Role of the core-valence interaction for pseudopotential calculations with exact exchange

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Standard normconserving pseudopotentials for the exact exchange energy functional of density functional theory exhibit a spurious long-range structure induced by the core-valence interaction. In this contribution the origin of this structure and its implications for the description of atoms, molecules, and solids is analyzed in detail. It is found that bond distances and energies obtained can be seriously in error, in particular for solids. Based on this analysis a parameter-free, self-consistent scheme for the elimination of the spurious feature is suggested. The resulting pseudopotentials predict binding properties of molecules and solids which, on average, are more accurate than those obtained with the corresponding local density approximation pseudopotentials.

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I. INTRODUCTION

The combination of density functional methods with the pseudopotential (PP) approach provides a theoretical framework for the numerical study of a large variety of complex electronic systems (Refs. 1–7). Such investigations are usually based on the local density (LDA) or the generalized gradient approximation (GGA) (Refs. 8 and 9) for the exchange-correlation (xc) energy functional $E_{\mathrm{xc}}$ of density functional theory (DFT).10 In recent years, also PP calculations with the exact exchange energy functional $E_x$ of DFT have been performed.11–14 The exact $E_x$,

$$E_x = -\frac{e^2}{\varepsilon_f} \sum_{i,j} \int d^3r \frac{\phi_i^*(r) \phi_i(r) \phi_j^*(r') \phi_j(r')}{|r-r'|}$$

(with $\varepsilon_f$ being the Fermi energy), is the prototype of an implicit density functional (Ref. 15), in which not (only) the density $n$, but rather the Kohn-Sham (KS) orbitals $\phi_k$ are used to characterize the functional. For such functionals the multiplicative xc potential $v_{\mathrm{xc}}(r) = \delta E_{\mathrm{xc}}/\delta n(r)$ has to be evaluated indirectly via the optimized potential method (OPM).16 With this procedure the nonlocal character of the Fock term (1) is absorbed into the construction of $v_{\mathrm{xc}}(r)$. As a consequence, the OPM is computationally much more demanding than the calculation of the LDA or GGA xc potential, even if one resorts to the efficient (and accurate) Krieger-Li-Iafrate (KLI) approximation to the full OPM.17 The use of PP’s is thus particularly attractive for calculations with orbital-dependent xc functionals.

For PP applications of the exact $E_x$ there still exist two obstacles: On the one hand, an appropriate correlation contribution to complement the exact $E_x$ has not yet been established,18–25 although some promising concepts have been put forward recently.21–24 In practice, the exact $E_x$ has either been applied without any correlation contribution ($\chi$-only) (Ref. 26–30) or with LDA or GGA correlation functionals.31,11,32,14

The second difficulty is connected with the construction of PP’s: Standard normconserving PP’s (Refs. 33–35) on the basis of the exact $E_x$ are found to develop a spurious long-range structure.11,12 In applications this feature acts as an additional, spurious force on neighboring ions, so that structural optimizations on the basis of such PP’s can be seriously in error (compare Secs. III and IV). In order to cure this deficiency a posteriori damping of the spurious contribution has been suggested.11,12 The introduction of additional parameters via the damping function, however, leads to some arbitrariness of the resulting molecular or bulk data. As an alternative, normconserving PP’s generated via an atomic LDA calculation have been utilized in molecular PP calculations with exact exchange.14 The use of different xc functionals for PP construction and the polyatomic calculation can, however, lead to significant errors36 (see also Sec. IV).

Clearly, an accurate and generally accepted procedure for handling the xc tail has to be established before OPM-based PP calculations can become a standard tool. On the basis of a detailed analysis of the normconserving PP’s obtained for the exact $E_x$ via the OPM (subsequently denoted by OPM-PP), we suggest in this contribution a parameter-free method for the elimination of the spurious contribution to the PP.

We first present a very brief outline of the construction of OPM-PP’s within the Troullier-Martins (TM) scheme,35 emphasizing the aspects by which OPM-PP’s differ from LDA-PP’s (Sec. II). In Sec. III we examine the properties of the resulting unmodified normconserving OPM-PP’s for atoms and molecules, using the corresponding all-electron (AE) OPM (Ref. 30) as well as AE and PP LDA data as comparative standards.37 While the results for atoms, obtained with the unmodified OPM-PP’s, are rather satisfactory, the molecular and bulk data clearly indicate the need for a modification of the OPM-PP’s. In Sec. IV the asymptotic form of the OPM-PP’s is studied in detail. We first verify explicitly that the long-range structure originates from the core-valence interaction, while differences between the valence pseudoorbitals and AE orbitals in the core region are of minor importance. We then examine the a posteriori damping pre-
scription for the xc tail. It is shown that variation of the damping function leads to a spread of molecular and bulk results which is not much smaller than the deviation of the unmodified PP results from the AE data. To resolve this ambiguity, we finally introduce a parameter-free PP construction scheme in Sec. V.

II. CONSTRUCTION OF NORM-CONSERVING OPM PSEUDOPOTENTIALS

In this section we briefly summarize the construction of norm-conserving PP’s for the exact exchange (I). In the first step the screened PP must be generated from AE results for the atom of interest. One thus starts with an AE OPM calculation for the atomic ground state, which differs from a standard LDA calculation by the evaluation of the exchange potential \( v_x \) via the OPM.\textsuperscript{16,20} In this method \( v_x \) is obtained from the product of the inverse of the static KS response function \( \chi \) and a source term \( \Lambda \), whose main ingredient is the functional derivative of \( E_x \) with respect to the KS orbitals,

\[
v_x(r) = \int d^3 r' \chi_{s}^{-1}(r,r') \Lambda_{x}(r'), \tag{2}
\]

\[
\chi_{x}(r,r') = - \sum_{\epsilon_i \approx \epsilon_F} \phi_i^*(r) G_i(r,r') \phi_i(r') + \text{c.c.}, \tag{3}
\]

\[
\Lambda_{x}(r) = - \sum_{l} \int d^3 r' \phi_i^*(r) G_l(r,r') \frac{\delta E_x}{\delta \phi_i^*(r')} + \text{c.c.}, \tag{4}
\]

\[
G_l (r,r') = \sum_{j \neq l} \frac{\phi_j (r) \phi_j^*(r')}{\epsilon_j - \epsilon_l}. \tag{5}
\]

\[
\frac{\delta E_x}{\delta \phi_i^*(r')} = - e^2 \sum_{\epsilon_j \approx \epsilon_F} \phi_j (r') \int d^3 r \frac{\phi_j^*(r) \phi_i(r)}{|r-r'|}. \tag{6}
\]

