

## 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  $v_{ps,lj}^{sc}$ . 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  $v_{ps,lj}^{sc}$  gives the unscreened PP,

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

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

While for explicitly density-dependent  $E_{xc}$  the evaluation of  $v_{xc}([n], r) = \delta E_{xc} / \delta n(r)$  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

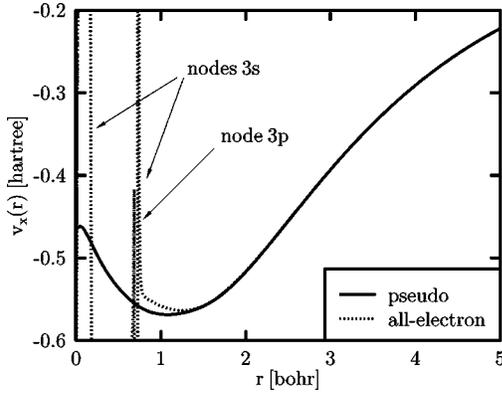


FIG. 1. Internal  $v_x$  of valence electrons for Si, obtained by solution of Eq. (3) for all-electron and pseudo-orbitals.

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

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

$n_{ps}$  does not uniquely determine the complete set of  $\varphi_{lj}^{ps}$  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  $\varphi_{lj}^{ps}$  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  $\varphi_{lj}^{ps}$  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,

$$\begin{aligned} & \int d^3 r' \frac{\delta n_{ps}(\mathbf{r})}{\delta v_{ps}^{sc}(\mathbf{r}')} v_{xc}([n_{ps}], \mathbf{r}') \\ &= \int d^3 r' \sum_{lj} \frac{\delta \varphi_{lj}^{ps}(\mathbf{r}')}{\delta v_{ps}^{sc}(\mathbf{r}')} \frac{\delta E_{xc}}{\delta \varphi_{lj}^{ps}(\mathbf{r}')} + \text{c.c.}, \end{aligned} \quad (3)$$

i.e., to define  $\delta n_{ps}$  as the response of the density if the same perturbation  $\delta v_{ps}^{sc}$  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  $\varphi_{lj}^{ps}$ . Although the two  $v_x$  differ completely in the core region (with the  $v_x$  of the all-electron valence orbitals

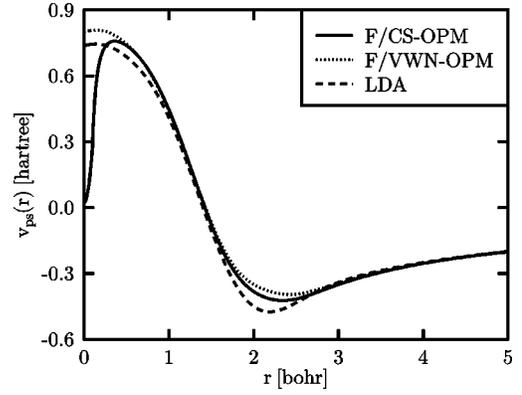


FIG. 2. Pseudopotential  $v_{ps}$  for the 3s orbital of Na: OPM results for two functionals, i.e., the combinations of the exact exchange ( $F$ ) with either the CS [11] or the VWN [12] correlation functional, in comparison with LDA result.

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  $v_x^{\text{LDA}}$ , and in addition one has  $v_c^{\text{LDA}} < v_c^{\text{CS}} < 0$ . 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 ( $\Delta r_e$ ) and energies ( $\Delta D_e$ ) obtained with pseudopotentials resulting from two different atomic valence configurations (see text): Fock/VWN-OPM versus LDA results.

	$\Delta r_e$		$\Delta D_e$	
	OPM	LDA	OPM	LDA
Li <sub>2</sub>	0.0	-1.0	0.6	3.0
Na <sub>2</sub>	0.3	-0.7	-0.7	5.2
K <sub>2</sub>	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<sub>2</sub> 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 <sub>2</sub>	5.05	5.03	(-0.4)	5.22	(3.4)	4.97	(-1.7)
Na <sub>2</sub>	5.82	5.73	(-1.5)	5.99	(3.0)	5.45	(-6.4)
K <sub>2</sub>	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 <sub>2</sub>	2.35	2.35	(-0.1)	2.36	(0.6)	2.34	(-0.4)
P <sub>2</sub>	3.58	3.58	(0.1)	3.62	(1.1)	3.55	(-0.8)
Si <sub>2</sub>	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 <sub>2</sub>	1.05	1.04	(-0.7)	0.94	(-10)	1.04	(-1.1)
Na <sub>2</sub>	0.72	0.84	(17)	0.75	(5)	0.88	(23)
K <sub>2</sub>	0.51	0.61	(20)	0.55	(7)	0.69	(35)
HF	5.87	6.86	(17)	6.72	(15)	6.71	(14)
C <sub>2</sub>	6.21	7.32	(18)	6.77	(9)	6.78	(9)
P <sub>2</sub>	5.03	6.25	(24)	5.67	(13)	5.95	(18)
Si <sub>2</sub>	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  $\text{Si}_2$  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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