PHYSICAL REVIEW B VOLUME 60, NUMBER 20 15 NOVEMBER 1999-II

Importance of nonlinear core corrections for density-functional based pseudopotential calculations

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(Received 12 May 1999; revised manuscript received 1 July 1999)

We have investigated the importance of nonlinear core corrections (NLCC) for accurate density-functional based pseudopotential (PSP) calculations. The quality of the PSP approach is assessed by comparing it to accurate all-electron calculations. It is found that a correct description of spin-polarized states requires the NLCC, even for first-row atoms. This is essential for simulations on magnetic systems and reaction processes that involve radicals. The NLCC is also essential for a realistic description of elements with more long-range core states such as alkali atoms. We propose a functional form for the partial NLCC, which is feasible in plane-wave calculations and suggest a scheme for choosing the default cutoff radius. [S0163-1829(99)02043-3]

I. INTRODUCTION

Modern implementations of electronic structure methodologies can be divided into two groups. On one side, there are all-electron (AE) approaches that consider both core and valence electrons explicitly in the calculation. Since core electrons are strongly localized, these methods need to employ localized basis functions such as augmented plane waves (APW),[1] linearized muffin-tin orbitals (LMTO),[2] Slater-type orbitals (STO's), or Gaussian orbitals.[3–6] Alternatively, one can construct pseudopotentials (PSP's) which effectively project out the core states from the problem while retaining the physical properties of the valence region. Extensive discussions and reviews of this approach have appeared in Refs. 7–11. Many pseudopotential applications employ a plane-wave basis set[12–14] but a variety of local-orbital based implementations exist as well.[15–22] Recently, there has also been a lot of work aimed at mesh-based approaches.[23–28] Nevertheless, many PSP applications use plane waves. The size of the basis needed for a calculation of this type depends strongly on the shape (hardness) of the atomic pseudopotentials. Several approaches have been proposed to construct soft pseudopotentials, which minimize the numerical costs while retaining the accuracy of the approach.[29–32]

Although the aspect of PSP softness is vital for practical applications based on plane-wave basis sets, the more important problem is pseudopotential transferability, i.e., the ability of the PSP to reproduce all-electron results for electronic configurations that differ from the one used for its construction. By definition, all PSP's that are created from first principles reproduce the all-electron eigenvalues of the electronic reference state used in the PSP construction. This is usually the spin-averaged ground state of the corresponding atom. However, most atoms have spin-polarized ground states and the PSP must be transferable in order to describe these states accurately. Similar problems arise when atoms are placed in a molecular environment and donate or accept electrons.

If the density-functional formalism is used in the usual Kohn-Sham approach,[33,34] the total energy expression contains the term $E_{xc}[\rho_{\uparrow}(\boldsymbol{r}),\rho_{\downarrow}(\boldsymbol{r})]$, a nonlinear functional that accounts for the exchange-correlation energy of the electrons in the system. The $\rho_{\uparrow}(\boldsymbol{r})$ and $\rho_{\downarrow}(\boldsymbol{r})$ are the spin-up and spin-down densities, which may be written as a sum of core and valence contributions. However, in simple pseudopotential methods, $\rho_{\sigma}(\boldsymbol{r})$ is replaced by the density associated with the pseudovalence orbitals $\rho_{\sigma}^{val}(\boldsymbol{r})$ only. This approximation corresponds to a linearization of the E_{xc} functional, which is only valid if the valence density in the core region does not change much when the atomic electronic configuration is altered. For this reason, Louie *et al.*[35] introduced a scheme that takes the nonlinear nature of the E_{xc} functional into account by explicitly adding a core charge density, i.e., replacing $\rho_{\sigma}^{val}(\boldsymbol{r})$ by $\rho_{\sigma}^{val}(\boldsymbol{r})+0.5\,\rho^{c}(\boldsymbol{r})$. This correction to the standard PSP approach is commonly known as the nonlinear core correction (NLCC). It only needs to be applied to the exchange-correlation part of the total energy functional since the linearization is valid for all other terms (Coulomb potential etc.).

Turning towards the discussion of an appropriate choice for ρ^{c}, it can be expected that the most reliable description will be obtained if the PSP and AE exchange-correlation potentials are identical for all those regions of space where PSP and AE valence densities are the same or similar. This way, possible sources of error will be limited to the core region close to the nucleus where the all-electron and pseudovalence densities may differ substantially due to the pseudization of the valence orbitals (while the all-electron valence states have nodes, the corresponding pseudovalence

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states are nodeless). For larger distances, however, AE and PSP valence densities are identical. Consequently, one has to require that ρ^c is equivalent to the true AE core charge density outside a well-chosen cutoff radius r_{core}. One possible choice is to set $r_{core}=0$ (full NLCC). However, this approach is not feasible for plane-wave-based applications since the full core density is strongly localized. For this reason, the true core density is usually replaced by an arbitrary but smooth function for $r \leqslant r_{core}$. The questions that remain to be answered are: (a) How important is the NLCC for different atomic species, (b) are core relaxation effects significant, and (c) what is the best choice for r_{core}?

