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Pseudopotentials from orbital-dependent exchange-correlation functionals

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Norm-conserving pseudopotentials are generated on the basis of the optimized potential method (OPM), combining the exact exchange with two different correlation functionals, i.e., the orbital-dependent form of Colle and Salvetti (CS) [Theor. Chim. Acta **37**, 329 (1975)] and the local density approximation (LDA). Application of both types of OPM pseudopotentials to a number of diatomic molecules leads to substantially different predictions for spectroscopic constants, thus indicating the importance of a suitable choice for the correlation functional to be used in the OPM context. Moreover, while the CS values are closer to the experimental data, our results nevertheless indicate that a really adequate correlation functional for use with the exact exchange is not yet available. In any case, both variants of the OPM-based pseudopotentials show an improved transferability compared with standard LDA pseudopotentials. [S1050-2947(98)03811-6]

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Many electronic structure calculations for molecules and solids are based on density functional theory, in which all complex many-body effects are absorbed into the exchange (x) and correlation (c) energy functional E_{xc}. While the standard approach to E_{xc} is the local density approximation (LDA), orbital-dependent forms of E_{xc}, for which the corresponding multiplicative xc potentials v_{xc} are obtained via the optimized potential method (OPM) [1], allow the exact treatment of the x-only energy E_x, so that only the c part E_c has to be approximated. As was shown for atoms [2,3] and solids [4–6], this results in significant improvements upon the LDA. However, OPM calculations for complex systems are computationally very demanding and still at the beginning. In order to reduce the computational cost, the use of pseudopotentials (PP's) suggests itself.

In most cases PP's are constructed from explicitly density-dependent E_{xc}, like the LDA [7] or the generalized gradient approximation (GGA) (see, e.g., [8,9]). As an alternative, recently a combination of a Dirac-Fock calculation for the atomic core and an approximate OPM calculation for the valence electrons, utilizing the Krieger-Li-Iafrate (KLI) scheme [10] for the exact E_x and the LDA or GGA for E_c, has been used to generate PP's [5]. It is well known, however, that the success of the LDA to some extent relies on a cancellation of errors between its x and c parts. As soon as the exact E_x (the Fock term) is utilized, one can no longer benefit from this type of error cancellation, so that the use of a particularly accurate form of E_c seems recommendable. As such, the Colle-Salvetti (CS) functional [11], which has been shown to give excellent E_c for light atoms [3], offers itself. In this contribution we present a *consistent* construction of norm-conserving PP's on an OPM basis, extending the PP approach of [7] to the combination of the Fock term with the orbital-dependent CS functional. The important role of the c functional used in the PP construction is investigated in detail by comparing the Fock CS PP's with PP's calculated from the combination of the exact E_x with the LDA for E_c [in the form of Ref. [12]—Vosko, Wilk, and Nusair (VSN)]: We demonstrate that the molecular results obtained with OPM-PP's depend rather sensitively on this input to the PP construction scheme and that an adequate correlation functional for use with the exact E_x is not yet available.

The PP scheme of [7] starts with an all-electron calculation (for which the relativistic OPM [13] is used in this work), employing a spherical average for open shells. In the case of the LDA, the PP's are usually constructed from the tabulated atomic configurations of [7], in which excited levels are stabilized by partial ionization and fractional occupation. This procedure is necessary because in the LDA the exchange potential v_x decays exponentially for large r, so that some excited levels of interest would be unbound if the ground state of the neutral atom was used. For the OPM, on the other hand, the correct asymptotic behavior of the exact v_x leads to much more realistic unoccupied levels, allowing the use of the ground-state configuration for all PP's. We have thus examined both sets of reference configurations here, the differences between the resulting PP's being a rough measure of their transferability. For each valence level with quantum numbers lj a PP is constructed so that its lowest (nonrelativistic) eigenstate agrees with the properly normalized upper component of the all-electron spinor beyond a suitably chosen core radius $r_{c,lj}$ (the $r_{c,lj}$ of [7] have been used throughout). The nodeless pseudo-wave-function is then modified inside the core to achieve norm conservation, leading to the corresponding screened PP $v^{sc}_{ps,lj}$. Finally, subtraction of the valence Hartree and xc potentials, i.e., $v_H[n]$ and $v_{xc}[n]$, evaluated for the (pseudo)valence density n_{ps}, from $v^{sc}_{ps,lj}$ gives the unscreened PP,

