RAPID COMMUNICATIONS

PHYSICAL REVIEW B **80**, 161205(R) (2009)

Relevance of core-valence interaction for electronic structure calculations with exact exchange

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(Received 6 August 2009; published 23 October 2009)

The role of the core-valence interaction in electronic structure calculations with the exact exchange of density-functional theory is investigated by comparison of pseudopotential with all-electron results for diamond and lithium. The same full-potential framework is applied in the case of both approaches, checking carefully the convergence of all results. It is found that the all-electron band structures of both prototype solids are well reproduced by the pseudopotential scheme. While for lithium with its rather polarizable core minor deviations between pseudopotential and all-electron bands are observed, the differences are marginal for diamond. The corresponding band gaps differ by less than 0.1 eV. This result gives further credence to the use of pseudopotentials in combination with the exact exchange.

DOI: 10.1103/PhysRevB.80.161205 PACS number(s): 71.15.Mb, 71.27.+a, 71.20.Be, 31.15.E−

Density-functional calculations with the exact exchange (EXX) have attracted considerable attention during the last decade (for an overview, see Ref. 1). This interest has primarily been triggered by the observation that the EXX approach yields band gaps in much better agreement with experiment than the corresponding local-density approximation (LDA) or generalized gradient approximation (GGA) data.[2–4] Improved gaps were found both with all-electron (AE) calculations on the basis of the atomic-sphere approximation[2] as well as with full-potential plane-wave pseudopotential (PP) calculations.[3–5] The EXX-PP scheme gives realistic gaps even for the transition-metal monoxides FeO and CoO,[6] which are predicted to be metallic by the LDA and GGA. Moreover, the exact exchange provides the basis for an orbital-dependent treatment of correlation, which—unlike the LDA and GGA—leads to correlation potentials in good agreement with exact reference results.[7–10]

Recently, however, this general perception of improvement by the EXX approach has been questioned by the first full-potential linearized-augmented-plane-wave (LAPW) calculations with the exact exchange.[11] In many cases, including such elementary solids as diamond, the LAPW band gaps turned out to be much larger than the corresponding PP values. As a result, the LAPW gaps for *sp* semiconductors agree much less with experimental data than their PP counterparts. On the other hand, the LAPW gaps for diamond and the noble gas solids are closer to experiment than the PP gaps. The discrepancy between PP and LAPW data was attributed to the missing core-valence interaction in the PP approach.[11]

Clearly, a realistic picture of the merits and shortcomings of the EXX scheme is of prime importance for future development of density-functional theory. Therefore, in this contribution the role of the core-valence interaction in EXX calculations is studied in detail. Two prototype solids are investigated, diamond and lithium, applying the same full-potential method to both the PP and the AE problems. It is found that the complete EXX band structures of both solids are well reproduced by the PP technique. The difference between the PP and the AE gaps of diamond amounts to less than 0.1 eV, with the AE gap being smaller than the PP gap.[12] The present results indicate that the differences between the LAPW and PP band gaps observed for diamond[11] cannot be due to the omission of the core-valence exchange in PP calculations. In fact, the core-valence interaction appears to be slightly less important for the EXX functional than for the LDA, at least in the case of lithium. This finding is consistent with earlier results for atomic excitation energies and spectroscopic constants of diatomic molecules.[13]

The core of any EXX calculation is the evaluation of the exact exchange potential v_{x}. In the case of periodic systems v_{x} can be written as[4]

$$v_{\mathrm{x}}(\boldsymbol{G}) = \sum_{\boldsymbol{G}'} \chi_{\mathrm{s}}^{-1}(\boldsymbol{G},\boldsymbol{G}')\Lambda_{\mathrm{x}}(\boldsymbol{G}'), \tag{1}$$

where χ_{s}^{-1} is the inverse of the static Kohn-Sham (KS) response function χ_{s} for a strictly periodic perturbation,

$$\chi_{\mathrm{s}}(\boldsymbol{G},\boldsymbol{G}') = \sum_{\boldsymbol{k}\alpha\alpha';\alpha'\neq\alpha} \frac{\Theta_{\boldsymbol{k}\alpha}-\Theta_{\boldsymbol{k}\alpha'}}{\epsilon_{\boldsymbol{k}\alpha}-\epsilon_{\boldsymbol{k}\alpha'}} \times \sum_{\boldsymbol{G}''} c_{\boldsymbol{k}\alpha}^{\dagger}(\boldsymbol{G}'')c_{\boldsymbol{k}\alpha'}(\boldsymbol{G}''+\boldsymbol{G}) \times \sum_{\boldsymbol{G}'''} c_{\boldsymbol{k}\alpha'}^{\dagger}(\boldsymbol{G}''')c_{\boldsymbol{k}\alpha}(\boldsymbol{G}'''-\boldsymbol{G}'), \tag{2}$$

