states of the Ce\(^{3+} \) ion, as well as for a proper calculation of the 4f \( \rightarrow \) 5d transition energies of Ce\(^{3+} \) and Ce\(^{4+} \)-doped \( \text{Cs}_2\text{NaYCl}_6 \). Similarly, a [Xe,4f] frozen core of neutral Pa is shown to be sufficient for a good description of \( \zeta_{5f} \) and \( \zeta_{6d} \) in the respective 5f\(^{1–2}F\) and 6d\(^{1–2}D\) states of the Pa\(^{4+} \) ion, as well as for a proper calculation of the 5f \( \rightarrow \) 6d transition energies of Pa\(^{4+} \)-doped \( \text{Cs}_2\text{ZrCl}_6 \). Similar behaviour is observed in Pr\(^{3+} \)-doped \( \text{Cs}_2\text{NaYCl}_6 \) and U\(^{4+} \)-doped \( \text{Cs}_2\text{ZrCl}_6 \). In consequence, we propose here the use of relativistic [Kr] core AIMPs produced in neutral atoms for the calculation of 4f and 5d states of lanthanide ions in ionic hosts, and the use of relativistic [Xe,4f] core AIMPs produced in neutral atoms for the calculation of 5f and 6d states of actinide ions in ionic hosts (even though [Xe,4f,5d] core AIMPs produced in the actinide ions seem to be sufficient in this case [16]). Here we examine these relativistic core AIMPs for the lanthanide elements Ce to Lu and the actinide elements Th to Lr, together with the corresponding optimized Gaussian valence basis sets.
2. *Ab initio* model potentials and valence basis sets

The *ab initio* model potential method (AIMP) is an effective core potential method based on the Huzinaga–Cantu equation [17], whose details are fully described in [1, 2, 18]. The details for lanthanide and actinide elements are described in [5]. Very briefly, it is a practical means for implementing the frozen core approximation without relying on any pseudo-orbital transformation. Given a Hamiltonian of an atom, a parametrization of its core operators in order to reproduce valence atomic properties is never done in the AIMP method. Instead, these operators are substituted by simpler ones (the AIMPs) which are high quality approximations of them produced by a simple recipe. (1) If the operator to be approximated is a long range local operator then it is substituted by a local operator as simple as possible; this is the case for the atomic core Coulomb operators. (2) If the operator to be approximated is a short range local or non-local operator, then it is substituted by a spectral representation of it; this is the case for the atomic core exchange operators and the mass–velocity and Darwin operators of Cowan and Griffin [3]. After this substitution, the AIMP valence-only Hamiltonian of an atom is fully defined and its (Gaussian) valence basis set is optimized according to standard variational procedures used in the all-electron methods of quantum chemistry. The AIMP method leads to approximate valence orbitals with the correct nodal structure. If the chosen Hamiltonian is non-relativistic, the application of the AIMP recipe leads to the non-relativistic AIMP method, NR-AIMP [1]. Different choices of relativistic Hamiltonian have led to the relativistic scheme by eliminating small components AIMP, RESC-AIMP [19], to the second-order Douglas–Kroll–Hess [20, 21] no-pair AIMP (NP-AIMP) [22, 23] and to the spin-free Cowan–Griffin AIMP (CG-AIMP) [24] and its spin–orbit extension, the Wood–Boring AIMP (WB-AIMP) [18]. The core AIMPs produced and monitored in this paper correspond to the latter choice: spin-free CG-AIMP and spin–orbit WB-AIMP.

The core AIMPs corresponding to a [Kr,4d] core of the lanthanide elements and to a [Xe,4f,5d] core of the actinide elements were published in [5] together with Wood–Boring [4] spin–orbit operators and optimized Gaussian valence basis sets. Here we extend this tabulation to the [Kr] and [M] cores of the lanthanide elements and the [Xe,4f] core of the actinide elements. The optimized basis sets are minimal basis sets of the size shown in Table 1. It should be noted that, when they are used in molecular calculations, their flexibility can be enhanced by adding or releasing the outermost primitives and by extension with appropriate functions, such as polarization and diffuse functions, in a fashion identical to all-electron calculations. The only, minor, change with respect to the full procedure of [5] is the following. Instead of the spin–orbit correction of the basis sets, which consisted of a change in the innermost orbital coefficient, followed by renormalization, such that the orbital spin–orbit coupling constant was identical to that corresponding to the numerical Cowan–Griffin atomic orbital [18], here we chose not to touch the valence orbitals but to change the core projection constants (in the AIMP term $\Sigma_{2e}^{core}(-2\varepsilon_c)\phi_\varepsilon(\phi_\varepsilon)$, see [5], equation (4)) from the nominal value $(-2\varepsilon_c)$ to another one, $B_c$, which gives orbital spin–orbit coupling constants close to the numerical ones. In this case, only the $B_{3d}$ of the lanthanide elements and the $B_{4d}$ and $B_{4f}$ constants of the actinide elements have been chosen different from $-2\varepsilon_c$. All these data are available from the authors [25] and as a supplementary data set [26].