$$v_{ps,lj}(r)=v^{sc}_{ps,lj}(r)-v_H([n_{ps}],r)-v_{xc}([n_{ps}],r), \quad (1)$$

in which all interaction effects between the valence electrons are eliminated.

While for explicitly density-dependent E_{xc} the evaluation of $v_{xc}([n],\boldsymbol{r})=\delta E_{xc}/\delta n(\boldsymbol{r})$ is straightforward also for $n=n_{ps}$, the situation is somewhat more complicated for orbital-dependent E_{xc}, for which the functional derivative has to be evaluated indirectly via the OPM. In the all-electron case one uses the unique correspondence between n and the Kohn-Sham (KS) orbitals to replace $\delta E_{xc}/\delta n$ by

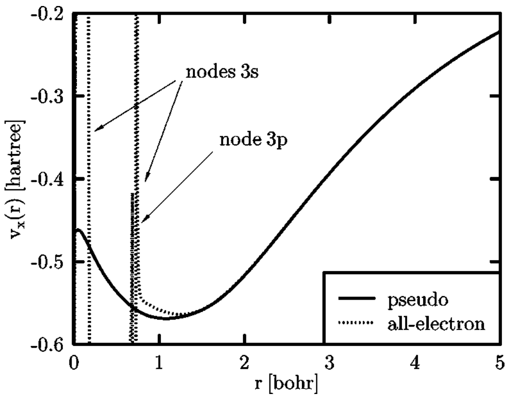

FIG. 1. Internal v_x of valence electrons for Si, obtained by solution of Eq. (3) for all-electron and pseudo-orbitals.

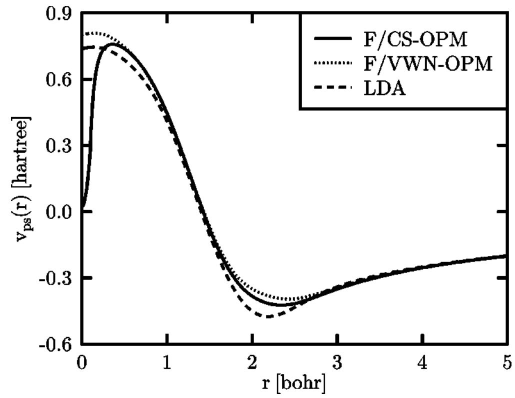

FIG. 2. Pseudopotential v_{ps} for the $3s$ orbital of Na: OPM results for two functionals, i.e., the combinations of the exact exchange (F) with either the CS [11] or the VWN [12] correlation functional, in comparison with LDA result.

functional derivatives of E_{xc} with respect to the orbitals. However, as for $r<r_{c,lj}$ the pseudo-orbitals φ_{lj}^{ps} belong to different $v_{ps,lj}^{sc}$,

$$\left\{-\frac{\hbar^2\nabla^2}{2m}+v_{ps,lj}^{sc}\right\}\varphi_{lj}^{ps}=\epsilon_{lj}\varphi_{lj}^{ps}, \qquad (2)$$

n_{ps} does not uniquely determine the complete set of φ_{lj}^{ps} from a rigorous point of view. On the other hand, in the physically relevant valence region all $v_{ps,lj}^{sc}$ are identical with the all-electron potential, and the φ_{lj}^{ps} are identical with the corresponding all-electron orbitals. Moreover, the basic concept of PP's implies that the form of the pseudo-orbitals in the core region is essentially irrelevant for their physical properties (as long as the orbitals are norm conserving and smooth—compare [5]). Consequently, one would expect that in spite of the nonlocality of E_{xc} the form of the φ_{lj}^{ps} for $r<r_{c,lj}$ does not substantially affect $v_{xc}[n_{ps}]$ in the valence regime. This suggests to rely on the standard form of the OPM [1,13] for the calculation of the internal v_{xc} of the pseudo-orbitals,

