Ultrasoft pseudopotentials for lanthanide solvation complexes: Core or valence character of the 4*f* electrons

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The 4*f* electrons of lanthanides, because of their strong localization in the region around the nucleus, are traditionally included in a pseudopotential core. This approximation is scrutinized by optimizing the structures and calculating the interaction energies of $Gd^{3+}(H_2O)$ and $Gd^{3+}(NH_3)$ microsolvation complexes within plane wave Perdew-Burke-Ernzerhof calculations using ultrasoft pseudopotentials where the 4*f* electrons are included either in the core or in the valence space. Upon comparison to quantum chemical MP2 and CCSD(T) reference calculations it is found that the explicit treatment of the 4*f* electrons in the valence shell yields quite accurate results including the required small spin polarization due to ligand charge transfer with only modest computational overhead. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2191498]

INTRODUCTION

At the heart of lanthanide complexation chemistry[1] is the common belief that the so-called "4*f* electrons" do not participate in coordinative bonds with ligands, which are thus considered to be largely electrostatic. And indeed, the rather compact but energetically high-lying 4*f* orbitals are incontestably shielded from the environment by the more diffuse 5*s* and 5*p* closed shells. In quantum mechanical studies, this chemical inactivity translates into semiempirical models where the lanthanide cation is represented by a central model potential,[2] or into *ab initio* methods resorting to pseudopotentials (PPs) that include the 4*f* electrons within a frozen core.[3,4] The unimportance of the role played by the 4*f* electrons in the complexation of lanthanides may then be reinforced by comparing to reference calculations that mix a small-core pseudopotential (i.e., putting the 4*f*, 4*s*, 4*p*, and 4*d* electrons into the valence space) with a density functional.[5] However, such calculations certainly invite caution as these PPs are not adjusted to density functional theory (DFT) all-electron (AE) data.[6] Moreover, second-order Møller-Plesset perturbation theory (MP2) calculations[7,8] using a PP that includes the 4*f* electrons into the valence space[9] in conjunction with an extended basis set have revealed the existence of some charge transfer between the 4*f* orbitals of a Gd^{3+} cation and the oxygen atoms of coordinating water molecules; this effect is found to increase with the number of solvating water molecules. These authors also established that the stabilizing exchange interaction between the $(4f_\alpha)^7$ shell and the formally unoccupied $5d_\alpha$ spin orbitals enhances the ability of the latter to accept α-spin density from the ligand, leading to a measurable spin polarization. It therefore appears that the question of the chemical inertness of the 4*f* electrons is not completely settled.

On pratical grounds, the explicit treatment of the 4*f* electrons increases the number of active electronic degrees of freedom, requires better basis sets, introduces open-shell complications, and thus adds considerable to the computation cost of such calculations. If bulk aqueous solution is the targeted medium, an additional difficulty arises when the convenient plane wave (PW) basis set is used to represent such a liquid within periodic boundary conditions. Indeed, expanding these strongly peaked 4*f* orbitals in terms of PWs requires many reciprocal space vectors and thus high plane wave cutoffs. However, the pseudization of the valence wave functions advantageously reduces the plane wave cutoff. This is best achieved with Vanderbilt's ultrasoft (US) pseudopotentials,[10–13] which allow for large cutoff radii (i.e., exceeding the outermost maximum of the radial all-electron wave function) without sacrificing transferability. Whether the 4*f* electrons are part of the valence[14] or kept in the core,[15] USPPs for lanthanides have, however, been restricted so far to solid state applications. The objective of the present work is rather to focus on small gadolinium(III) complexes whose properties can also be computed with high-level quantum chemistry methods in order to set the stage for a more detailed *ab initio* study of their dynamic properties in aqueous solution.

ULTRASOFT PSEUDOPOTENTIALS AND 4*f* ELECTRONS: GADOLINIUM

The quest for smooth pseudized wave functions led Vanderbilt[10] to the construction of a new family of PPs that relax the familiar norm-conservation constraint (i.e., the equality of the norms of the AE and pseudized atomic wave functions, ψ_i and ϕ_i, respectively, inside the core region). The price to pay besides the more complex formalism is then to optimize the Kohn-Sham orbitals $\phi_{n\mathbf{k}}$ under a generalized orthonormality condition and to recover the valence electron density according to

$$n_v(\mathbf{r}) = \sum_{n\mathbf{k}} |\phi_{n\mathbf{k}}(\mathbf{r})|^2 + \sum_{ij} \rho_{ij} Q_{ij}(\mathbf{r}), \qquad (1)$$

where ρ_{ij} are $\phi_{n\mathbf{k}}$-dependent weights and $Q_{ij}(\mathbf{r})$ are augmentation functions defined by

$$Q_{ij}(\mathbf{r}) = \psi_i^*(\mathbf{r})\psi_j(\mathbf{r}) - \phi_i^*(\mathbf{r})\phi_j(\mathbf{r}). \quad (2)$$