The technical details of AE OPM calculations for atoms have been discussed in Refs. 27 and 20, to which we refer the reader for further information. Note that this procedure is readily extended to orbital-dependent correlation functionals.

Given the self-consistent AE OPM solution, i.e., the AE orbitals (AEO’s) \( \phi_i^{AE}(r) = \phi_{nl}^{AE}(r) Y_{lm}(\Omega) / r \), the corresponding eigenvalues \( \epsilon_i \), and the total AE potential \( v_x^{AE} \), the construction of the screened PP for the case of the exact \( E_x \) proceeds as for the LDA. For this purpose we have used the TM scheme,\textsuperscript{35,38} applying the cutoff radii \( r_{c,l} \) listed in Table I (the same \( r_{c,l} \) have been used for all PP variants discussed subsequently). Rather hard values have been chosen for \( r_{c,l} \) in order to ensure converged PP results. For each valence level with angular momentum \( l \) the TM scheme provides a (nodeless) radial pseudoo orbital (PO) \( \varphi_{ps,l} \), which is identical with \( \varphi_{nl}^{AE} \) for \( r \geq r_{c,l} \), together with the associated screened PP \( v_{ps,l}^{n} \), which, in the valence region, is identical with \( v_x^{AE} \).

In a second step the interaction among the valence electrons must be eliminated from \( v_{ps,l}^{n} \). If \( v_{xc} \) were a linear functional of the density, this goal could be achieved exactly by linear unscreening:

\[
v_{ps,l}^{n}(r) = v_{ps,l}^{AE}(r) - v_{H} [n_{ps,l}; r] - v_{xc} [n_{ps,l}; r]. \tag{7}
\]

Here \( v_{H}[n_{ps,l}] \) is the Hartree potential of the valence electrons with pseudodensity \( n_{ps,l} \):

\[
v_{H} [n_{ps,l}; r] = e^2 \int d^3 r' \frac{n_{vs,l}(r')}{|r-r'|}, \tag{8}
\]

\[
n_{ps,l}(r) = \sum_{occ, val, orb} \Theta |\varphi_{ps,l,r}(r)\rangle. \tag{9}
\]

(\( \Theta \) denotes the occupation number of the subshell with angular momentum \( l \)). \( v_{xc}[n_{ps,l}] \) is the xc potential corresponding to \( n_{ps,l} \), which, in the case of the exact exchange, has to be evaluated by solution of Eqs. (2)–(6) with the valence PO’s (Ref. 39). The sums over \( i \) in Eqs. (3) and (4) and \( j \) in Eq. (6) are thus restricted to the valence states and all quantities are calculated with the PO’s (the form of Eqs. (2)–(6) for spherical systems is explicitly specified in Appendix A of Ref. 20—for the evaluation of \( G_l \), Eq. (A54) of Ref. 20 has been used in combination with the pseudostates).

However, the exact \( E_{xc} \) is a nonlinear functional of \( n \), so that the unscreening (7) implies a linearization of the xc contribution to the core-valence interaction. In the unscreening procedure the nonlinearity can be taken into account via nonlinear core corrections (NLCC’s),\textsuperscript{40}

\[
u_{ps,l}^{NLCC} (r) = v_{ps,l}^{AE} (r) - v_{H} [n_{ps,l}; r] - v_{xc} [n_{ps,l} + n_{e}^{AE}; r], \tag{10}
\]

i.e., by inclusion of the AE core density \( n_{e}^{AE} \) in the nonlinear part of the unscreening potential. As a consequence, \( n_{e}^{AE} \) has to be included also in the evaluation of the molecular or bulk.
TABLE II. Ionization potentials of first- and second-row atoms: PP vs AE results (Ref. 53) (all energies in eV).

<table>
<thead>
<tr>
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xc potential and energy. In principle, this nonlinear approach can also be used for the exact $E_x$. In this case $v_x[n_{v,ps} + n_{c}]$ is obtained by solution of Eqs. (2)-(6) for the combination of valence PO’s and core AEO’s.

III. RESULTS FOR NORM-CONSERVING OPM PSEUDOPOTENTIALS

In this section we investigate the performance of norm-conserving $x$-only OPM-PP’s generated by the procedure outlined in Sec. II without any further modification. The quantities considered are atomic ionization potentials (IP’s), intrashell transfer energies (for both first and second row atoms), the energy gain obtained by allowing nonspherical density shapes for open shell atoms, and molecular ground-state properties. In all cases an unambiguous comparative standard can be provided by AE calculations with the exact $E_x$. For comparison we also list corresponding LDA results, both for the case of linearly unscreened LDA-PP’s and for LDA-PP’s including NLCC’s.41–43 The general conclusion, substantiated by the detailed results, is that the core-valence interaction plays a minor important role for the case of the exact exchange functional as compared to the LDA, which suggests a high transferability of the linearly unscreened OPM-PP’s. In addition, we find that the inclusion of NLCC’s consistently improves results in the case of the LDA-PP’s, as pointed out before.44,45

The IP’s of the PP and AE OPM calculations (Table II) agree very closely, the deviations being of the order of 0.01 eV with a maximum of 0.05 eV found for P. This pattern is confirmed by the good agreement of the corresponding PP and AE orbital eigenvalues, where again the deviation is largest for P (10 mhartree for the $3s_1$ state). In the case of the LDA, on the other hand, the differences between the AE and linearly unscreened PP results are of the order of 0.1 eV. In order to achieve the same level of accuracy as observed for the OPM-PP’s the inclusion of NLCC’s is necessary. These results suggest that the ground states of both neutral atoms and positive ions are well described by the linearly unscreened OPM-PP’s.