### Table 1. Core/valence partitions and valence basis sets used for the lanthanide and actinide element

<table>
<thead>
<tr>
<th>Label</th>
<th>Core orbitals</th>
<th>Valence orbitals</th>
<th>Minimal valence basis set</th>
<th>Recommended contraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce-Lu$^a$ [Kr,4d]</td>
<td>K,L,M,4s,4p,4d</td>
<td>5s,5p,4f,5d,6s</td>
<td>(14s10p9d8f)/[2s1p1d1f]</td>
<td>[6s5p5d4f]</td>
</tr>
<tr>
<td>Ce-Lu$^b$ [Kr]</td>
<td>K,L,M,4s,4p</td>
<td>4d,5s,5p,4f,5d,6s</td>
<td>(14s10p10d8f)/[2s1p2d1f]</td>
<td>[6s5p6d4f]</td>
</tr>
<tr>
<td>Ce-Lu$^b$ [M]</td>
<td>K,L,M</td>
<td>4s,4p,4d,5s,5p,4f,5d,6s</td>
<td>(14s10p10d8f)/[3s2p2d1f]</td>
<td>[7s6p6d4f]</td>
</tr>
<tr>
<td>Th-Lr$^a$ [Xe,4f,5d]</td>
<td>K,L,M,N,5s,5p,5d</td>
<td>6s,6p5f,6d,7s</td>
<td>(14s10p11d9f)/[2s1p2d1f]</td>
<td>[6s5p5d4f]</td>
</tr>
<tr>
<td>Th-Lr$^b$ [Xe,4f]</td>
<td>K,L,M,N,5s,5p</td>
<td>5d,6s,6p,5f,6d,7s</td>
<td>(14s10p12d9f)/[2s1p2d1f]</td>
<td>[6s5p6d4f]</td>
</tr>
</tbody>
</table>

$^a$ Reference [5].  
$^b$ This work.
the 6d\textsuperscript{1}–2D state of Pa\textsuperscript{4+}. This latter core potential was used to calculate the local structure and spectroscopy of the Pa\textsuperscript{4+}-doped Cs\textsubscript{2}ZrCl\textsubscript{6} solid, leading to excellent agreement with available experimental data [16]. Similar deficiencies in the neutral atom [Kr,4d]/[Xe,4f,5d]-core potentials have been found for other lanthanide and actinide ions in studies of the f–d spectroscopy of Cs\textsubscript{2}NaYCl\textsubscript{6}:Ce\textsuperscript{3+} [27] and Cs\textsubscript{2}ZrCl\textsubscript{6}:U\textsuperscript{4+} [28]. The option of producing the corresponding [Kr,4d]/[Xe,4f,5d] cores in the ions rather than in the neutral atoms has been analysed. However, it is neither generally valid, as we show here for Ce\textsuperscript{3+}, nor desirable. Consequently, we have conducted a study of the transferability of core \textit{ab initio} model potentials obtained for neutral lanthanide and actinide elements to the calculation of the f\textsuperscript{n} and f\textsuperscript{n}/C\textsubscript{0}1d\textsuperscript{1} manifolds of their ions (in the gas phase and embedded in host crystals) using different core/valence partitions. The goal is to establish what is the largest core capable of reaching uniform high accuracy for both manifolds. We present next the results of this study for the Ce\textsuperscript{3+} and Pa\textsuperscript{4+} free ions and for the Cs\textsubscript{2}NaYCl\textsubscript{6}:Pr\textsuperscript{3+}, Cs\textsubscript{2}NaYCl\textsubscript{6}:Ce\textsuperscript{3+}, Cs\textsubscript{2}ZrCl\textsubscript{6}:Pa\textsuperscript{4+}, and Cs\textsubscript{2}ZrCl\textsubscript{6}:U\textsuperscript{4+} crystals. All the calculations were performed with the Molcas-5 program system [29].