As these functions are localized in the core region, the second term of the right-hand side of Eq. (1) is so "hard" that they are first expressed as a sum over all the permissible total angular momenta,[10–12]

$$Q_{ij}(\mathbf{r}) = \sum_{l=|l_i-l_j|}^{l_i+l_j} \sum_{m=-l}^{l} c_{lm}^{ij} Y_{lm}(\theta,\phi) Q_{ij}^l(r), \quad (3)$$

where the Clebsch-Gordan coefficients c_{lm}^{ij} are defined by the real Gaunt integrals,[16]

$$c_{lm}^{ij} = \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi Y_{l_i m_i}^*(\theta,\phi) Y_{l_j m_j}(\theta,\phi) Y_{lm}^*(\theta,\phi). \quad (4)$$

In Eq. (3), the augmentation functions were made l dependent and preserve the corresponding spherical multipolar moments. They are then smoothened inside an inner cutoff radius by means of an expansion in polynomials of r. We have modified the CPMD program package[17,18] in order to calculate the Clebsch-Gordan coefficients in a convenient way, namely, by integrating directly Eq. (4) via the Lebedev-Laïkov [19] spherical quadrature formula,

$$c_{lm}^{ij} = \sum_{k=1}^N w_k Y_{l_i m_i}^*(\theta_k,\phi_k) Y_{l_j m_j}(\theta_k,\phi_k) Y_{lm}^*(\theta_k,\phi_k), \quad (5)$$

with the number of points of the octahedral symmetric mesh N set to 74 to ensure the angular integration of polynomials of order less than or equal to 13 with a relative accuracy of 2×10^{-14} [since the order must obey the relation $n=2m+1$, $m=1,2,\ldots,15$ (Ref. 19) and the f angular momentum implies that max $l+l_i+l_j=12$], and where w_k are the associated normalized weights. For comparison, the PWSCF suite of programs [20] performs this quadrature with random uniform deviates on the unitary sphere.

Using this implementation, two "small core" (SC) PPs, where the $4f$ electrons belong to the valence space, and two "large core" (LC) PPs were generated[21] based on AE calculations on the spherically symmetric atom using the Perdew-Burke-Ernzerhof[22] (PBE) gradient corrected exchange-correlation functional including scalar relativistic effects (in the Koelling-Harmon approximation:[23] mass-velocity term and Darwin shift are retained but not spin-orbit coupling). As our target systems are formally trivalent Gd complexes, the reference (spin averaged) electronic configurations were $[1s^2-4d^{10}]4f^75s^25p^{5.5}5d^{0.5}$ for the SC USPPs (Ref. 24) and $[1s^2-4d^{10},4f^7]5s^25p^6$ (i.e., ground state of Gd^{3+}) for the LC USPPs. When included in the core, the $4f$ orbitals overlap with the $5s$ and $5p$ valence orbitals, so that the unscreening procedure that removes the valence contribution to the nonlinear density-dependent exchange-correlation potential can be a source of inaccuracy. This problem was circumvented during the pseudopotential PW calculations on Gd(III) complexes by applying a nonlinear core correction[25] (NLCC) which consists in calculating the core plus valence exchange-correlation energy with the core electron density being replaced by a smooth function up to a
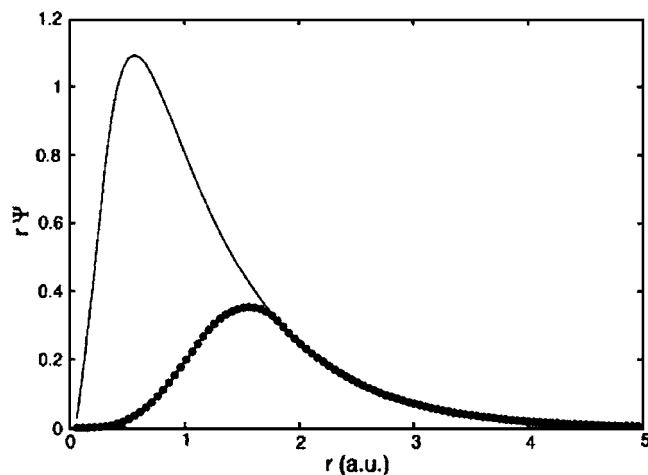