$$\int d^3r'\frac{\delta n_{ps}(\boldsymbol{r})}{\delta v_{ps}^{sc}(\boldsymbol{r}')}v_{xc}([n_{ps}],\boldsymbol{r}')$$
$$=\int d^3r'\sum_{lj}\frac{\delta\varphi_{lj}^{ps}(\boldsymbol{r}')}{\delta v_{ps}^{sc}(\boldsymbol{r})}\frac{\delta E_{xc}}{\delta\varphi_{lj}^{ps}(\boldsymbol{r}')}+\text{c.c.}, \qquad (3)$$

i.e., to define δn_{ps} as the response of the density if the same perturbation δv_{ps}^{sc} is added to all $v_{ps,lj}^{sc}$ [note that the E_{xc} used in this work do not depend on the KS eigenvalues, so that no corresponding term appears in Eq. (3)]. We just remark that nonlinear core corrections [14] can be easily incorporated in this scheme by including the frozen all-electron core states in Eq. (3).

The assumption of an approximate decoupling of the core and valence regimes which underlies Eq. (3) can be tested by solving Eq. (3) for two sets of valence orbitals which only differ in the core region. In Fig. 1 we thus compare the v_x resulting from Eq. (3) for the valence electrons of Si obtained with (i) the original all-electron wave functions and (ii) the φ_{lj}^{ps}. Although the two v_x differ completely in the core region (with the v_x of the all-electron valence orbitals diverging at their nodes, as indicated in Fig. 1), they agree almost perfectly in the relevant bonding regime, thus clearly supporting the assumption of decoupling (the cutoff radii are 0.97 bohr for the $3s$ and 1.46 bohr for the $3p$ level).

The unscreened v_{ps} resulting from both combinations of orbital-dependent x and c functionals for the $3s$ orbital of Na are shown in Fig. 2 in comparison with their LDA counterpart. One finds that v_{ps} becomes more shallow when going from the LDA to the Fock/CS and finally to the Fock/VWN (combination of exact exchange with VWN correlation) variant of the OPM. At the same time, the position of the minimum of v_{ps} is shifted to larger r values. Differences of the same size are obtained, e.g., for K, while they are smaller for C and Si (though not being negligible), demonstrating that the OPM does not just lead to modifications of the same magnitude and form for all elements. This varying impact results from a subtle cancellation of much larger differences between the corresponding v_{ps}^{sc} and $v_{xc}[n_{ps}]$: In the valence regime the exact v_x of the OPM, which completely cancels the ''spurious'' self-interaction in v_H, is much more attractive than v_x^{LDA}, and in addition one has $v_c^{\mathrm{LDA}}<v_c^{\mathrm{CS}}<0$. Taking the difference between the eigenvalue of the highest occupied orbital and the experimental ionization potential (IP) as quality criterion, the Fock/CS OPM leads overall to the most realistic v_{xc} [3]. However, for a number of atoms (as, e.g., F) the exact v_c must be repulsive in the valence regime, as the exact x-only eigenvalues [2] are larger than the experimental IP's (compare [15]). Thus for these atoms even the sign of the CS correlation potential is incorrect in the valence regime, so that the resulting Fock/CS PP's in spite of the improved v_x are not necessarily more realistic than LDA-PP's [16].