3.1. Free ion calculations

Table 2 gives the results of spin-free relativistic CG-AIMP calculations on the f\textsuperscript{1–2F} and d\textsuperscript{1–2D} electronic states of the Ce\textsuperscript{3+} and Pa\textsuperscript{4+} free ions corresponding to core potentials that have been obtained either in the ions or in the neutral atoms using different core/valence partitions. Their quality can be assessed by comparison with the results of spin-free relativistic all electron numerical Cowan–Griffin Hartree–Fock (CG-HF) calculations [3], also included in table 2. Table 3 and figure 1 include the results of all-electron CG-HF calculations on both the neutral Ce and Pa and the free ions Ce\textsuperscript{3+} and Pa\textsuperscript{4+}, which are useful for analyses.

The changes in the expected values of \(r\) and \(r/C\textsubscript{0}\), and in the spin–orbit coupling constants, \(\zeta\), of the outermost orbitals of Ce\textsuperscript{3+} and Pa\textsuperscript{4+} relative to their neutral atom values are shown to be much larger for Pa\textsuperscript{4+} than for Ce\textsuperscript{3+} in table 3. The shrinking of the Pa\textsuperscript{4+} 6d orbital

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Table 2. Results of spin-free relativistic calculations of radial expectation values (in atomic units), orbital spin–orbit coupling constants \(\zeta\) (in cm\textsuperscript{–1}), ionization potentials IP(nf) (in eV), and \(f \rightarrow d\) electronic transition energy (in cm\textsuperscript{–1}) for Ce\textsuperscript{3+} and Pa\textsuperscript{4+} free ions.

<table>
<thead>
<tr>
<th>Core</th>
<th>Ce\textsuperscript{3+} 5d\textsuperscript{1–2D}</th>
<th>Pa\textsuperscript{4+} 6d\textsuperscript{1–2D}</th>
<th>All electron numerical CG-HF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[Kr,4d]</td>
<td>[Kr,4d]</td>
<td>[Kr]</td>
</tr>
<tr>
<td>Ce\textsuperscript{3+}</td>
<td>(r)\textsubscript{4f}</td>
<td>1.034</td>
<td>1.021</td>
</tr>
<tr>
<td></td>
<td>(r)\textsubscript{5f}</td>
<td>4.351</td>
<td>4.442</td>
</tr>
<tr>
<td></td>
<td>(\Delta E_{f \rightarrow d})</td>
<td>40 900</td>
<td>46 140</td>
</tr>
<tr>
<td>Pa\textsuperscript{4+}</td>
<td>(r)\textsubscript{5f}</td>
<td>1.374</td>
<td>1.359</td>
</tr>
<tr>
<td></td>
<td>(r)\textsubscript{6f}</td>
<td>5.527</td>
<td>5.690</td>
</tr>
<tr>
<td></td>
<td>(\Delta E_{f \rightarrow d})</td>
<td>30 19</td>
<td>46 17</td>
</tr>
<tr>
<td></td>
<td>IP(5f)</td>
<td>345 711</td>
<td>350 455</td>
</tr>
<tr>
<td></td>
<td>IP(6f)</td>
<td>302 519</td>
<td>303 801</td>
</tr>
<tr>
<td></td>
<td>(\Delta E_{f \rightarrow d})</td>
<td>43 192</td>
<td>46 653</td>
</tr>
</tbody>
</table>
The spin–orbit coupling constant $\zeta_{6d}$ makes its spin–orbit coupling constant $\zeta_{6d}$ more than double. Also, the four ionizations in Pa$^{4+}$ are accompanied by a contraction of the 5d outer core orbital which, being small, is significant enough to make the Pa [Xe,4f,5d] core to fail completely in the calculation of $\zeta_{6d}$ of Pa$^{4+}$ ($6d^{1-2}D$) (table 2) and to lead to poor values of $\zeta_{6f}$ of Pa$^{4+}$ ($5f^{1-2}F$) and the 6d ionization potential of Pa$^{4+}$ ($6d^{1-2}D$), IP(6d), and 5f ionization potential of Pa$^{4+}$ ($5f^{1-2}F$), IP(5f), and, as a consequence, of the 5f → 6d electronic transition, $\Delta E_{f-d}$ (note that $\Delta E_{f-d} = \text{IP}(6d) - \text{IP}(5f)$). All this suggested the production of the [Xe,4f,5d] core potential in the Pa$^{4+}$ ion; in view of the extremely poor value of $\zeta_{6d}$ its 6d$^{1-2}D$ state rather than its 5d$^{1-2}F$ state was chosen for this purpose [16]. The results of this AIMP appear in table 2 and show its very good quality and transferability to the Pa$^{4+}$ 5f$^{1-2}F$ electronic state. Alternatively, the transferability of the neutral Pa core potential is very much improved if the 5d orbitals are promoted to the valence, this leading to the Pa [Xe,4f] core AIMP (table 2). The overall improvement in the results, together with the very high transferability of the Pa$^{4+}$ [Xe,4f,5d] core AIMP to the 5f$^{1-2}F$ state, indicate that most of the effect comes from a more realistic modelling of the 5d–6d interactions in the Pa$^{4+}$ ion, either explicitly, being the 5d orbitals in the valence (Pa [Xe,4f] CG-AIMP calculations), or as a frozen core orbital obtained in the 6d$^{1-2}D$ state of the Pa$^{4+}$ ion (Pa$^{4+}$ [Xe,4f,5d] CG-AIMP calculations).