For the intrashell transfer two types of excitations are examined (Table III): On the one hand, the minority spin ($\uparrow$) $s$ electron is transferred into the majority spin ($\downarrow$) $p$ orbital, so that the excited state has a larger spin polarization (magnetic moment) than the ground state ($s\rightarrow p$ transfer). In the second case a $p\rightarrow p$ electron goes into the $p\downarrow$ state, reducing the magnetic moment ($p\rightarrow p$ transfer). Given the rather accurate ground-state energies documented by the IP’s of Table II, the $s\rightarrow p\downarrow$ and $p\downrightarrow p\downarrow$ transfer energies mainly probe the description of the excited states and thus the performance of the PP’s in a different chemical environment. For both types of excitations the agreement between AE OPM and OPM-PP results is very close. Similar agreement is found for the LDA-PP’s with NLCC’s, while the transfer energies are much less accurate if the nonlinearity of the LDA functional is neglected.

The energy gain resulting from the transition from a spherical to a nonspherical atomic density is emphasized once again the role of the core-valence interaction. The presence of the (essentially) spherical core density stabilizes a spherical valence density relative to a nonspheri-

TABLE III. $s\rightarrow p$ and $p\rightarrow p$ transfer energies of first- and second-row atoms: PP vs AE results (Ref. 53) (in eV).

<table>
<thead>
<tr>
<th></th>
<th>$s\rightarrow p\downarrow$</th>
<th>$p\rightarrow p\downarrow$</th>
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TABLE IV. Difference between ground-state energies obtained with nonspherical and spherical densities for first-row atoms (all energies in meV). The calculations for the exact exchange are consistently based on the KLI approximation (Ref. 17).

<table>
<thead>
<tr>
<th>Mode</th>
<th>LDA AE</th>
<th>OPM</th>
<th>Mode</th>
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The spectroscopic constants obtained for 15 first- and second-row diatomic molecules are listed in Tables V and VI for the LDA and Tables VII and VIII for the exact exchange. The average absolute deviations of the PP bond lengths \( R_e \) and dissociation energies \( D_e \) from the AE values are slightly smaller for the OPM-PP’s than for the linearly unscreened LDA-PP’s, though both average errors are larger than those obtained with the LDA-PP’s plus NLCC’s. The distribution of errors shows that for the LDA-PP without NLCC’s the deviations are largest for molecules whose constituents are “strongly” spin polarized, with nitrogen and phosphorus being the prime examples: N₂ is responsible for roughly one-third of the total average error of 0.24 eV found for the first row; P₂ even accounts for half of the average error of the second-row molecules. For these systems \( D_e \) is clearly underestimated by LDA-PP’s without NLCC’s, as a consequence of an overestimation of the atomic ground-state energies. As in the case of the atomic excitation energies the difficulties of the LDA-PP’s with high-spin states are resolved by inclusion of NLCC’s (Ref. 44). In the case of the OPM, on the other hand, the errors are only half as large as those of the linearly unscreened LDA-PP’s for N₂ and P₂, but slightly larger for O₂. The different pattern of errors indicates that for the OPM-PP’s the deviations do not primarily originate from a poor description of spin polarization (which would have to be corrected by NLCC’s). Obviously, the rather substantial differences between the AE and PP dissociation energies (e.g., for C₂ or O₂) demand a more detailed analysis of the OPM-PP’s.

IV. DETAILED ANALYSIS OF OPM PSEUDOPOTENTIALS FOR AI

As a prototype of all OPM-PP’s we consider the second-row element Al. The \( s, p, \) and \( d \) components of the PP are compared with the corresponding linearly unscreened LDA-PP in Figs. 1(a)–1(c). For the \( s \) component one observes only a small shift of the PP minimum from the LDA value of 1.55–1.58 bohr, consistent with the corresponding change in the \( r \) expectation value of the \( 3s \) orbital; otherwise, the PP’s are rather similar. The \( p \) component reflects the more pronounced shell structure produced by the exact exchange potential. In the PP description this requires a slightly enhanced separation of the valence shell from the core shells. As a consequence, the OPM-PP is more repulsive than the LDA-PP.

In order to emphasize the differences between the OPM-PP and the LDA-PP in the valence region we plot in Fig. 2 the quantity

\[ r v_p(r) + Z_{ion} e^2 \]

for the \( p-\)PP (beyond the maximum \( r_e \) all PP components are identical by construction). As already noted by Bylander and Kleinman, the OPM-PP’s contain a spurious long-range

<table>
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<th>OPM</th>
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<td>-0.351</td>
</tr>
<tr>
<td>PP+NLCC</td>
<td>0.006</td>
<td>-0.085</td>
<td>-14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiH</td>
<td>AE</td>
<td></td>
<td>PP</td>
<td>-0.115</td>
<td>0.077</td>
</tr>
<tr>
<td>PP+NLCC</td>
<td>0.005</td>
<td>-0.046</td>
<td>-53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FH</td>
<td>AE</td>
<td></td>
<td>PP</td>
<td>0.004</td>
<td>-0.122</td>
</tr>
<tr>
<td>PP+NLCC</td>
<td>0.003</td>
<td>-0.025</td>
<td>-16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>AE</td>
<td></td>
<td>PP</td>
<td>-0.003</td>
<td>-0.378</td>
</tr>
<tr>
<td>PP+NLCC</td>
<td>0.000</td>
<td>-0.067</td>
<td>-2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>PP</td>
<td>0.026</td>
<td>0.235</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>deviation</td>
<td>PP+NLCC</td>
<td>0.003</td>
<td>0.044</td>
<td>12</td>
<td></td>
</tr>
</tbody>
</table>
component beyond the leading, electrostatic \(-Z_{\text{ion}}e^2/\mathbf{r}\) term, which is not present for LDA-PP’s. Even without NLCC’s the LDA-PP shows only a small peak in the vicinity of the cutoff radius, which vanishes within 1 bohr. In addition, the inclusion of the NLCC’s in the LDA-PP leads to a clean \(-Z_{\text{ion}}e^2/\mathbf{r}\) behavior for all \(r > r_{\text{c,l}}\). This is the desired asymptotic form, as the ionic core interacts with the valence electrons around neighboring ionic cores and in the bonding region as a pure point charge.