FIG. 1. $4f$ AE (solid) and pseudized (circles) radial wave functions (times r) of Gd^{3+} ($[1s^2-4d^{10}]4f^75s^25p^{5.5}5d^{0.5}$ electronic configuration), with a cutoff radius equal to 1.9 a.u.

cutoff radius where the exact core electron density is restored (otherwise the convergence in reciprocal space would be slow). The same analysis can hold for the overlap between the $4s$, $4p$, and $4d$ core orbitals and the $4f$ valence orbital so that we apply a NLCC to one of the SC USPPs as well. Moreover, Porezag *et al.*[26] also showed that such a correction improves the transferability of spin-neutral pseudopotentials.[26] The corresponding cutoff radius was set to 0.6 a.u. for the LC USPP and to 0.95 a.u. for the SC USPP (in order to obtain better convergence properties, *vide infra*). All PPs were constructed with two reference energies per angular momentum channel such that the local part of the PPs has correct scattering properties in the f channel; the cutoff radius was set to 2.5 a.u. for the local PP, and 2.0 a.u. for all the angular momentum channels but f, where it was set to 1.9 a.u; the inner cutoff radius was set to 1.06 a.u. for the SC USPPs and to 1.00 a.u. for the LC USPPs. A comparison between the $4f$ AE and pseudized radial wave functions is shown in Fig. 1

COMPUTATIONAL DETAILS

Convergence of the plane wave basis set

As the systems under study were not neutral, all plane wave calculations were performed with an isolated box 15 $\times 15 \times 15$ Å^3 large, with the Hockney Poisson solver. The quality of a PW basis depends only on the energy cutoff and, moreover, such a basis set does not suffer from the basis set superposition error (BSSE).[18] As a first test of the SC USPPs, we compute the total integrated absolute value of the local spin polarization,

$$\zeta = \int d\mathbf{r} \left| \frac{\rho_\alpha(\mathbf{r}) - \rho_\beta(\mathbf{r})}{\rho_\alpha(\mathbf{r}) + \rho_\beta(\mathbf{r})} \right|, \quad (6)$$

for the triply charged gadolinium ion, Gd^{3+}.

As can be observed in Fig. 2 the value of ζ nicely approaches the target value of seven stemming from the seven unpaired $4f$ electrons localized on the Gd^{3+} ion upon increasing the cutoff; in particular, a value of only 25 Ry already
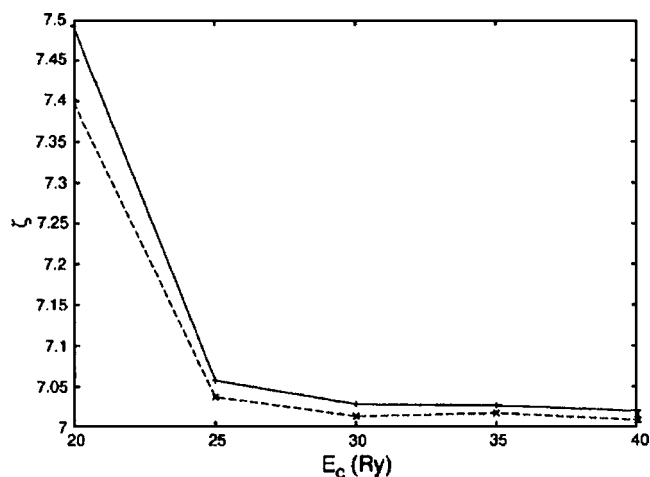
FIG. 2. Convergence of the total integrated absolute value of the local spin polarization for Gd^{3+} (SC USPP without NLCC in solid line, and with NLCC in dashed line).

FIG. 4. Convergence of the interaction energy (solid line and left axis) and optimized ion-ligand distance (dashed line and right axis) for the $Gd^{3+}(H_2O)$ complex with the large core ultrasoft pseudopotential including NLCC.

yields an acceptable PP quality. This is especially true for the SC USPP that includes the NLCC correction.