As we move from the actinide series to the lanthanide series, the lack of transferability of the corresponding [Kr,4d] core potential of the neutral atom to the Ce$^{3+}$ ($4d^{1-2}F$) and Ce$^{3+}$ ($5d^{1-2}D$) states is also shown (the errors are, though, smaller and IP(5d) and $\zeta_{6f}$ are good, but the results are poor overall). Unfortunately, the transferability of the corresponding Ce$^{3+}$–$2D$ [Kr,4d] core potential to Ce$^{3+}$ ($4f^{1-2}F$) disappears now: $\zeta_{6f}$ and, especially, IP(4f), are not good, with the error of the latter being directly transferred to $\Delta E_{f-d}$. Now, the small spatial separation between the 4f and the 4d orbitals (figure 1, table 3) enhances the importance of the 4f–4d interactions with respect to the corresponding 5f–5d interactions in the actinides, and makes the small differences shown by the 4d orbital in Ce$^{3+}$ ($4f^{1-2}F$) and Ce$^{3+}$ ($5d^{1-2}D$) more important than the corresponding ones in the actinides. Accordingly, when the 4d outer core orbitals are promoted to the valence, the [Kr] core CG-AIMP obtained in the neutral Ce atom guarantees excellent transferability. As can be seen in table 2, further enlargement of the valence space is found to be unnecessary for the properties under study here, and the Ce [M] core and Ce [Kr] core CG-AIMP results are essentially equivalent.

Table 3. Results of spin-free relativistic all electron numerical CG-HF calculations of radial expectation values (in atomic units) and spin–orbit coupling constants (in cm$^{-1}$) of the outermost d and f orbitals of Ce, Ce$^{3+}$, Pa, and Pa$^{4+}$.

<table>
<thead>
<tr>
<th></th>
<th>Ce (I)</th>
<th>Ce$^{3+}$ ($2F,2D$)</th>
<th>Pa (I)</th>
<th>Pa$^{4+}$ ($2F,2D$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\langle r \rangle_{4d}$</td>
<td>0.745</td>
<td>0.745, 0.738</td>
<td>0.911</td>
<td>0.904, 0.899</td>
</tr>
<tr>
<td>$\langle r \rangle_{5d}$</td>
<td>37.1</td>
<td>37.1, 37.8</td>
<td>50.6</td>
<td>51.4, 52.0</td>
</tr>
<tr>
<td>$\langle r \rangle_{4f}$</td>
<td>1.091</td>
<td>1.020</td>
<td>1.769</td>
<td>1.370</td>
</tr>
<tr>
<td>$\langle r \rangle_{5f}$</td>
<td>4.182</td>
<td>4.457</td>
<td>3.853</td>
<td>5.437</td>
</tr>
<tr>
<td>$\zeta_{6f}$</td>
<td>748</td>
<td>800 (7.0)</td>
<td>1344</td>
<td>1914 (42)</td>
</tr>
<tr>
<td>$\zeta_{6d}$</td>
<td>3.022</td>
<td>2.266</td>
<td>3.471</td>
<td>2.356</td>
</tr>
<tr>
<td>$\zeta_{5d}$</td>
<td>548</td>
<td>1017 (86)</td>
<td>3.006</td>
<td>6.812</td>
</tr>
<tr>
<td>$\zeta_{5f}$</td>
<td>2.021</td>
<td>3.724</td>
<td>1337</td>
<td>3042 (128)</td>
</tr>
<tr>
<td>$\zeta_{4f} - \zeta_{4d}$</td>
<td>0.346</td>
<td>0.275, 0.282</td>
<td>0.858</td>
<td>0.466, 0.471</td>
</tr>
</tbody>
</table>