The appearance of the long-range feature in OPM-PP’s can be understood in the following fashion: In the valence region the screened PP’s are identical with \(n_{c}^{\text{AE}}\) densities. In the valence region the xc contribution to the unscreened PP’s \(n_{v,\text{ps}}\) is thus given by the difference

\[
v_{\text{xc}}([n_{c}^{\text{AE}}; r] - [n_{v,\text{ps}}; r]). \tag{11}\]

For local and gradient-corrected functionals this difference vanishes by construction as soon as \(n_{c}^{\text{AE}}\) starts to decay exponentially. The ionic PP’s thus show a clean \(-Z_{\text{ion}}e^2/\mathbf{r}\) behavior in the asymptotic region (no structure is introduced by \(v_{\text{Hf}}([n_{c}^{\text{AE}} + n_{v}^{\text{AE}}]; r] - [n_{v,\text{ps}}; r])\). In the case of exact exchange, on the other hand, the density in the core region affects the exchange potential in the valence regime via Eq. (6), so that the difference (11) does not vanish even for rather

\[
\begin{array}{ccc}
\text{Mode} & R_e & D_e & \omega_e \\
\hline
\text{Na}_2 & \text{AE} & 5.673 & 0.883 & 162 \\
\text{PP} & 0.121 & 0.039 & 3 \\
\text{PP} + \text{NLCC} & 0.011 & 0.007 & 1 \\
\hline
\text{Cl}_2 & \text{AE} & 3.738 & 3.626 & 564 \\
\text{PP} & 0.005 & 0.105 & 2 \\
\text{PP} + \text{NLCC} & 0.004 & 0.023 & 4 \\
\hline
\text{Na} & \text{AE} & 5.673 & 0.883 & 162 \\
\text{PP} & 0.121 & 0.039 & 3 \\
\text{PP} + \text{NLCC} & 0.011 & 0.007 & 1 \\
\hline
\text{Cl}_2 & \text{AE} & 3.738 & 3.626 & 564 \\
\text{PP} & 0.005 & 0.105 & 2 \\
\text{PP} + \text{NLCC} & 0.004 & 0.023 & 4 \\
\hline
\text{Na}_2 & \text{AE} & 5.673 & 0.883 & 162 \\
\text{PP} & 0.121 & 0.039 & 3 \\
\text{PP} + \text{NLCC} & 0.011 & 0.007 & 1 \\
\hline
\text{Cl}_2 & \text{AE} & 3.738 & 3.626 & 564 \\
\text{PP} & 0.005 & 0.105 & 2 \\
\text{PP} + \text{NLCC} & 0.004 & 0.023 & 4 \\
\hline
\end{array}
\]

TABLE VI. As in Table V for second-row dimers.
large values of $r$. The nonlocal nature of the exact $E_x$ thus leads to a long-range xc component in the ionic PP. This xc tail is found in the OPM-PP's of all first- and second-row atoms.\textsuperscript{50} For polyatomic systems this feature leads to a spurious contribution to the interaction energy of an ion with the valence electrons around neighboring centers. This unphysical energy shift accounts for the different patterns of errors observed for OPM-PP's and LDA-PP's (Tables V–VIII).

In order to pinpoint the origin of the spurious feature a number of variants of the OPM-PP's have been investigated. In the first variant the unscreening potential $v_x[n_v^{AE}]$ in Eq. (7) is calculated by solution of Eq. (2) with only the valence AEO's taken into account in $\chi_v$ and $\Lambda_v$ [but $G_e$ is still evaluated via Eq. (5)]. The PP obtained in this way is very similar to the standard PP in the asymptotic region (Fig. 2). The spurious tail is not sensitive to the marked differences between PO's and AEO's in the core region (nor to variation of the cutoff radius\textsuperscript{51}). It is thus not due to an incomplete optimization of the PO's and cannot be remedied by inclusion of further subsidiary conditions in the construction of the PP, as long as linear unscreening is applied.

As a first example of nonlinear unscreening we consider a variant where the complete AE exchange potential is subtracted from the screened PP together with the valence AE Hartree potential. The result, shown in Fig. 3, is a PP free of any long-range structure, which confirms the conclusion that the nonlinearity of the core-valence interaction is the origin of the spurious feature.

In a second nonlinear unscreening variant, the exchange component of the unscreening potential is generated from a