Although the NLCC has been used extensively in a variety of different applications, the above questions have rarely been addressed directly. There is some work stressing the increased importance of the NLCC for gradient-corrected density functionals[36–38] and a very recent publication dealing with PSP transferability for transition metal atoms.[39] In that paper, the authors found that the standard pseudopotential approach was incapable of reproducing all-electron s-d transfer energies in transition metals even if nonlinear core corrections were applied. They introduced spin-dependent PSP's to obtain a better transferability. We will discuss these results in our paper and show that an accurate description of transition metals is possible without adding the additional complication of a spin-dependent pseudopotential. However, our paper includes not only transition metals but also a variety of other atomic species since our main goal is a systematic study aimed at determining the quantitative and possibly qualitative differences between PSP's with and without the NLCC. In Sec. III, we report results for atoms found in the first row and sixth column of the Periodic Table. Trends for alkali- and transition-metal atoms will be discussed as well. We will show that the discrepancies between all-electron and pseudopotential methods can be easily understood and corrected.

II. METHOD

All results have been obtained using the density-functional formalism[33,34] and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.[40] Both the generalized-gradient approach (GGA-PBE) and the local spin-density approximation (LSDA) contained in the PBE functional have been used. For the pseudopotential construction and atomic calculations, a highly accurate numerical code was employed. The PSP eigenvalues for the reference states usually deviate from their all-electron counterparts by 1 meV or less. For all elements, the spin-averaged ground state of the spherically symmetric atom has been used as the reference state for the PSP construction. While it is possible to chose reference states that are closer to electronic configurations found in solids or molecules, the main objective of this paper is to test PSP transferability. For a transferable PSP, the exact choice of the reference state should be of minor importance.

Our results are based on pseudopotentials constructed with a modified Troullier-Martins (TM) scheme.[32] The difference between the new and the original TM approach is that the pseudo-wave functions match function value and first to sixth derivative at the cutoff radius r_{cut} whereas the original TM method only matched up to the fourth derivative. In order to fulfill the additional conditions, the TM wave-function ansatz was extended to include two more polynomial terms. This modified approach leads to PSP's that are more easily integrable since the discontinuity at $r=r_{cut}$ appears only in the fifth derivative of the PSP (not in the third derivative as is the case for the original TM scheme). The cutoff radii for the PSP construction have been chosen conservatively (see Table I). Note that since our modified TM method matches two additional derivatives at $r=r_{cut}$, the corresponding pseudo-wave functions are closer to their all-electron counterparts than with the original TM scheme (provided the same cutoff radius is used). PSP construction and calculations were performed with the same functionals to ensure consistency.

TABLE I. Cutoff radii (a_B) used for the pseudopotential construction. Mn^c corresponds to a conservative Mn pseudopotential, which includes the $3s$ and $3p$ semicore states in the valence basis.

	Li	B	C	N	O	F	S	Se	Mn	Mn^c
s	2.58	1.40	1.14	0.96	0.83	0.73	1.53	1.67	2.53	0.81
p	2.58	1.40	1.14	0.96	0.83	0.73	1.70	1.75	2.75	0.81
d	2.58	1.40	1.14	0.96	0.83	0.73	1.70	2.40	0.81	0.81

The original ansatz of Louie *et al.*[35] for the functional form of the NLCC core charge density has a discontinuity in the second derivative at $r=r_{core}$. In a PBE-GGA calculation, this would lead to a discontinuity in the pseudopotential itself, which is clearly undesirable. For this reason, we use a functional ansatz for ρ^c which is equivalent to the TM ansatz for a s-type pseudo-wave function

$$\rho^c(r)=\begin{cases} \exp\left\{ \sum_{i=0}^{7} c_i\, r^{2i} \right\} & r \leqslant r_{core} \\ \rho^c_{full} & r \geqslant r_{core} \end{cases} \tag{1}$$

and determine the c_i from the condition that function value and up to sixth derivative of $\rho^c(r)$ at $r=r_{core}$ are continuous and that the integral:

$$\int dr \left(\frac{d^2 \rho^c}{dr^2} \right)^2 \rightarrow \min \tag{2}$$

is minimized. We would like to note that TM (Ref. 32) proposed the functional form (1) for the pseudo-wave function in their method because it is very well representable in a plane-wave basis. Since we use the same ansatz for ρ^c our approach will be numerically efficient in plane-wave applications as well. Additionally, the condition (2) leads to a smooth behavior of ρ^c. Of course, the actual convergence of the results as a function of plane-wave cutoff energy depends on the choice for r_{core}, which will be discussed below.