*Percentage increase relative to the neutral atom values are given in parentheses.*
3.2. Embedded cluster calculations

In this section we present the results of embedded cluster calculations on the Cs$_2$NaYCl$_6$:Ce$^{3+}$, Cs$_2$NaYCl$_6$:Pr$^{3+}$, Cs$_2$ZrCl$_6$:Pa$^{4+}$, and Cs$_2$ZrCl$_6$:U$^{4+}$ materials. In all these crystals, the f-element ions are introduced as impurities that produce substitutional defects: Ce$^{3+}$ and Pr$^{3+}$ substitute for Y$^{3+}$ ions of the Cs$_2$NaYCl$_6$ host, whereas Pa$^{4+}$ and U$^{4+}$ substitute for Zr$^{4+}$ in Cs$_2$ZrCl$_6$. Therefore, all defect clusters are octahedral hexachloride complexes: (CeCl$_6$)$_3$$^{3-}$, (PrCl$_6$)$_3$$^{3-}$, (PaCl$_6$)$_2$$^{2-}$, and (UCl$_6$)$_2$$^{2-}$. Following the ab initio model potential (AIMP) embedded cluster method [2, 30], the quantum mechanical interactions between the defect clusters and their crystalline surroundings are modelled and built in the embedding AIMPs which are added to the cluster molecular orbitals and the embedding ion calculations which may be used to ensure a high degree of linear independence between the cluster molecular orbitals and the embedding ion orbitals [2, 34].

The core valence orbitals use the following spin-free relativistic core CG-AIMP and valence basis sets. The cores of the lanthanide and actinide ions are represented by the CG-AIMPs described and discussed in sections 2 and 3.1 (table 2); the valence basis sets and recommended contractions of table 1 are used. For Cl we use the [Ne] core CG-AIMP of [24], its valence basis set, extended with one p diffuse function for anion [32] and one d polarization function [33], is (7s7p1d)/[3s4p1d]. It is known that second neighbour basis functions are needed when the cluster has next neighbour cations in the directions of the bonding axes, in order to ensure a high degree of linear independence between the cluster molecular orbitals and the embedding ion orbitals [2, 34]. This is the case with the Na$^+$ cations in the (100) directions in the Cs$_2$NaYCl$_6$ elpasolite structure. Consequently, the (CeCl$_6$)$_3$$^{3-}$ and (PrCl$_6$)$_3$$^{3-}$ embedded cluster calculations use the (7s4p)/[1s1p] functions corresponding to the 2s and 2p atomic orbitals of the Cs$_2$NaYCl$_6$:Na$^+$ embedded ion calculations which are carried out to obtain the embedding AIMP [31]. In the Cs$_2$ZrCl$_6$ crystal the crystallographic sites of Na$^+$ in Cs$_2$NaYCl$_6$ are vacant, and the use of basis functions in such vacant sites has no effect on the electronic structure of the embedded cluster other than enlarging the size of the basis set; therefore, they are not used.