For a number of elements we have found sizeable kinks in the Fock/CS PP's for very small r (see Fig. 2). This structure originates from the CS contribution to $v_{xc}[n_{ps}]$, required for Eq. (1). However, this unphysical feature, which is due to the specific form of the semiempirical CS functional (and sensitively depends on the choice of $r_{c,lj}$), does not affect molecular results as the valence density is negligible in this region. To illustrate this point we have generated an alternative set of Fock/CS PP's for Na by extrapolating their form in the vicinity of $r=0.5$ bohr smoothly to the origin, thereby eliminating the kinks. This leads to Fock/CS PP's which are

TABLE I. Percentage deviations of bond lengths (Δr_e) and energies (ΔD_e) obtained with pseudopotentials resulting from two different atomic valence configurations (see text): Fock/VWN-OPM versus LDA results.

	Δr_e		ΔD_e	
	OPM	LDA	OPM	LDA
Li_2	0.0	−1.0	0.6	3.0
Na_2	0.3	−0.7	−0.7	5.2
K_2	0.9	2.2	−0.5	5.0

almost indistinguishable from their Fock/CS VWN counterparts for $r<0.5$ bohr. The energy surfaces for Na_2 resulting from both versions of the Fock/CS PP's via the calculational scheme described below differ by less than 10^{-3} eV, thus justifying the smoothing procedure (clearly, one would expect that a first-principles, orbital-dependent E_c [17] does not require any smoothing—all Fock/CS data given below have been obtained with the original unmodified Fock/CS PP's). On the other hand, in the bonding regime the OPM-PP's do not show any artificial structures as have been reported for GGA's [8]. Consequently the OPM allows the construction of soft PP's, which is an important criterion for plane-wave calculations.

In order to examine the impact of the orbital-dependent treatment of *xc* effects in PP's on chemical binding, we have studied a number of diatomic molecules, employing the local spin density approximation (LSDA) in all molecular calculations. This scheme has been chosen for two reasons: On the one hand, the application of orbital-dependent methods to molecules or solids is computationally very involved, so that it is presently limited to very small or highly symmetric systems. In order to utilize the OPM-PP's, e.g., in molecular-dynamics simulations one would have to combine them with a conventional density-functional treatment of the valence electrons in the molecular computation, thus using the OPM only to construct an optimal Fock space for the molecular problem. In this respect, our results demonstrate what can be gained by simply replacing the standard LDA-PP's by OPM-PP's in presently available codes, i.e., without any additional computational cost. On the other hand, the above scheme allows us to separate the relevance of the *xc* functional for the form of the PP's, whose analysis is our main objective, from that for the actual molecular calculations. Note that this procedure is consistent as the internal atomic *xc* contributions of the valence electrons are eliminated from the final v_{ps} via Eq. (1) [18].

We have solved the two-center KS equations on a prolate spheroidal mesh, expanding the KS orbitals in terms of Hylleraas basis functions (see [19]). In all calculations *j*-averaged PP's ($v_{ps,l}=[(l+1)v_{ps,l,l+1/2}+lv_{ps,l,l-1/2}]/(2l+1)$) have been applied, taking the PP for the highest l as a local potential (for H we have used the exact Coulomb potential, rather than a PP).

First of all, we have examined the dependence of the molecular results on the atomic configuration used for the construction of $v_{ps,lj}$. From both the configurations of [7] and

TABLE II. Bond lengths r_e and energies D_e for diatomic molecules: Comparison of Fock/CS-OPM and Fock/VWN-OPM with LDA pseudopotentials (the percentage of deviation from experiment are given in parentheses). r_e and D_e (zero-point energy is subtracted) have been obtained by a fit to a Morse potential. Experimental values are taken from [23].