We have also calculated the interaction energy and the optimized Gd–O distance of the microsolvated $Gd^{3+}(H_2O)$ complex as a function of PW cutoff using the SC and LC USPPs (see Figs. 3 and 4, respectively).

Except for the SC USPP that includes NLCC, for which an almost converged Gd–O distance can only be obtained for at least 30 Ry, increasing the cutoff from 20 to 25 Ry is sufficient to converge also these properties to a useful accuracy. In addition, although our calculations were not symmetry constrained, the C_{2v} and C_{3v} symmetries of the water and ammonia molecules (the latter data are not shown) are very well reproduced and no significant tilt angle (i.e., angle between the Gd–O/Gd–N axis and the dipole moment axis of H_2O/NH_3) is observed. From these convergence checks we conclude that the calculation of these properties is converged to a satisfactory level at 30 Ry for the SC USPP that includes NLCC and at 25 Ry for the other USPPs.
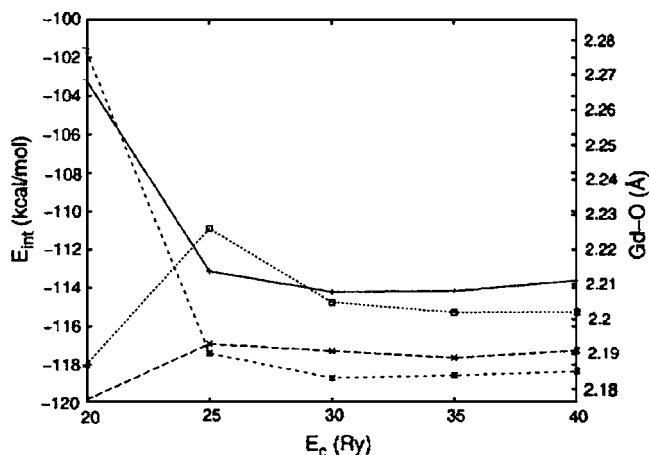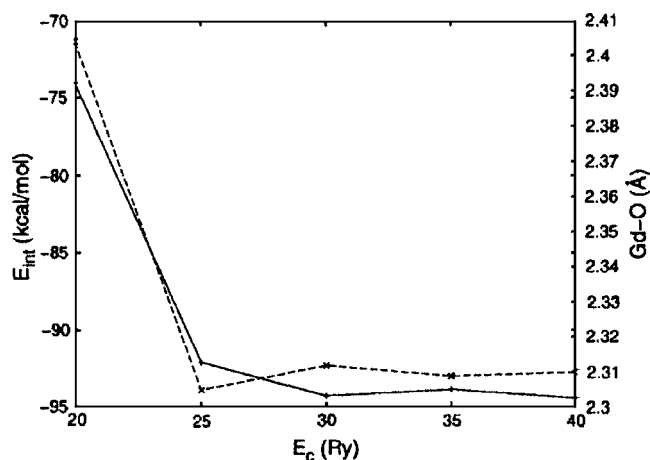
FIG. 3. Convergence of the interaction energy (on left axis, "plus" sign without NLCC and "star" sign with NLCC) and optimized ion-ligand distance (on right axis, "cross" sign without NLCC and "box" sign with NLCC) for the $Gd^{3+}(H_2O)$ complex with the small core ultrasoft pseudopotential.

Reference calculations using Gaussian basis sets

Prior to an analysis of the role of the $4f$ electrons in the complexation of gadolinium, we will first establish the transferability of the new USPPs. Accordingly, we will compare our results with data obtained from "effective core potential" (ECP) calculations using Gaussian basis sets. In order to calculate interaction energies corrected for the BSSE the minimum of a potential energy surface will then be determined not by direct optimization but rather by interpolation between points separated by 0.1 Å. The BSSE was evaluated from an adaptation of the *a posteriori* counterpoise correction method of Boys and Bernardi.[27]

We used ECPs of various sizes from the Stuttgart/ Cologne group (with their associated basis sets) and from Cundari and Stevens[9] (with the augmented triple-ζ basis set developed by Glendening and Petillo[7]). Thus, our LC USPPs will be compared with a large (and frozen) core ECP (Refs. 3 and 4) of same size, while our SC USPPs will be compared with either an ECP of same size[9] or with an ECP that puts in addition the $4s$, $4p$, and $4d$ orbitals into the valence space.[28–30] All calculations were performed with the MOLPRO quantum chemistry package[31] with the default numerical integration grid for DFT. Finally, it is stressed that the USPPs were constructed from atomic AE calculations using the *identical* electronic structure method (i.e., Kohn-Sham DFT together with the PBE functional) whereas the ECPs to be used with the Gaussian basis sets in PBE, MP2, and CCSD(T) calculations were constructed from Hartree-Fock atomic reference calculations.