The potential energy surfaces of selected local electronic states of the embedded clusters have been obtained by performing complete active space self-consistent field (CASSCF) calculations [35] where the valence molecular orbitals of main character 4f/5f and 5d/6d constitute the active orbital space. We shall refer to this type of calculation as CASSCF (f,d). This space leads to open-shell restricted Hartree–Fock wavefunctions in the case of the f$^1$ (CeCl$_6$)$_3$$^{3-}$ and (PaCl$_6$)$_2$$^{2-}$ embedded clusters; we present here the results of the lowest f$^1$ state, $^2$A$_{2u}$, and the ligand field split d$^1$ excited states: $^2$T$_{2g}$ and $^2$E$_g$. A much larger manifold of states is obtained in the case of the (PrCl$_6$)$_3$$^{3-}$ and (UCl$_6$)$_2$$^{2-}$ isoelectronic defect clusters, which may be grouped into three different manifolds labelled according to the following 'superconfigurations': f$^2$, f$^1$d$^1$(t$_{2g}$)$^1$, and f$^1$d$^1$(e$_g$)$^1$. The potential energy surfaces of all states belonging to a given super configuration are found to be virtually parallel, that is, they show very close values of impurity–ligand equilibrium distance $R_e$, and totally symmetric vibrational frequency $\omega_{v1g}$. The f$^2$ manifold includes all cluster electronic states that stem from the f$^2$ free ion terms split by the actual interactions in the octahedral embedding cluster. Since the O$_6$ crystal field splitting of the d orbitals is much larger than that of the f orbitals, the two f$^1$d$^1$(t$_{2g}$)$^1$ and f$^1$d$^1$(e$_g$)$^1$ manifolds arise as two sets of virtually parallel potential energy surfaces whose bond lengths are considerably different from one set to the other, namely, smaller for the f$^1$d$^1$(t$_{2g}$)$^1$ manifold, which reveals the relative stabilization of the d(eg) ($\pi$ antibonding) orbitals and destabilization of the d(e$_g$) ($\sigma$ antibonding) orbitals in the octahedral crystalline environment. As a showcase, we present the CASSCF (f,d) results of all spin-triplet electronic states of the Cs$_2$ZrCl$_6$:U$^{4+}$ system in figure 2. The values of the UCl equilibrium distance and totally symmetric vibrational frequency of the states belonging to each of the three manifolds can be summarized, using mean values and root-mean-square deviations, as follows: f$^2$, 2.674 ± 0.003 Å (316 ± 1) cm$^{-1}$.

![Figure 2. Potential energy surfaces of the spin-triplet electronic states of Cs$_2$ZrCl$_6$:U$^{4+}$ calculated at the CASSCF(f,d) level using the [Xe,4f,5d] core CG-AIMP obtained in the 5f$^1$6d$^1$-1/2D state of the U$^{4+}$ free ion.](image-url)
$t^1d(t_{2g})^1$, $2.646 \pm 0.003 \text{ Å (320 \pm 1) cm}^{-1}$; $t^1d(e_g)^1$, $2.713 \pm 0.003 \text{ Å (305 \pm 1) cm}^{-1}$. Consequently, in what follows we present the results of the lowest electronic state (high spin) of each manifold as a representative member of it.

The accurate calculation of the local structure and spectroscopy of these materials extends beyond the spin-free relativistic CASSCF (f,d) level described above [16], which does not include the important spin–orbit or dynamic electron correlation effects. Without these methodological requirements it is not possible to directly compare the theoretical results with the experiments to validate the methods; however, it is still possible to reveal whether or not a given choice of core/valece partition and CG-AIMP is transferable to the calculation of the potential energy surfaces of the three $f^1$, $f^{n-1}d(t_{2g})^1$, and $f^{n-1}d(e_g)^1$ manifolds, which is the purpose of this work. Nevertheless, spin–orbit correlated calculations that use the spin-free CASSCF (f,d) level as a starting point and their experimental counterparts will be referred to, whenever possible, in order to establish references for accuracy checks of the spin-free CASSCF (f,d) results.

The results of the CG-AIMP calculations on Cs$_2$ZrCl$_6$:PaCl$_6$$^{2-}$ obtained using the [Xe,4f,5d] core of the Pa$^{4+}$, presented in table 4, can be used as a reference for accuracy, given that full spin–orbit correlated calculations have been carried out using this core AIMP and compare very well with experiment [13, 16]. The same is true for the CG-AIMP calculations which use the [Kr] core AIMPs obtained in neutral Ce [27].