\begin{table}
\begin{tabular}{cccc}
\hline
\textbf{Mode} & $R_v$ (bohr) & $D_v$ (eV) & $\omega_v$ (cm$^{-1}$) \\
\hline
\textbf{Na$_2$} & \\
AE & 6.050 & 0.034 & 155 \\
OPM-PP & -0.010 & -0.020 & -1 \\
LDA-PP & -0.537 & 0.009 & 18 \\
SC-OPM-PP & -0.039 & -0.018 & 0 \\
\textbf{Al$_2$} & \\
AE & 4.801 & 0.397 & 313 \\
OPM-PP & 0.025 & -0.079 & -12 \\
LDA-PP & -0.136 & 0.041 & 13 \\
SC-OPM-PP & 0.025 & -0.022 & -2 \\
\textbf{Si$_2$} & \\
AE & 4.184 & 1.786 & 575 \\
OPM-PP & 0.003 & -0.042 & -3 \\
LDA-PP & -0.093 & 0.121 & 14 \\
SC-OPM-PP & 0.000 & 0.004 & 1 \\
\textbf{P$_2$} & \\
AE & 3.492 & 1.614 & 918 \\
OPM-PP & 0.004 & -0.102 & -8 \\
LDA-PP & -0.092 & 0.165 & 18 \\
SC-OPM-PP & 0.001 & -0.016 & -5 \\
\textbf{S$_2$} & \\
AE & 3.514 & 2.154 & 821 \\
OPM-PP & 0.008 & -0.062 & -7 \\
LDA-PP & -0.048 & 0.122 & 14 \\
SC-OPM-PP & 0.001 & 0.021 & 1 \\
\textbf{Cl$_2$} & \\
AE & 3.727 & 0.715 & 613 \\
OPM-PP & 0.019 & -0.039 & -10 \\
LDA-PP & -0.038 & 0.010 & 8 \\
SC-OPM-PP & 0.002 & -0.006 & 2 \\
\hline
\textbf{Average deviation} & \\
OPM-PP & 0.012 & 0.058 & 7 \\
LDA-PP & 0.158 & 0.089 & 14 \\
SC-OPM-PP & 0.011 & 0.015 & 2 \\
\hline
\end{tabular}
\caption{As in Table VII for second-row dimers (Refs. 49 and 54).}
\end{table}
The long-range structure of the third variant remains essentially unchanged if the 1s contribution to $\delta E_x/\delta \phi_i$ is neglected (see Fig. 3). This last partial nonlinear unscreening variant would constitute the most economic nonlinear scheme.

Unfortunately, nonlinear unscreening is not a very attractive option in practice, in particular within the frequently used plane-wave-pseudopotential scheme. A plane-wave representation of the core states requires extremely high energy cutoffs, even if one restricts oneself to the outermost core shell. The concept of NLCC’s is only useful together with a smooth truncation of the core density $n_{c,\text{AE}}$ below some core-cutoff radius $r_{\text{NLCC}}$. Without this truncation the representation of $n_{c,\text{AE}}$ in terms of basis functions and integrations over the strongly peaked full $n_{c,\text{AE}}$ become exceedingly difficult. It is not clear a priori whether a corresponding smooth truncation of the core orbitals is compatible with the nonlocal nature of the Fock term. One would at least expect that $r_{\text{NLCC}}$ has to be chosen much smaller than in the case of the LDA, in order to account for the nonlocality of the exact $E_x$. Given the limited success of nonlinear unscreening with the elimination of the spurious tail and the limited importance of nonlinear contributions to the core-valence interaction for the transferability of OPM-PP’s, it thus seems that one has to stay with linear unscreening.

Consequently the question arises how one can handle the unphysical xc tail within the linear unscreening scheme. Two schemes of this nature are found in the literature. Kim and co-workers suggest OPM calculations on the basis of LDA-PP’s. While this scheme avoids all problems related to the spurious xc tail from the outset, the use of different xc functionals in the PP construction and the polyatomic calculation does not yield sufficiently accurate results (see Tables VII and VIII—compare Ref. 36).

Bylander and Kleinman suggested to damp the long-range structure a posteriori. In order to test the sensitivity of polyatomic results to the form of the damping function we have used two different damping functions for the calculation of the properties of both the Al dimer and bulk Al. The OPM-PP’s obtained for Gaussian and power law damping,

$$
\begin{align*}
    v_{\text{ps}}(r) &= \begin{cases} 
        v_{\text{ps}}(r) & \text{for } r \leq r_d, \\
        f(r) = \exp[-(r-r_d)^2/l_d^2] & \text{for } r \geq r_d,
    \end{cases}
    \\
    f_G(r) &= \begin{cases} 
        f_G(r) & \text{for } r \leq r_d, \\
        f_p(r) = \exp[-(r-r_d)^2/l_d^2] & \text{for } r \geq r_d,
    \end{cases}
\end{align*}
$$

are shown in Fig. 4. Rather different characteristics have been chosen for the individual functions. The weak power law damping with an onset at 2.3 bohr and a damping length of $l_d=5$ bohr only reduces the amplitudes of the spurious oscillations. On the other hand, the Gaussian damping with $l_d=0.3$ bohr essentially switches off any structure for $r > r_d$. Choosing $r_d=2.3$ bohr, one thus simulates the asymptotic behavior of a PP with NLCC’s. The larger value of $r_d=5.7$ bohr only eliminates the minimum around $r = 8.4$ bohr, so that the comparison of the two Gaussians...
TABLE IX. Spectroscopic constants of Al₂ obtained from exact exchange: various damping variants in comparison with unmodified OPM-PP and AE results (Refs. 49 and 54).

<table>
<thead>
<tr>
<th>Mode</th>
<th>Damping function</th>
<th>r₅ [bohr]</th>
<th>l₅ [bohr]</th>
<th>R₅ [bohr]</th>
<th>D₅ [eV]</th>
<th>ω₅ [cm⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP</td>
<td>Unmodified</td>
<td>4.826</td>
<td>0.318</td>
<td>301</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP</td>
<td>Padé</td>
<td>2.3</td>
<td>5.0</td>
<td>4.817</td>
<td>0.316</td>
<td>302</td>
</tr>
<tr>
<td>PP</td>
<td>Gaussian</td>
<td>5.7</td>
<td>0.3</td>
<td>4.813</td>
<td>0.359</td>
<td>303</td>
</tr>
<tr>
<td>PP</td>
<td>Gaussian</td>
<td>2.3</td>
<td>1.5</td>
<td>4.793</td>
<td>0.381</td>
<td>311</td>
</tr>
<tr>
<td>PP</td>
<td>Gaussian</td>
<td>2.3</td>
<td>0.3</td>
<td>4.773</td>
<td>0.429</td>
<td>318</td>
</tr>
</tbody>
</table>

Expt.       | 4.660            | 1.57      | 350       |

The corresponding spectroscopic constants for Al₂ are listed in Table IX. A comparatively wide range of results is obtained. For the weak damping via the Padé function one finds almost the same results as with the unmodified PP. For the Gaussian damping the differences are more pronounced. However, while the damping length of 1.5 bohr leads to the Gaussian damping the differences are more pronounced. This part of the tail is not probed in Al₂, which explains the different signs of the error in the equilibrium distances. Unfortunately, the spread of results among the various damped PP's is also substantial.