After generating the PSP's we performed calculations on atoms and molecules using the Gaussian-orbital based density-functional code NRLMOL developed by Pederson, Porezag, and Jackson.[5,6,21] This method is based on an accurate numerical integration scheme. Besides the expansion of the wave functions into Gaussian orbitals, no additional approximations are used. The program allows for mixed all-electron and pseudopotential descriptions within the same calculation, i.e., some atoms may be treated within an all-electron scheme while others may be described with PSP's. This feature can be used to isolate the effect of pseudopotentials for single atoms in a larger structure. We have employed very large basis sets and checked that all results are converged with respect to basis set size.

III. RESULTS AND DISCUSSION

While the transferability of a pseudopotential should always be checked for the particular system or problem that is investigated, there are systematic tests that can be performed for each individual atom before focusing on the more complicated condensed matter applications. For many applications, spin-polarized electronic states are important. We give results for atomic spin polarization energies in Secs. III A and III B. The problem of *s*-*d* transfer energies in transition metals will also be addressed. Finally, we use the example of LiF to discuss possible sources of error, which only arise when atoms are placed in a molecular or solid environment.

For all atomic species investigated here we have performed all-electron calculations and pseudopotential calculations without the NLCC, with a partial NLCC using different core radii r_{core}, and with the full NLCC. Not surprisingly we find that the order of magnitude of the deviations between the AE and PSP approaches depends strongly on the atomic species. Data that show the convergence of the results as a function of r_{core} can only be given for a few selected examples since journal space is limited. However, our calculations have revealed two important points: (1) Reducing r_{core} always improves the agreement between the AE and PSP methods (and thus increases PSP transferability); and (2) for small values of r_{core}, the results are converged, i.e., independent of r_{core}. In Sec. III D we will suggest a simple way for choosing the largest possible r_{core}, which leads to converged results. However, more importantly, our findings show that applying the full NLCC is the most accurate approach and therefore it is frequently used here.

A. Spin-polarization energies for atoms in the first row and oxygen column

First-row atoms are characterized by a single 1*s* core shell. For B through Ne, this core shell is strongly localized. Therefore, it is usually assumed that these elements can be treated without the NLCC. However, Fig. 1 shows that due to the localized nature of the valence states there is still a significant overlap between valence and core charge densities. Therefore, it is not entirely clear if nonlinear core-valence interactions may be completely ignored. One particularly interesting question is if the energy difference between the spin-averaged reference state used in the pseudopotential construction and the (typically spin polarized) atomic ground state is accurately described. In the following, this energy difference will be called spin-polarization energy (SPE). Spin-polarized states may occur in simulations of reaction processes between molecules, radicals, and surfaces and it is important that they are described accurately. The spin-polarized atomic ground state is also the reference state for calculations of binding energies.

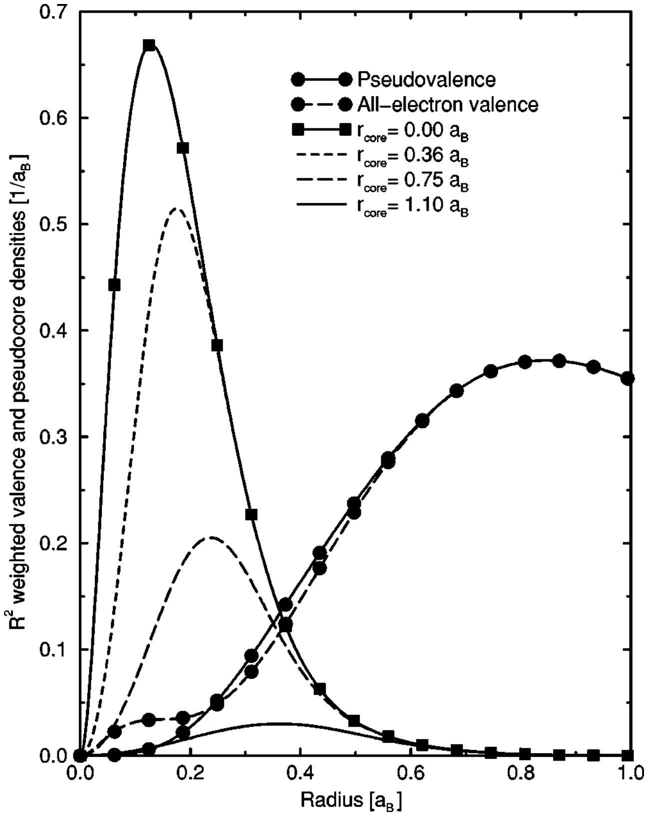

FIG. 1. Oxygen valence and core densities for different NLCC core radii. Results have been obtained with the GGA-PBE functional.