Altogether, the results of the four systems presented in tables 4 and 5 show that the local structure

<table>
<thead>
<tr>
<th>Core</th>
<th>CG-AIMP</th>
<th>Ce$^{3+}$ 5d$^1$ 2D</th>
<th>[Kr,4d]</th>
<th>[Kr,4d]</th>
<th>[Kr]</th>
<th>[M]</th>
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<tr>
<td>(CeCl$_6$)$^{3-}$</td>
<td>4f$^1$</td>
<td>$^2A_{2u}(^2F)$</td>
<td>$R_e$</td>
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<td>$^2T_{2g}(^2D)$</td>
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<tr>
<td></td>
<td>5d($e_g$)$^1$</td>
<td>$^2E_g(2^2D)$</td>
<td>$R_e$</td>
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<td></td>
<td>$^2T_{2g} \rightarrow ^2E_g$</td>
<td>(10D$_q$)</td>
<td>$T_e$</td>
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<td>21849</td>
<td>21296</td>
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<table>
<thead>
<tr>
<th>Core</th>
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<th>Pa$^{4+}$ 6d$^1$ 2D</th>
<th>[Xe,4f,5d]</th>
<th>[Xe,4f,5d]</th>
<th>[Xe,4f]</th>
<th>[Xe,4f]</th>
</tr>
</thead>
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<tr>
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<td>$^2A_{2u}(^2F)$</td>
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<td>2.683</td>
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<td>2.682</td>
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<td>$\omega_{a_1g}$</td>
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<td>$R_e$</td>
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<tr>
<td></td>
<td>$^2T_{2g} \rightarrow ^2E_g$</td>
<td>(10D$_q$)</td>
<td>$T_e$</td>
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<td>57246</td>
<td>53438</td>
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Tables 4 and 5 present the CASSCF(f,d) values of the impurity ligand equilibrium distances $R_e$ and totally symmetric vibrational frequencies $\omega_{a_1g}$ of the lowest states of the $f^1$, $d(t_{2g})^1$, and $d(e_g)^1$ configurations of Cs$_2$NaYCl$_6$:Ce$^{3+}$ and Cs$_2$ZrCl$_6$:Pa$^{4+}$ (note that the $d(t_{2g}) \rightarrow d(e_g)$ transition is in this case the familiar $10D_q$ crystal field parameter [36]) and of the lowest 2S+1 = 3 states of the $f^2$, $f^1d(t_{2g})^1$, and $f^1d(e_g)^1$ configurations of Cs$_2$NaYCl$_6$:Pr$^{3+}$ and Cs$_2$ZrCl$_6$:U$^{4+}$, together with the difference of energy minima between them.

Table 4. Results of spin-free relativistic CASSCF(f,d) calculations of spectroscopic constants $R_e$ (in Å), $\omega_{a_1g}$ and $T_e$ (in cm$^{-1}$) and zero-phonon 10D$_q$ electronic transition (in cm$^{-1}$), for Cs$_2$NaYCl$_6$:CeCl$_6$$^{3-}$ and Cs$_2$ZrCl$_6$:PaCl$_6$$^{2-}$ using different core/valece partitions.
parameters $R_e$ and $\omega_{a_{1g}}$ are largely insensitive to the core AIMP used. This is also the case for the $d_{(t^2_g)}$ and $d_{(e_g)}$ electronic transitions. That is, the problem of transferability of a core AIMP manifests itself only when the f–d energy differences are calculated which, as a matter of fact, are shown to follow quite closely the tendencies of the f–d electronic transition of the respective free ions (cf. tables 4 and 2). Consequently, the conclusions relative to the transferability of core AIMPs that may be driven from the embedded cluster results are a replica of those commented on for the free ion calculations. For the actinide impurity ions, two transferable CG-AIMPs lead to comparable accuracy: the $[\text{Xe,4f,5d}]$ core potential obtained for the $f^{n+1}d^1$ state of the ion and the $[\text{Xe,4f}]$ core potential of the neutral actinide. For the lanthanide impurity ions, transferability is attained only when the 4d orbitals are treated explicitly using the $[\text{Kr}]$ core AIMPs of the neutral atoms, whereas the promotion of the 4s and 4p orbitals to the valence is shown to be unnecessary (cf. [M] core results in table 4).