RESULTS AND DISCUSSION

The transferability and accuracy of the Gd USPPs will be judged by looking at structural and energetic results obtained on the $Gd^{3+}(H_2O)$ and $Gd^{3+}(NH_3)$ microsolvation complexes compiled in Tables I and II, respectively. The main data have been grouped into two blocks in which the $4f$ electrons are either included in the valence (group I) or in the core (group II) space.

TABLE I. Calculated structural and energetic data of the $Gd^{3+}(H_2O)$ complex.

Method[a]	Gd PP[b]	Gd–O[c]	E_{int}[d]
Group I ("small core")			
UKS/PBE	$[1s^2-3d^{10}]$ ECP	2.22	−117.25
UKS/PBE	$[1s^2-4d^{10}]$ USPP w NLCC	2.20	−118.67
UKS/PBE	$[1s^2-4d^{10}]$ ECP	2.21	−107.75
UKS/PBE	$[1s^2-4d^{10}]$ USPP w/o NLCC	2.19	−113.13
MP2	$[1s^2-3d^{10}]$ ECP	2.19	−104.54
MP2[e]	$[1s^2-4d^{10}]$ ECP	2.18	−105.15
CCSD(T)	$[1s^2-4d^{10}]$ ECP	2.19	−103.23
Group II ("large core")			
KS/PBE	$[1s^2-4d^{10},4f^7]$ ECP	2.22	−106.84
KS/PBE	$[1s^2-4d^{10},4f^7]$ USPP w/o NLCC	2.26	−115.69
KS/PBE	$[1s^2-4d^{10},4f^7]$ USPP w/NLCC	2.31	−92.08
CCSD(T)	$[1s^2-4d^{10},4f^7]$ ECP	2.25	−93.7
Group III (core polarization)			
UKS/PBE	$[1s^2-4d^{10},4f^7]$ CPP	2.10	−130.2
CCSD(T)	$[1s^2-4d^{10},4f^7]$ CPP	2.22	−101.0

[a]KS=spin-unpolarized (closed-shell) Kohn-Sham, and UKS=unrestricted spin-polarized (open-shell) Kohn-Sham.
[b]Energy cutoff for plane wave expansion set to 25 Ry for all USPPs but the $[1s^2-4d^{10}]$ USPP with NLCC for which it is set to 30 Ry.
[c]Gd-0 distance in Å.
[d]Interaction energy in kcal/mol.
[e]Reference 7.

Within group I, we first expect that the USPP (with no NLCC) should be similar to the ECP that shares the same core size. This is more apparent in the case of ammonia, with corresponding interaction energies only differing by 2.6%, whereas the difference amounts to 5.8% with respect to the ECP with the smaller core. However, we also expect that the agreement with the latter PP should be more favorable if the USPP is corrected with the NLCC. And indeed, the absolute errors on the corresponding interaction energies are then reduced to only 1.2% and 1.3% for water and ammonia, respectively. Having established the validity of our SC USPPs, we now judge their accuracy in comparison with post-Hartree-Fock methods. It appears that PBE can overbind up to approximately 15 kcal/mol with respect to the CCSD reference calculations, the $[1s^2-4d^{10}]$ ECP/PBE calculation providing the smallest error (i.e., about 5 kcal/mol). However, such an overbinding tendency is a known feature of GGA calculations and therefore should not be corrected by any pseudopotential (whose aim is really to reproduce all-electron data). The small errors obtained from the

TABLE II. Calculated structural and energetic data of the $Gd^{3+}(NH_3)$ complex (see Table I).