The sensitivity of the bulk properties to the asymptotic tail (and thus to the choice of the damping function) can be understood most easily if one examines the PP’s (minus the electrostatic component) in momentum space:

\[ w_{ps}(\mathbf{k}) = \int \frac{d^3r}{r} \exp(i\mathbf{k} \cdot \mathbf{r}) \left[ \mathbf{v}_{ps}(r) + \frac{Z_{\text{ion}}^2}{r} \right]. \]

In \( w_{ps}(\mathbf{k}) \) the asymptotic behavior of the OPM-PP’s is noticeable as a small dip at \( k=0 \) (see Fig. 5). This long-wavelength limit is not relevant for the total KS potential of a solid and thus does not affect the electronic structure (for Al with \( a=7.5 \) bohr the smallest nonvanishing reciprocal lattice vector equals 1.45 bohr⁻¹). It does, however, affect the cohesive properties via the long-range component of the electron-ion interaction energy, \( E_{\text{coh}} \).

TABLE X. Equilibrium lattice constant \( a \), cohesive energy \( E_{\text{coh}} \), and bulk modulus \( B \) of fcc Al obtained from exact exchange: various damping variants in comparison with unmodified OPM-PP, self-consistent OPM-PP (SC-OPM-PP), and LDA results (Refs. 49, 56, and 54) (the experimental values have been taken from Ref. 36). \( E_{\text{xc}} \) denotes the functional used in the bulk PP calculation. Also given is the long-wavelength limit of the \( d \) component of the PP in momentum space, Eq. (12), which determines the long-range contribution to the electron-ion interaction, Eq. (13).

<table>
<thead>
<tr>
<th>( x )</th>
<th>( E_{\text{xc}} )</th>
<th>Damping function</th>
<th>( r₅ ) [bohr]</th>
<th>( l₅ ) [bohr]</th>
<th>( w_{ps,d}(k=0) ) [hartree×bohr³]</th>
<th>( a ) [bohr]</th>
<th>( E_{\text{coh}} ) [eV/atom]</th>
<th>( B ) [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exact</td>
<td>unmodified</td>
<td>2.3</td>
<td>5.0</td>
<td>-0.754</td>
<td>7.65</td>
<td>1.77</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td>Exact</td>
<td>Padé</td>
<td>2.3</td>
<td>0.3</td>
<td>-0.526</td>
<td>7.69</td>
<td>1.53</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>Exact</td>
<td>Gaussian</td>
<td>2.3</td>
<td>1.5</td>
<td>-0.218</td>
<td>7.77</td>
<td>1.35</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>Exact</td>
<td>Gaussian</td>
<td>5.7</td>
<td>0.3</td>
<td>0.444</td>
<td>7.94</td>
<td>0.94</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>Exact</td>
<td>SC-OPM-PP</td>
<td>-0.689</td>
<td>7.79</td>
<td>1.37</td>
<td>71</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LDA</td>
<td>LDA</td>
<td>AE</td>
<td></td>
<td></td>
<td>7.52</td>
<td>84</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LDA</td>
<td>LDA</td>
<td>LDA-PP</td>
<td></td>
<td>-2.62</td>
<td>7.47</td>
<td>4.04</td>
<td>86</td>
<td></td>
</tr>
<tr>
<td>LDA</td>
<td>LDA</td>
<td>LDA-PP+NLCC</td>
<td>2.806</td>
<td>7.48</td>
<td>4.05</td>
<td>88</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Expt.    | 7.65            | 3.39           | 77            |

*Reference 55.

The corresponding cohesive properties of bulk Al (Table X) are even more sensitive to the asymptotic form of the PP. One first of all observes that the unmodified PP underestimates the experimental lattice constant by 0.55 bohr and overestimates the bulk modulus by almost a factor of 2. In spite of the fact that one should not expect an \( x \)-only calculation to reproduce the experimental data of a metal, this large deviation shows that OPM-PP’s are not usable for bulk calculations without an elimination of the xc tail. All damping variants enlarge the lattice constant \( a \) by more than 0.5 bohr and reduce the cohesive energy by more than 2 eV, thus improving the agreement with experiment and LDA-PP results (also given in Table X). Obviously, the very small \( a \) predicted by the unmodified PP is due to the attractive part of the spurious tail around 10 bohr, which is sufficiently suppressed even by the weak Padé damping. This part of the tail is not probed in Al₂, which explains the different signs of the error in the equilibrium distances. Unfortunately, the spread of results among the various damped PP’s is also substantial.