### 4. Conclusion

Relativistic ab initio model potentials (AIMPs) based on Cowan–Griffin atomic calculations and their corresponding optimized valence basis sets have been produced in this work for Ce to Lu using the $[\text{Kr}]$ and $[\text{M}]$ cores and for Th to Lr using the $[\text{Xe,4f}]$ core. Their transferability to the calculation of selected atomic and molecular properties of $3^+$ and $4^+$ ions in states of the $f^0$ and $f^{n-1}d^1$ configurations has been studied using as test cases the Ce$^{3+}$ and Pa$^{4+}$ free ions and the $\text{Cs}_2\text{NaYCl}_6(\text{CeCl}_6)^3^-$, $\text{Cs}_2\text{NaYCl}_6(\text{PrCl}_6)^3^-$, $\text{Cs}_2\text{ZrCl}_6(\text{PaCl}_6)^2^-$, and $\text{Cs}_2\text{ZrCl}_6(\text{UCl}_6)^2^-$ embedded clusters. The CASSCF method for the f and d active orbital space has been used to obtain the cluster energies and wavefunctions embedded in ab initio model potential representations of the surrounding host crystals. The results of the atomic calculations show that the $[\text{Kr}]$/$[\text{Xe,4f}]$ core CG-AIMPs are capable of producing uniform high accuracy in the spin–orbit coupling constants $\zeta_t$ and $\zeta_d$ and $f \to d$ electronic transition energies. They are also capable of producing accurate values of the

### Table 5. Results of spin-free relativistic CASSCF(f,d) calculations of spectroscopic constants $R_e$ (in Å), $\omega_{a_{1g}}$, and minimum to minimum transition energies $T_e$ (in cm$^{-1}$) for $\text{Cs}_2\text{NaYCl}_6(\text{PrCl}_6)^3^-$ and $\text{Cs}_2\text{ZrCl}_6(\text{UCl}_6)^2^-$ using different core/valence partitions.

<table>
<thead>
<tr>
<th>Core</th>
<th>$R_e$ (Å)</th>
<th>$\omega_{a_{1g}}$ (rad s$^{-1}$)</th>
<th>$T_e$ (cm$^{-1}$)</th>
</tr>
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<tbody>
<tr>
<td>$[\text{Kr},4d]$</td>
<td>2.726</td>
<td>307</td>
<td>48270</td>
</tr>
<tr>
<td>$[\text{Kr}]$</td>
<td>2.730</td>
<td>308</td>
<td>42869</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Core</th>
<th>$R_e$ (Å)</th>
<th>$\omega_{a_{1g}}$ (rad s$^{-1}$)</th>
<th>$T_e$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Xe,4f,5d}]$</td>
<td>2.670</td>
<td>316</td>
<td>33516</td>
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<tr>
<td>$[\text{Xe,4f}]$</td>
<td>2.669</td>
<td>316</td>
<td>32753</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Core</th>
<th>$R_e$ (Å)</th>
<th>$\omega_{a_{1g}}$ (rad s$^{-1}$)</th>
<th>$T_e$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Xe,4f,5d}]$</td>
<td>2.714</td>
<td>306</td>
<td>65990</td>
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<tr>
<td>$[\text{Xe,4f}]$</td>
<td>2.711</td>
<td>305</td>
<td>65351</td>
</tr>
</tbody>
</table>
local structural parameters (impurity–ligand bond-lengths $R_v$, and totally symmetric vibrational frequencies $\omega_{11}$) and $f \to d$ electronic transitions in the embedded cluster systems. The same properties have been calculated using larger and smaller cores. The larger [Kr,4d]/[Xe,4f,5d] core CG-AIMPs of the lanthanide/actinide elements produced in a previous work also are shown to be very accurate in the calculation of the local structure parameters ($R_v, \omega_{11}$) and 10Dq electronic transition of the embedded cluster systems, but they are shown to fail in producing a balanced high quality in the transition of the embedded cluster systems, but they are shown to fail in producing a balanced high quality in the atomic orbital spin–orbit coupling constants ($\xi_t, \xi_g$) and (atomic and molecular) $f \to d$ electronic transitions. This lack of transferability of the 4d/5d orbitals of the lanthanide/actinide elements between $f$ and $d$ valence states of their respective ions is a manifestation of the different interactions of the 4d/5d orbitals of the lanthanoids/actinoids with the 4f/5f and 5d/6d orbitals, of very different spatial nature. The smaller [M] core CG-AIMP results obtained for the lanthanide free and embedded ions show that the promotion of the 3s and 4p orbitals to the valence is not necessary.

This work was partly supported by a grant from Ministerio de Ciencia y Tecnología, Spain (Dirección General de Investigación, PB98-0108).

References
[25] Detailed core AIMP and valence basis set data libraries in electronic format are available from the authors upon request or directly at http://www.iam.es/quinica/aimp/Data/AIMPLibs.html (see also [29]).
[26] See the online edition of this issue.
[27] Seijo, L., and Barandiáran, Z., unpublished.