Figure 2 shows the errors in the PSP based spin-polarization energies for Li and B though F as calculated within both LSDA and GGA-PBE. Results are shown for calculations including the full NLCC and no NLCC. Errors are measured with respect to the corresponding all-electron values. The deviations are largest for N, which has a fully polarized 2*p* shell and a total SPE of 3.02 eV within LSDA and 3.12 eV within GGA-PBE. If no NLCC is applied, the SPE errors amount to about 10% of the total SPE. Interestingly, the errors are larger for nonspherical atoms (which are usually lower in energy than the spherical ones, especially within GGA-PBE). This is due to the fact that the valence densities in nonspherical atoms are more localized than in spherical ones. The total SPE error can be as large as 0.3 eV (for N and O within GGA-PBE). Errors of this magnitude will lead to discrepancies of approximately 0.6 eV if binding energies for homonuclear dimers are calculated. For example, the AE GGA-PBE dissociation energy for O_2 is 6.2 eV whereas it is determined to be 5.7 eV in the PSP approach without the NLCC. At this point, it should be noted that the experimental binding energy of O_2 is only 5.2 eV. However, the discrepancy between the AE and experimental results has to be attributed to deficiencies in modern density functionals and the pseudopotential calculation should reproduce the AE results since it is based on the same theory.

Including the NLCC greatly improves the performance of the PSP approach, leading to a maximum deviation of only 0.02 eV (for the SPE of N). Hence, it can be concluded that SPE's of first-row atoms are very well described if a full NLCC is applied. The question which remains to be answered is how the SPE error depends on the choice of the

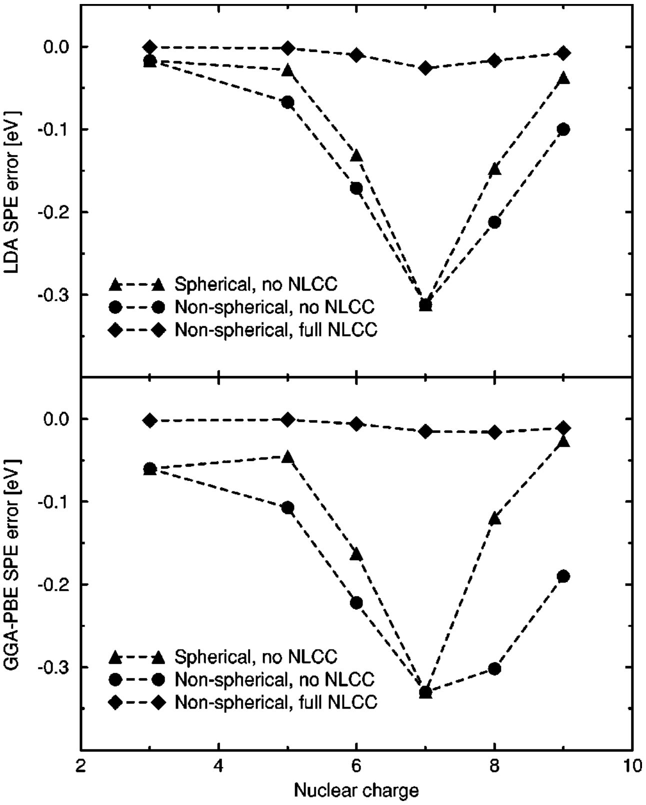

FIG. 2. Errors in the atomic spin-polarization energies with respect to all-electron values as calculated with the full NLCC and without NLCC. Results are given for both spherical and nonspherical atoms. GGA-PBE predicts nonspherical atomic ground state densities except for Li and N.

core radius if only a partial NLCC is applied. Table II shows results for a GGA-PBE calculation on oxygen (the behavior is very similar for the other first-row atoms as well). The corresponding core densities are displayed in Fig. 1. For core radii of about $0.4a_\mathrm{B}$ or smaller, the spin-polarization energies determined with a partial NLCC do not differ from the full NLCC results. Turning towards heavier atoms, Table III presents the calculated data for the sulphur and selenium atoms, which have the same number of valence electrons as oxygen but a more diffuse charge distribution. The errors for S and Se are smaller than for O. Again, including the NLCC leads to an excellent agreement with the all-electron results.

TABLE II. Atomic GGA-PBE spin-polarization energies (eV) for oxygen as calculated with all-electron and PSP methods using the NLCC and different core radii r_{core} (first line, given in a_B). $r_{core}=\infty$ corresponds to a neglect of the NLCC.