The sensitivity of the bulk properties to the asymptotic tail (and thus to the choice of the damping function) can be understood most easily if one examines the PP’s (minus the electrostatic component) in momentum space:

\[ w_{ps}(\mathbf{k}) = \int \frac{d^3r}{r} \exp(i\mathbf{k} \cdot \mathbf{r}) \left[ \mathbf{v}_{ps}(r) + \frac{Z_{\text{ion}}^2}{r} \right]. \]

In \( w_{ps}(\mathbf{k}) \) the asymptotic behavior of the OPM-PP’s is noticeable as a small dip at \( k=0 \) (see Fig. 5). This long-wavelength limit is not relevant for the total KS potential of a solid and thus does not affect the electronic structure (for Al with \( a=7.5 \) bohr the smallest nonvanishing reciprocal lattice vector equals 1.45 bohr⁻¹). It does, however, affect the cohesive properties via the long-range component of the electron-ion interaction energy, \( E_{\text{coh}} \).
due to the fact that the resulting \( w \) is not equal for different \( \Omega \) and \( \Omega' \). This potential is defined as \( \phi_{nl}^{\text{mod}}(r) = \phi_{nl}^{\text{ae}}(r) - \phi_{nl}^{\text{mod}}(n_{v,ps}, r) \) and \( \phi_{nl}^{\text{mod}}(n_{v,ps}, r) \) has the correct asymptotic behavior (compare \( \phi_{nl}^{\text{ae}} - \phi_{nl}^{\text{mod}}(n_{v,ps}, r) \) with \( \phi_{nl}^{\text{ae}} - \phi_{nl}^{\text{mod}}(n_{c,ps}, r) \) in Fig. 3). The form of \( \phi_{nl}^{\text{mod}}(r) \) for \( r < r_{c, l} \) is irrelevant for the following. This potential is then used to generate a set of modified reference orbitals \( \phi_{nl}^{\text{mod}} \) in step (4). As the TM scheme only uses the reference orbitals in the valence region, suitable \( \phi_{nl}^{\text{mod}} \) can be obtained by inward integration of the radial KS equations, using \( \phi_{nl}^{\text{mod}} \) as total potential and the original AE eigenvalues as energy parameters:

\[
\left\{ -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + \epsilon_{nl}^{\text{AE}}(r) \right\} \phi_{nl}^{\text{mod}}(r) = \epsilon_{nl}^{\text{AE}} \phi_{nl}^{\text{mod}}(r).
\]

The inward integration via a standard finite difference method is started by applying the boundary condition

\[
\phi_{nl}^{\text{mod}}(r \to \infty) \sim r^{1/2} \epsilon_{nl}^{\text{AE}} \exp[-2 \epsilon_{nl}^{\text{AE}} r].
\]

for sufficiently large \( r \) values. In addition, one requires the norm of \( \phi_{nl}^{\text{mod}} \) in the valence region to be identical to that of the original AE orbital:

\[
\int_{r_{c, l}}^{\infty} dr |\phi_{nl}^{\text{mod}}(r)|^2 = \int_{r_{c, l}}^{\infty} dr |\phi_{nl}^{\text{AE}}(r)|^2.
\]

These conditions and the fact that \( \phi_{nl}^{\text{mod}} \) is dominated by the \(- e^2/r\) behavior of the exchange component in \( \epsilon_{nl}^{\text{AE}} \) guarantee that the resulting \( \phi_{nl}^{\text{mod}} \) are extremely close to the AEO’s for \( r > r_{c, l} \). In step (5) the TM procedure is repeated, using \( \phi_{nl}^{\text{mod}} \) as reference potential and \( \phi_{nl}^{\text{mod}} \) as reference orbitals. The result are new PO’s, a new screened PP \( \psi_{nl}^{\text{mod}} \), and new unscreening potentials \( \psi_{nl}^{\text{mod}} \) for all values of \( r \).
As a consistent scheme is based on standard PP quantities no new cutoff radii are not larger than those resulting from different components. However, even the differences observed for these two components, on the other hand, are clearly more affected by the self-consistent procedure. The ps component, which, overall, is rather similar to the unmodified PP, is free of any spurious long-range structure by virtue of Eq. (14). In addition, the specific choice (14) guarantees that the self-consistent application of the unscreened potential leads to a nonelectrostatic perturbation of the SC-OPM-PP's give essentially the same results as the unmodified PP's, including NLCC's. The spurious oscillations at 3–20 bohr are not reduced by roughly a factor of 2 and compare favorably with the errors obtained with LDA-PP's including NLCC's.

A direct comparison of SC-OPM-PP and AE OPM results is possible in the molecular case. The spectroscopic constants found with the SC-OPM-PP's for our set of diatomic molecules are included in Tables VII and VIII. They are, overall, much closer to the AE OPM values than those found with the unmodified OPM-PP's; the average deviations are reduced by roughly a factor of 2 and compare favorably with the errors obtained with LDA-PP's including NLCC's.

For the atomic properties examined in Sec. III the SC-OPM-PP's give essentially the same results as the unmodified PP's. The spurious oscillations at 3–20 bohr are not relevant for the atomic ground and low-lying excited states considered.

VI. SUMMARY AND CONCLUSIONS

The standard procedure for norm-conserving pseudopotentials implies a linearization of the core-valence interaction. In the case of the nonlocal exact exchange this linearization leads to a nonelectrostatic perturbation of the \(-Z_{\text{ion}}e^2/\mathbf{r}\) behavior of the ionic PP in the valence region. Although this spurious long-range tail decays much faster than \(1/\mathbf{r}\), it effectively acts like a small additional “ionic” force between neighboring atoms. As the spurious tail oscillates as a function of the distance from an atom, this artificial force can either be attractive or repulsive, so that either a bond length reduction or an increase can be observed in dif-
different chemical environments (for instance, for bulk Al and the Al dimer). As the range of the tail is of the order of 20 bohr, not only nearest neighbors experience it. This means that bulk results are much more affected by the spurious feature than those for diatomic molecules.

In the case of the LDA-PP’s the nonlinearity of the xc functional can be taken into account by inclusion of nonlinear core corrections. We have verified that a suitable nonlinear unscreening scheme can reduce the size of the spurious structure substantially. On the other hand, all atomic properties considered indicate that the nonlinearity of the core-valence interaction is less relevant in the case of the exact exchange than for the LDA. In particular, the lowest excitation energies which are a measure of the transferability of the PP’s are almost as accurate as those obtained from LDA-PP’s with nonlinear core corrections. In view of the high price to be paid for the inclusion of core states in OPM-PP calculations these observations call for a procedure within the framework of linear unscreening.