Method	Gd PP	Gd–N[a]	E_{int}
Group I ("small core")			
UKS/PBE	$[1s^2-3d^{10}]$ ECP	2.34	−138.46
UKS/PBE	$[1s^2-4d^{10}]$ USPP w NLCC	2.35	−136.51
UKS/PBE	$[1s^2-4d^{10}]$ ECP	2.34	−127.08
UKS/PBE	$[1s^2-4d^{10}]$ USPP w/o NLCC	2.33	−130.40
MP2	$[1s^2-3d^{10}]$ ECP	2.33	−124.34
MP2[b]	$[1s^2-4d^{10}]$ ECP	2.32	−121.28
CCSD(T)	$[1s^2-4d^{10}]$ ECP	2.33	−122.40
Group II ("large core")			
KS/PBE	$[1s^2-4d^{10},4f^7]$ ECP	2.36	−126.93
KS/PBE	$[1s^2-4d^{10},4f^7]$ USPP w/o NLCC	2.41	−128.68
KS/PBE	$[1s^2-4d^{10},4f^7]$ USPP w/NLCC	2.49	−109.02
CCSD(T)	$[1s^2-4d^{10},4f^7]$ ECP	2.40	−111.46
Group III ("core polarization")			
UKS/PBE	$[1s^2-4d^{10},4f^7]$ CPP	2.23	−146.90
CCSD(T)	$[1s^2-4d^{10},4f^7]$ CPP	2.36	−118.80

[a]Gd–N distance in Å.
[b]Reference 7.

$[1s^2-4d^{10}]$ ECP/PBE calculation is probably an artifact stemming from the non-negligible interactions between the $4f$ and the $4s$, $4p$, and $4d$ orbitals. Concerning the ion-ligand distances, the PBE/USPP calculations correctly reproduce the MP2 and CCSD(T) values (the maximum error is only 0.02 Å). We will now examine the results obtained with larger cores in order to check whether computational time could be saved.

Distances within group II are all larger and (absolute) interaction energies smaller (for a given method) than within group I. However, we remark a close proximity first between the ECP/PBE results (both the interaction energies and the distances) in group II and the PBE results in group I obtained with the $[1s^2-4d^{10}]$ ECP, and then between the USPP/PBE interaction energies in group II and in group I, both obtained without NLCC (the distances for water and ammonia being, respectively, 0.07 and 0.08 Å too large in group II). In order to increase the ability of these "large core" PPs to reproduce "small core" data, we have considered for both of them two corrections different in nature. For the USPP, this is the NLCC, whereas for the ECP it consists in correcting the absence of polarization of the core due to the charges of the valence electrons and of all other cores. This polarization has been taken into account by adding an effective core polarization potential (CPP) in the Müller *et al.* framework.[32] The parameters of the CPP for the Gd^{3+} ion were already determined in a previous work.[33] Surprisingly, the USPP/PBE with NLCC results in a worse agreement, even producing the largest ion-ligand distances and the smallest (absolute) interaction energies (although the error on the latter with respect to ECP/CCSD(T) is lower than 2%). PBE calculations using CPPs, which are reported within group III, produce worse results too but just in the opposite direction, namely, leading to the shortest ion-ligand distances and the largest (absolute) interaction energies. In contrast, when the CCSD(T) method is used, a better agreement with group I is observed. We interpret this failure by emphasizing the importance of combining the right pseudopotential with the right method (according to the target property): clearly, while this CPP is very well suited to post-HF calculations (see also Ref. 34), it cannot be used safely within DFT to determine with accuracy geometries and interaction energies. Eventually, the failure of both corrections limits the efficiency of both LC pseudopotentials (within DFT) to the accuracy priorly achieved.

We conclude this section by a comment on the role of the $4f$ electrons in the complexation. Clearly, the error on the metal-ligand distance becomes very small as soon as the $4f$ electrons are treated explicitly. A further evidence for their participation in the complexation is the contribution to the total integrated absolute value of the local spin polarization due to the presence of the ligand, which is 0.033 (i.e., $\zeta = 7.047$) for H$_2$O and 0.059 (i.e., $\zeta = 7.073$) for NH$_3$ at 30 Ry using our SC USPP with NLCC. By comparison, the LC USPPs lead to a contribution of zero by definition. Indeed, this result can be interpreted as a net charge transfer of α-spin density from the ligand to the Gd(III) ion.[7] Thus, these fine details can only be captured when the $4f$ electrons are treated in the valence shell.

CONCLUSIONS

In summary, we have constructed Vanderbilt's ultrasoft pseudopotentials for gadolinium, where the $4f$ electrons belong either to the core or to the valence space. Using small complexes, we have established that PBE calculations with the small-core USPPs can compete with CCSD(T) reference calculations using equivalent pseudopotentials. If one would like to perform calculations with the large-core USPPs (mainly because of the closed shell configuration and reduced computational cost), it is necessary to keep in mind that only a qualitative behavior could be obtained and that a large error on both geometry and interaction energy could appear.

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