	AE	0.00	0.36	0.75	1.10	∞
SPE	−1.86	−1.88	−1.88	−1.95	−2.07	−2.16
Err.		−0.02	−0.02	−0.09	−0.21	−0.30

TABLE III. Atomic spin-polarization energies (eV) for S and Se as calculated with all-electron and PSP methods. The core radii of $0.92a_\mathrm{B}$ (S) and $1.25a_\mathrm{B}$ (Se) lead to converged results. $r_{core}=\infty$ corresponds to a neglect of the NLCC.

	LSDA			GGA-PBE		
			Sulphur			
	AE	0.92	∞	AE	0.92	∞
SPE	−0.75	−0.76	−0.83	−0.99	−0.98	−1.05
			Selenium			
	AE	1.25	∞	AE	1.25	∞
SPE	−0.63	−0.63	−0.72	−0.82	−0.81	−0.91

As has been demonstrated in the preceding paragraphs, neglecting the nonlinear behavior of the core-valence interactions leads to an overestimation of the total energy magnitude of the spin-polarized states. This behavior may be easily understood if one considers that the only explicitly spin-dependent energy contribution in a density-functional calculation is the exchange-correlation energy, which is dominated by the local exchange term

$$E_x=-\frac{3}{4}\left(\frac{6}{\pi}\right)^{1/3}\int d\boldsymbol{r}[\rho_\uparrow(\boldsymbol{r})^{4/3}+\rho_\downarrow(\boldsymbol{r})^{4/3}]. \tag{3}$$

Further, assuming that the same angular and radial states are occupied for spin-averaged and spin-polarized atoms, the total electron densities $\rho(\boldsymbol{r})=\rho_\uparrow(\boldsymbol{r})+\rho_\downarrow(\boldsymbol{r})$ in both systems will be very similar. Therefore, the energy difference between the spin-polarized and spin-averaged configuration may be approximated as

$$E_{SPE}\approx-\frac{3}{4}\left(\frac{6}{\pi}\right)^{1/3}\int d\boldsymbol{r}\left\{\left[\frac{\rho(\boldsymbol{r})+\Delta(\boldsymbol{r})}{2}\right]^{4/3}+\left[\frac{\rho(\boldsymbol{r})-\Delta(\boldsymbol{r})}{2}\right]^{4/3}-2\left[\frac{\rho(\boldsymbol{r})}{2}\right]^{4/3}\right\}, \tag{4}$$

where $\Delta(\boldsymbol{r})$ is the difference of the up- and down-spin densities. Using a Taylor expansion, Eq. (4) can be transformed into

$$E_{SPE}\approx-\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int d\boldsymbol{r}\sum_{j=1}^{\infty} t_{2j}\frac{\Delta(\boldsymbol{r})^{2j}}{\rho(\boldsymbol{r})^{2j-4/3}},$$

$$t_{2j}=\frac{2}{9},\frac{5}{243},\frac{44}{6561},\ \ldots>0. \tag{5}$$

Note that since the core states are always completely filled, they do not contribute to $\Delta(\boldsymbol{r})$ but they do contribute to $\rho(\boldsymbol{r})$. Hence, neglecting the core density in a pseudopotential calculation leads to a reduction of the denominator in Eq. (5) and consequently to a systematic overestimation of the magnitude of E_{SPE}.

B. Transition-metal atoms

Transition-metal atoms, especially those of the $3d$ series, have strongly localized d electrons. Further, it is known that reliable PSP's for transition metals need to incorporate nonlinear core corrections. For these reasons, it can be expected that the problems discussed in the preceding section will be even more severe for these systems. This is particularly true for Mn since it has a fully polarized d shell. Therefore, we

TABLE IV. Atomic LSDA spin-polarization energies (eV) for Mn as calculated with all-electron and PSP methods using different core radii r_{core} (first line, given in a_B). $r_{core}=\infty$ corresponds to a neglect of the NLCC.

AE	0.00	0.43	0.65	0.80	2.50	∞
−5.28	−5.31	−5.31	−5.40	−5.57	−7.58	−12.37

will focus our discussion on this element. Table IV shows results for the LSDA spin-polarization energies as calculated within the all-electron and PSP approaches using different core radii for the NLCC. The corresponding valence and core densities are displayed in Fig. 3. It is apparent that the PSP method without the NLCC gives completely unreasonable results. Further, the core radius must be chosen fairly small ($0.43a_\mathrm{B}$) in order to achieve converged results. However, if the NLCC is applied correctly, it leads to a very good agreement with the all-electron calculation.

In Ref. 39, the authors found that s-d transfer energies (i.e., the total energy differences between the atomic s^2d^n and s^1d^{n+1} electronic configurations) are described very poorly with PSP's even if the NLCC is applied. In particular, they determined the all-electron and the PSP+NLCC s-d transfer energies for Mn to be about 1 and 2 eV, respectively. We have calculated the same quantity and give the results in Table V. The all-electron and converged PSP+NLCC s-d transfer energies are found at 1.04 and 1.20 eV, respectively. Note that the error increases significantly if r_{core} is chosen too large. For example, the calculated PSP+NLCC s-d transfer energy determined with $r_{core}=2.50a_\mathrm{B}$ is 2.26 eV, similar to the result published in Ref. 39.