In this case a suitable modification of standard normconserving PP’s is required. The most simple modification is the \textit{a posteriori} damping of the tail.\textsuperscript{11} However, this procedure introduces new parameters into the PP’s, which leads to an uncertainty of the resulting polyatomic data. Our results for bulk aluminum show that this uncertainty is of the same order of magnitude (within a factor of 2–3) as the deviation of the original PP results from the AE data.

As an alternative, a modified PP construction scheme is introduced, which is free of any additional parameters. In this scheme the PP is determined in a self-consistent fashion which guarantees the correct ionic form of the unscreened PP. The spectroscopic constants obtained with the self-consistent PP’s for a set of first- and second-row molecules agree much better with the corresponding AE OPM data than those of the original PP’s. The average deviations found for the self-consistent PP’s are almost as small as those obtained for LDA-PP’s which include nonlinear core corrections, consistent with the findings for atoms. The combination of linear unscreening with the self-consistent PP generation thus seems to provide the appropriate basis for PP calculations with exact exchange.

\section*{Acknowledgments}

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\begin{thebibliography}{99}
\end{thebibliography}
In the case of the LDA the Hamann prescription


The derivation of the OPM equation

Precisely speaking, we have used the relativistic variant of the
M. Fuchs, M. Bockstedte, E. Pehlke, and M. Scheffler, Phys. Rev.

N. Troullier and J.L. Martins, Phys. Rev. B

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T. Kotani, Phys. Rev. B

E. Engel, A. Höck, and R.M. Dreizler, Phys. Rev. A


Note that the correct reference standard for the present PP study is provided by the corresponding AE data, rather than experiment: Of course, the PP cannot and should not correct the deficiencies of the approximation chosen for \( E_{v,c} \).

Precisely speaking, we have used the relativistic variant of the Troullier-Martins scheme introduced in Ref. 45 in the limit \( c \to \infty \). While for explicitly density-dependent \( E_{v,c} \) this procedure yields exactly the same PP's as the original Troullier-Martins approach, this is not generally true for orbital-dependent xc functionals. The difference originates from the average over all possible substates which is required to obtain a spherical exchange potential in the case of open-subshell atoms (see, e.g., Refs. 16 and 20). Even though the formalism is applied for \( c \to \infty \), the relativistic ground state corresponds to a well-defined \( j = l \pm 1/2 \). For open subshells with \( l \neq 0 \) the average thus extends over the \( 2j + 1 \) substates for this \( j \). On the other hand, the average includes all \( 2(2l + 1) \) substates of the subshell in the nonrelativistic situation. The spherical average is, however, applied both in the AE calculation and for the evaluation of \( v_{\rho,\psi}[n_{\rho,\psi}] \). In the final unscreened PP the effect thus essentially cancels.

The derivation of the OPM equation (2) relies on the one-to-one correspondence between the ground-state density, the associated total KS potential, and the set of KS orbitals. In the core region, however, the PO's correspond to different screened PP's, which play the role of the total KS potential in the unscreening procedure. Thus, as a matter of principle, the pseudovaleence density does not uniquely determine the complete set of PO's. The nonlocal nature of the PP therefore questions the legitimacy of Eq. (2). The same basic problem also exists for explicitly density-dependent functionals, for which, nevertheless, the standard expressions for \( v_{\rho} \) are routinely applied. Following this standard, we have used Eq. (2) for the calculation of \( v_{\rho}[n_{\rho,\psi}] \) in the case of exact exchange. This procedure is supported by the very limited sensitivity of \( v_{\rho}[n_{\rho,\psi}] \) to the form of the PO's in the core region (see Fig. 1 of Ref. 13).


In the case of the LDA the Hamann prescription (Ref. 34) has been utilized to construct PP's for the unoccupied 3\( d \) orbitals of the second-row atoms.

For the smoothly truncated core density we have used the form \( n_0 + \sum_{i=1}^{6} n_i r^i \) for \( r < r_{\text{NLCC}} \) with the cutoff radii \( r_{\text{NLCC}} \) given in Table I.


Note that the exact densities of open-shell atoms are nonspherical; see H.A. Fertig and W. Kohn, Phys. Rev. A 62, 052511 (2000).


For all molecular calculations prolate-elliptic coordinates and a Hylleraas-type two-center basis set have been employed (for the details see Ref. 30). For open-shell atoms we have consistently used atomic reference energies obtained from nonspherical densities for the evaluation of dissociation energies. Taking all sources of numerical inaccuracies, i.e., the basis set and grid sizes as well as the fit of the numerical energy surface to a Morse function, together, the resulting molecular bond lengths are converged to better than 0.002 bohr, the dissociation energies are correct within 0.002 eV, and vibrational frequencies are within 10 cm\(^{-1}\).

For the molecular and bulk OPM calculations the semianalytical KLI approximation (Ref. 17) has been utilized. The KLI approximation proved to be very accurate not only for atoms (Ref. 17), but also for molecules (Ref. 30) and the bulk. For the polyatomic systems it has the advantage that it allows the use of larger basis sets than the numerically much more involved full OPM. In practice, the KLI approximation thus usually provides ground-state energies for these systems which are lower than those obtained with the full OPM in combination with the necessarily more moderate basis sets (Ref. 30).

The xc tail obtained by use of the KLI approximation (Ref. 17) for the construction of the PP differs from the OPM tail. While it is of the same magnitude, it does not show the oscillatory behavior of the OPM tail (Ref. 51).


All calculations in Tables II and III are based on spherically averaged densities.

For \( v_{\text{loc}} \) we have always used the \( p\)-PP in the case of the first-row elements and the \( d\)-PP for the second-row atoms.


Plane-wave basis sets with energy cutoffs of 25–35 hartree have been used. The integrations over the Brillouin zone have been performed with the Monkhorst-Pack technique [H.J. Monkhorst and J.D. Pack, Phys. Rev. B 13, 5188 (1976)] using 44 special \( k \) points.