and the inhomogeneity is given by

$$\Lambda_{\mathrm{x}}(\boldsymbol{G}) = \sum_{\boldsymbol{k}\alpha\alpha';\alpha'\neq\alpha} \frac{\Theta_{\boldsymbol{k}\alpha}-\Theta_{\boldsymbol{k}\alpha'}}{\epsilon_{\boldsymbol{k}\alpha}-\epsilon_{\boldsymbol{k}\alpha'}} S_{\boldsymbol{k}\alpha\alpha'} \sum_{\boldsymbol{G}'} c_{\boldsymbol{k}\alpha}^{\dagger}(\boldsymbol{G}')c_{\boldsymbol{k}\alpha'}(\boldsymbol{G}'+\boldsymbol{G}), \tag{3}$$

$$S_{\boldsymbol{k}\alpha\alpha'} = -\frac{1}{\Omega}\sum_{\boldsymbol{k}''\alpha''}\Theta_{\boldsymbol{k}''\alpha''}\sum_{\boldsymbol{G}}\frac{4\pi e^2}{(\boldsymbol{k}-\boldsymbol{k}''+\boldsymbol{G})^2} \times \sum_{\boldsymbol{G}'} c_{\boldsymbol{k}\alpha'}^{\dagger}(\boldsymbol{G}')c_{\boldsymbol{k}''\alpha''}(\boldsymbol{G}'-\boldsymbol{G})\sum_{\boldsymbol{G}''} c_{\boldsymbol{k}''\alpha''}^{\dagger}(\boldsymbol{G}'')c_{\boldsymbol{k}\alpha}(\boldsymbol{G}''+\boldsymbol{G}). \tag{4}$$

Here, $c_{\boldsymbol{k}\alpha}(\boldsymbol{G})$ denotes the expansion coefficients of the Bloch states $\phi_{\boldsymbol{k}\alpha}$ on the reciprocal lattice,

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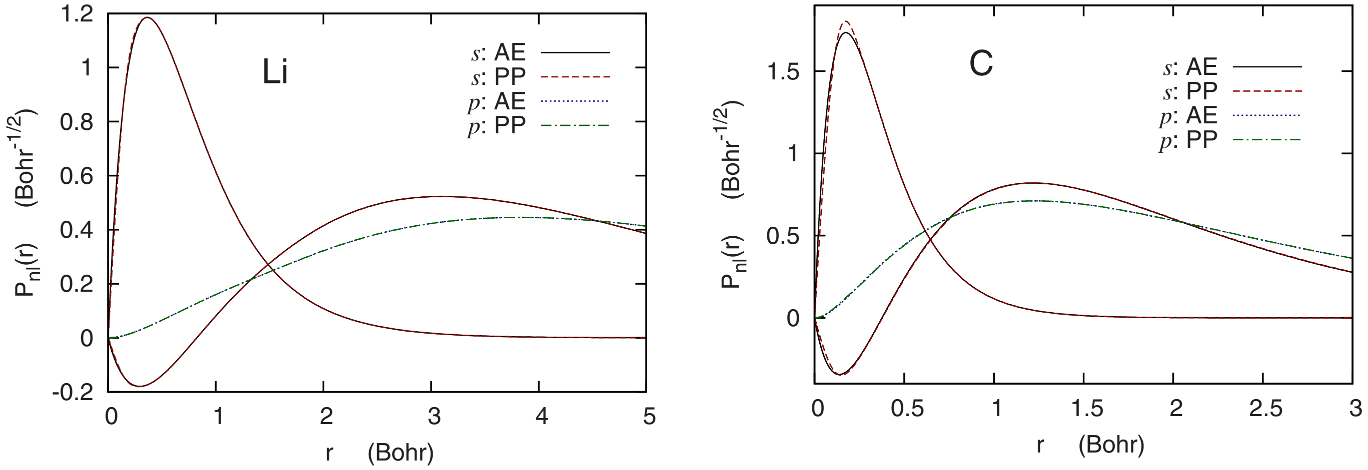