TABLE V. Atomic s-d transfer energies [eV] for Mn as with all-electron and PSP methods using different core radii r_{core} (first line, given in a_B). $r_{core}=\infty$ corresponds to a neglect of the NLCC. The Ar core line refers to a calculation where the $3sp$ electrons are treated as core electrons.

	AE	0.00	0.43	0.65	0.80	2.50	∞
Ar core	1.04	1.20	1.20	1.24	1.33	2.26	4.22
Ne core	1.04	1.06	1.06				1.35

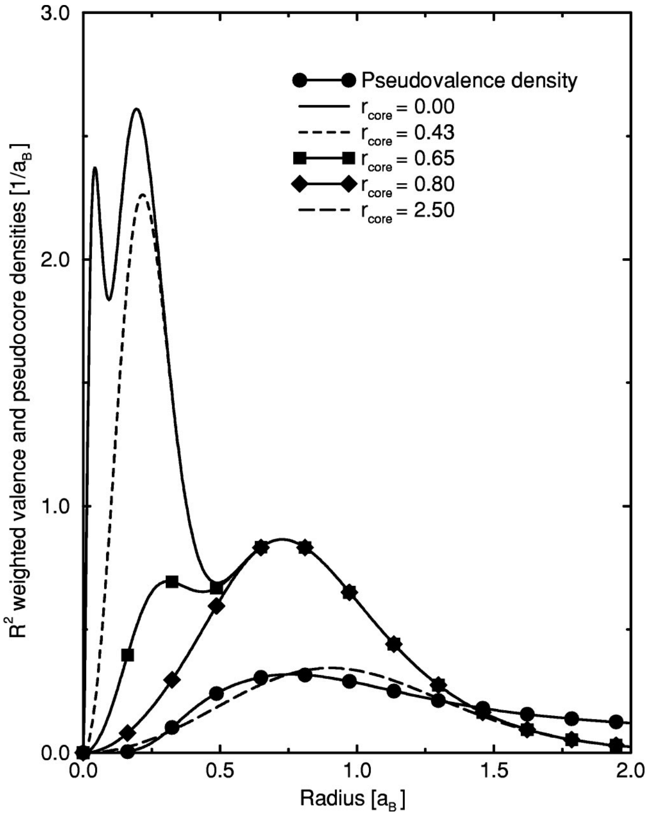

FIG. 3. Manganese valence and core densities for different NLCC core radii. Results have been derived within LSDA. The all-electron valence density (not displayed here) is almost identical to the pseudo valence density because the nodeless $3d$ state dominates for smaller distances.

Traditionally,[35] r_{core} has always been set approximately to where the core and pseudovalence densities are equal. For first-row and second-row atoms such as C, N, Al, or Si, this choice leads to converged results. For Mn, on the other hand, the traditional rule leads to a r_{core} of about $1.4a_\mathrm{B}$, which is much larger than the value needed for a converged result. The authors of Ref. 39 may have used the old and established prescription to determine r_{core}, which could explain the discrepancies between their and our data. The reason for the failure of the traditional approach in $3d$ transition metals is the strong spatial overlap of $3d$ valence and $3sp$ core states in the atom.

Although the NLCC leads to a much improved description of the s-d electron transfer, there is still a difference of 0.16 eV between PSP and all-electron results, which needs further discussion. Besides deviations arising from the necessary pseudization of the valence orbitals, the neglect of core relaxation needs to be addressed. The calculations presented so far were based on PSP's that assigned the $3s$ and $3p$ states to the core. However, as can be seen from Fig. 3, the spatial range of these states is very similar to that of the $3d$ electrons. Transferring an electron from the rather diffuse $4s$ state to the localized $3d$ state will increase the Coulomb repulsion in this area and hence lead to a relaxation of the $3s$ and $3p$ states. Assigning these states to the core makes such a relaxation impossible. For this reason, we have constructed a *conservative* pseudopotential for Mn, which includes the $3s$ and $3p$ states in the valence basis. As can be seen from Table V, the conservative approach leads to results which are in excellent agreement with the all-electron data. Therefore, it can be concluded that the PSP approach describes transition-metal atoms with a similar accuracy as other atom types if both nonlinear core-valence interactions and semicore relaxation effects are included in the method.

C. Lithium fluoride

While spin polarization or a change of the electronic configuration is one way to alter the atomic electron density, another way is the embedding of the atom into a solid, cluster, or molecule. It can be expected that the effects will be largest for atoms with a very diffuse low-density electronic charge distribution if they are combined with atoms characterized by compact localized states. Prominent examples for such systems are alkali-halogenide compounds such as LiF.