	r_e (bohr)						
	Expt.	Fock/CS-OPM		Fock/VWN-OPM		LDA	
Li_2	5.05	5.03	(−0.4)	5.22	(3.4)	4.97	(−1.7)
Na_2	5.82	5.73	(−1.5)	5.99	(3.0)	5.45	(−6.4)
K_2	7.38	7.39	(0.2)	7.69	(4.2)	6.84	(−7.4)
HF	1.73	1.76	(1.8)	1.76	(1.8)	1.76	(1.7)
C_2	2.35	2.35	(−0.1)	2.36	(0.6)	2.34	(−0.4)
P_2	3.58	3.58	(0.1)	3.62	(1.1)	3.55	(−0.8)
Si_2	4.24	4.30	(1.4)	4.37	(2.9)	4.27	(0.5)
	D_e (eV)						
	Expt.	Fock/CS-OPM		Fock/VWN-OPM		LDA	
Li_2	1.05	1.04	(−0.7)	0.94	(−10)	1.04	(−1.1)
Na_2	0.72	0.84	(17)	0.75	(5)	0.88	(23)
K_2	0.51	0.61	(20)	0.55	(7)	0.69	(35)
HF	5.87	6.86	(17)	6.72	(15)	6.71	(14)
C_2	6.21	7.32	(18)	6.77	(9)	6.78	(9)
P_2	5.03	6.25	(24)	5.67	(13)	5.95	(18)
Si_2	3.21	4.11	(28)	3.78	(18)	3.95	(23)

the ground-state configurations with unoccupied excited states, we have generated OPM-PP's and LDA-PP's for Li, Na, and K, restricting ourselves to sp components (and to the combination Fock/VWN of the OPM), and applied them to the corresponding dimers. The percentages of deviation between the resulting spectroscopic constants are listed in Table I. Although the ground-state configuration represents a rather extreme basis for LDA-PP's, Table I nevertheless demonstrates that LDA results are more sensitive to the atomic reference configuration than OPM data. This indicates that the error introduced by the linearization of the core-valence contribution to v_{xc} implied in Eq. (1) is much smaller for the exact v_x than for the LDA (a similar observation has been made for Hartree-Fock PP's [20]). Consequently, the transferability of OPM-PP's to other chemical environments should be better than that of LDA-PP's [21].

For a comparison with experimental data we thus contrast OPM-PP's from the ground-state configuration with LDA-PP's from the configurations in [7], including s, p, and d components. The equilibrium distances r_e and dissociation energies D_e resulting for some diatomic molecules are given in Table II. While the tendency of the standard LDA scheme to overbind is a well-known fact, the use of the exact exchange in the PP's weakens the bonds, consistent with Fig. 2. However, Fock/VWN PP's produce r_e, which are systematically larger than the experimental values. We attribute this behavior to the fact that in Fock/VWN the LDA's overestimation of atomic E_c and the corresponding deficiencies in v_c are no longer compensated by errors in E_x and v_x of opposite sign. Although the corresponding D_e are not completely unrealistic, these results clearly show that the exact E_x should not be combined with the LDA for E_c.

On the other hand, focusing on the PP's from the presently most reliable orbital-dependent scheme, the Fock/CS variant of the OPM, one finds that the bonds are weakened much less. As a consequence, the errors in r_e in most cases are significantly reduced when going from the Fock/LDA-PP's to the Fock/CS PP's. The only exceptions are Si_2 and HF, where even the LDA-PP's lead to an overestimation of r_e. It seems likely that these particular problems are related to the incorrect behavior of the CS correlation potential in the asymptotic regime of Si and F, thus indicating the need for a more accurate orbital-dependent E_c than the CS functional (the core polarization effects neglected in our calculation reduce r_e by less than 0.01 bohr [22] in the case of HF). As far as D_e is concerned, the picture is not as clear. While Fock/CS PP's slightly improve the D_e's of the alkali-metal dimers, they clearly overestimate the D_e's of the other molecules examined. These results suggest that in order to obtain the correct energetics of molecules, an OPM (or KLI) treatment of E_{xc} in the molecular calculations is mandatory. For such calculations consistent OPM-PP's should be particularly suited.

In any case, the substantial differences between the data obtained with Fock/CS and Fock/VWN PP's emphasize the importance of a suitable choice of the c functional to be used with the exact E_x. In fact, not only VWN but also the CS functional does not seem to be an ideal counterpart. It remains to be investigated whether the first-principles orbital-dependent E_c put forward in [17] can fill this gap.

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