FIG. 1. (Color online) Soft versus standard all-electron radial orbitals: (a) Li with $r_c=0.40$ bohr and (b) C with $r_c=0.35$ bohr.

$$\phi_{k\alpha}(\boldsymbol{r}) = \frac{e^{i\boldsymbol{k}\cdot\boldsymbol{r}}}{\sqrt{\Omega}}\sum_{\boldsymbol{G}} e^{i\boldsymbol{G}\cdot\boldsymbol{r}} c_{k\alpha}(\boldsymbol{G}), \tag{5}$$

and $\Theta_{k\alpha}$ is the occupation factor for the state $\boldsymbol{k}\alpha$ with energy $\epsilon_{k\alpha}$. Since this study focuses on the role of the core-valence interaction in v_x, the correlation potential is omitted in the comparison of AE- with PP-EXX results (as in Ref. 11). This allows one to extract the properties of the exact exchange as cleanly as possible. For integration over the first Brillouin zone, 44 special k points[14] have been applied for lithium and 28 for diamond. These choices ensure a high degree of convergence, leaving, e.g., an error of less than 5 meV in the band gap of diamond.

In the present work both the PP and the AE reference calculations are performed with the PP approach, utilizing norm-conserving EXX-PP, in which spurious long-range core-valence interactions are eliminated by self-consistent iteration.[13] For the actual PP calculations standard PP valence spaces and cutoff radii have been applied (Li: $r_{c,s}=r_{c,p}=2.8$ bohr; C: $r_{c,s}=r_{c,p}=1.2$ bohr). These PPs have been demonstrated to give excellent agreement with AE results for the spectroscopic constants of diatomic molecules.[13] The corresponding cutoff energy E_{cut} of the plane-wave basis was chosen to be 30 Ry for lithium and 80 Ry for diamond. For both systems the p-PP has been applied as local potential.

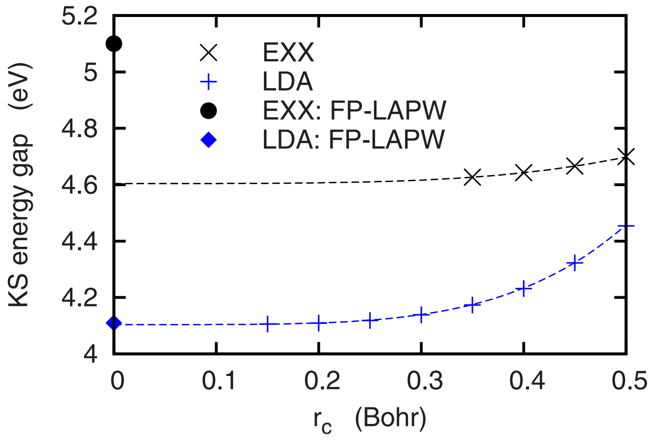

FIG. 2. (Color online) Fundamental KS band gap of diamond as a function of the AE cutoff radius r_c: LDA versus EXX-only results. Also shown are fits to the data at $r_c=0.35$ and 0.45 bohr, using Eq. (6), as well as the corresponding LAPW gaps (Refs. 11 and 15) (lattice constant $a=6.746$ bohr).

In the case of the AE calculations the PPs are only used to smoothen the cusp of the 1s wave function at the position of the nucleus, which implies that the same r_c is used for all angular momenta. In order to demonstrate that this smoothening does not significantly affect the distribution of the electrons, the corresponding atomic orbitals are compared with the standard AE orbitals in Fig. 1. Softened and standard AE orbitals are indistinguishable for the r_c chosen (Li: 0.40 bohr; C: 0.35 bohr), with the exception of the 1s state of C, for which a minor redistribution of the orbital density is observed for $r<r_c$. The softened AE orbitals have the advantage that they can be accurately represented by plane-wave basis sets with $E_{\text{cut}}=280$ Ry for lithium and $E_{\text{cut}}=640$ Ry for carbon.