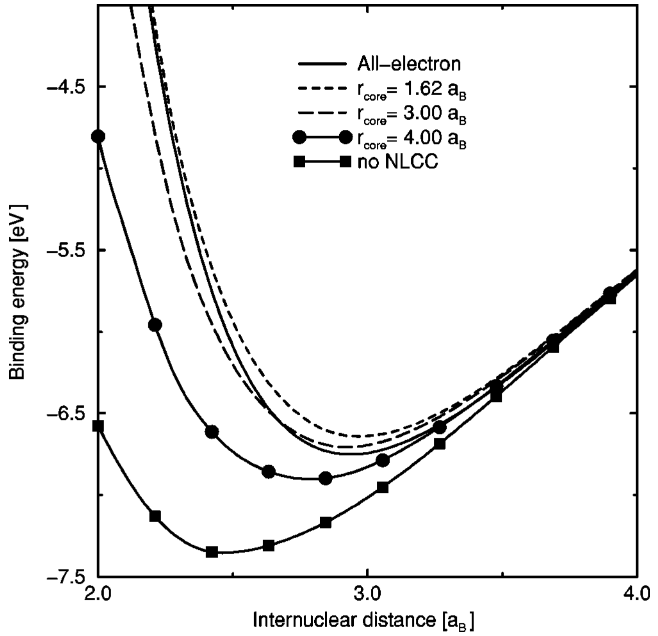

FIG. 4. LSDA cohesive energy as a function of internuclear distance for the LiF molecule. The PSP+NLCC results for $r_{core} = 1.62a_B$ are identical to the full NLCC.

In order to demonstrate the problems that occur for this combination of elements, we will focus on the LiF diatomic molecule. Figure 4 shows the cohesive energy of this molecule as a function of interatomic distance as calculated within LSDA. The PSP calculation without the NLCC overestimates the binding energy by about 1 eV and underestimates the bondlength by more than $0.5a_B$. Applying a full NLCC corrects this deficiency and leads to a good agreement with the all-electron result. The partial and full NLCC results agree for $r_{core} \leqslant 1.62a_B$. The remaining difference between the PSP+NLCC and AE data can be attributed to pseudization effects and the neglect of the 1s core relaxation. Note that in order to rule out additional sources of error, the F atom has also been treated in an all-electron fashion here.

Figure 5 illustrates the reason for the failure of the standard (non-NLCC) PSP approach for LiF. It displays the contribution of Li and F densities to the total molecular density for an internuclear distance of $2.30a_B$, which is about 20% shorter than the all-electron equilibrium distance but very close to the equilibrium distance if calculated in a PSP approach without the NLCC. Li has a rather diffuse 1s core state, which dominates the total atomic density for $r \leqslant 1.6a_B$. However, this is the spatial range of the bonding region in LiF and hence there is a strong overlap of the F valence and Li core charges. Note that there is a region where the Li pseudovalence density is almost two orders of magnitude smaller than both Li core and LiF pseudovalence densities. Clearly, a linearization of the core-valence interactions cannot be a good approximation in this case. For this reason, applying the NLCC is an absolute necessity for Li and other alkali atoms.

D. The choice of the NLCC core radius and its effect on the exchange-correlation potential

Based on the calculations presented in the preceding sections and the large amount of data that could not be included here we have drawn the following conclusions. First, when addressing the issue of PSP transferability, it should be sufficient to consider only the region of space where the PSP and AE valence densities are similar. Second, since the valence densities are a superposition of the corresponding valence orbital densities, we can focus our discussion on these orbitals. Third, for each relevant valence state there is a region (termed A) where AE and PSP orbitals are identical (for radii larger than the wave-function cutoff radius r_{cut}) and a region (termed C) where AE and PSP orbitals are completely unrelated (inside of the outermost node r_{node} of the AE state) or where the corresponding valence charge is negligible (for small radii). Between r_{node} and r_{cut} there is a transition region (termed B). One expects that the best possible transferability can be obtained if the PSP exchange-correlation potential is identical or similar to the AE exchange-correlation potential in regions A and B. This assumption is confirmed by our calculations, which have

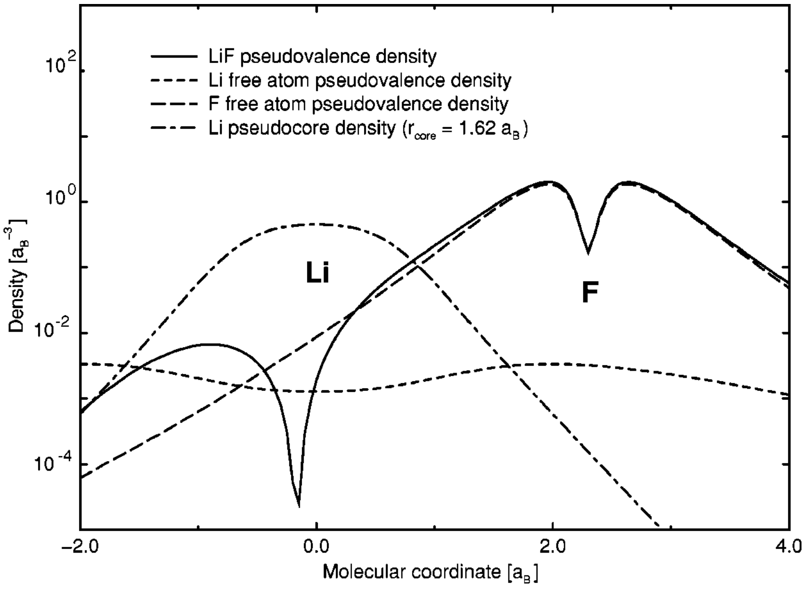

FIG. 5. LSDA electron densities in LiF compared to the free-atom densities for an internuclear distance of $2.30a_B$.

shown that in order to obtain converged results one has to construct the partial NLCC core charge density ρ^c so that it is identical to the full core charge density ρ_0^c in region A and a reasonable approximation of the latter in region B. One might guess that this condition can be fulfilled by setting $r_{core}=r_{cut}$ but this choice will often lead to unconverged results because ρ_0^c may change very rapidly in region B (see for example the Mn calculation with $r_{core}=0.80a_{\mathrm{B}}$). A more conservative choice for r_{core}, which we have found to work very well for all systems investigated here, is to define $r_{core}=(r_{cut}+r_{node})/2$. This simple relation should be evaluated for each relevant valence state $(s,p, \ldots)$ and then the smallest of all values should be used. For example, in the case of Mn we have the *s*, *p*, and *d* cutoff radii at $2.53a_{\mathrm{B}}$, $2.75a_{\mathrm{B}}$, and $0.81a_{\mathrm{B}}$, and the corresponding AE wave-function nodes at $1.07a_{\mathrm{B}}$, $1.16a_{\mathrm{B}}$, and $0.00a_{\mathrm{B}}$ (the $3d$ function is nodeless). The arithmetic averages $(r_{cut}+r_{node})/2$ of cutoff and node radii for *s*, *p*, and *d* are $1.80a_{\mathrm{B}}$, $1.96a_{\mathrm{B}}$, and $0.40a_{\mathrm{B}}$ and hence $r_{core}=0.40a_{\mathrm{B}}$.

We would like to remark that the above approach is rather conservative in the sense that it is aimed at achieving converged results even in the worst possible cases and not at finding a compromise between accuracy and numerical efficiency in plane-wave calculations. Larger r_{core} (and even no NLCC at all) are suitable for many applications but this should always be checked for every single system independently. Finally, by choosing r_{core} conservatively it is ensured that PSP and AE exchange-correlation potentials agree in all those regions of space where PSP and AE valence density are identical or similar. This seems to be the key for a good transferability. The fact that a further reduction of r_{core} towards $r_{core}=0$ (which will ultimately lead to a full NLCC) has no effect on the calculated results also indicates that the region close to the core is unimportant for the problems discussed above.

IV. SUMMARY AND CONCLUSIONS

We have investigated the importance of nonlinear core corrections for the transferability of norm-conserving Troullier-Martins pseudopotentials. Since other PSP's are constructed with similar techniques our results should also hold for other norm-conserving PSP's. It is found that the PSP approach without the NLCC is likely to be inaccurate if the electron density in the core region of a particular atom differs significantly from the density corresponding to the reference state used in the pseudopotential construction. We have demonstrated that altering the atomic spin state or embedding the atom into a heteronuclear compound may lead to such important changes. The application of the NLCC reduces the deviation of the PSP results from the all-electron data to a much smaller amount. Remaining errors can be explained by valence pseudization and core relaxation effects. The latter may be taken into account by including core or semicore states into the valence basis. Since it is hard to predict how big the effect of the NLCC will be for a particular system and since the NLCC adds a rather small overhead to the calculation, we suggest to *always* apply this correction. The simple approach for the choice of r_{core}, which was given in the preceding section should facilitate future PSP +NLCC applications.

ACKNOWLEDGMENTS

We thank Dr. D. Bird for providing and discussing his pseudopotential results. D.V.P. gratefully acknowledges support from the Alexander von Humboldt Foundation of Germany. This work was supported in part by the ONR Molecular Design Institute N0001498WX20709 and by National Science Foundation Grant No. DMR9627778.

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