The sensitivity of the AE results to the AE cutoff radii has

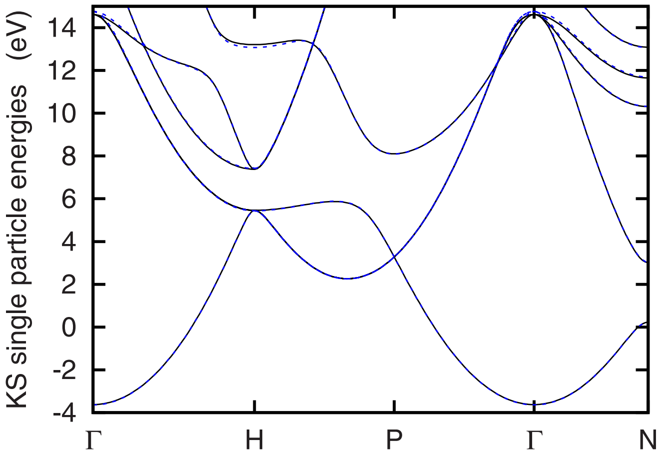

FIG. 3. (Color online) Band structure of lithium obtained by PP calculations with the exact exchange: AE (solid line) versus PP (dashed line) result ($a=6.60$ bohr).

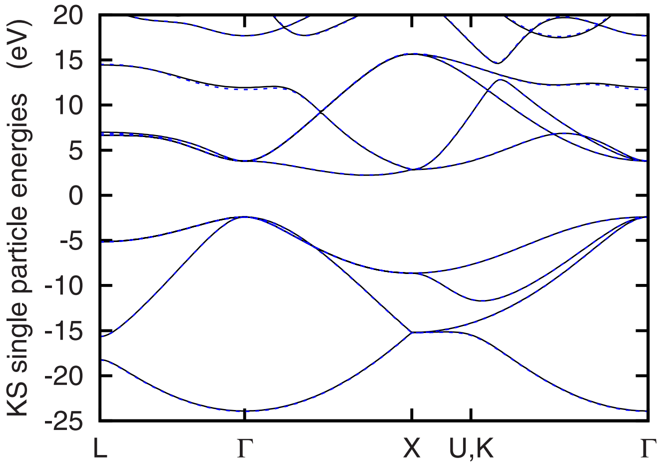

FIG. 4. (Color online) Same as Fig. 3 for diamond.

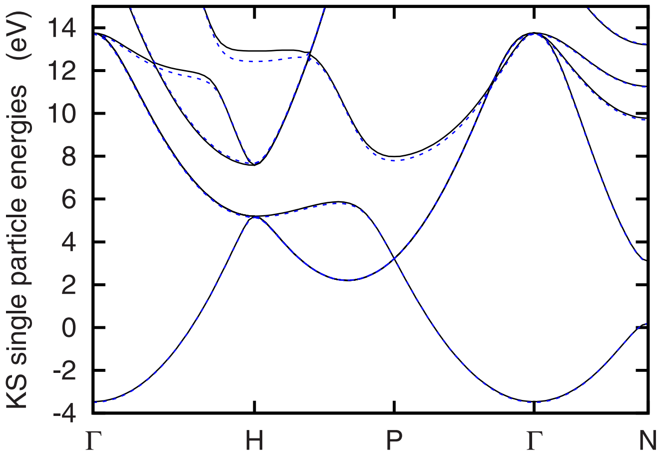

FIG. 5. (Color online) Same as Fig. 3 for LDA.

been carefully checked by variation. In the case of lithium the AE-EXX band structure does not change in any relevant way if r_c is increased by 0.1 bohr: the differences between the resulting valence-band energies are below 7 meV for all k points considered. In the case of diamond the sensitivity of the AE band structure to an increase in r_c is somewhat higher, as a result of the enhanced redistribution of the $1s$ density. When going from $r_c=0.35$ bohr to $r_c=0.45$ bohr, the valence- and lowest conduction-band energies vary by less than 70 meV, the core energies change by 185 meV—the fundamental band gap E_g increases by 40 meV (see Fig. 2) and the gap at the Γ point by less than 10 meV.

The difference between the band energies of diamond obtained with $r_c=0.35$ bohr and the true AE energies (corresponding to $r_c=0$) has been analyzed by LDA calculations. As demonstrated in Fig. 2, the LDA gap of 4.173 eV resulting from $r_c=0.35$ bohr differs by only 0.07 eV from the limit $r_c \to 0$, which is essentially reached for $r_c=0.15$ bohr (for this r_c an E_{cut} of 3200 Ry has been used). The dependence of E_g^{LDA} on r_c is excellently reproduced by the simple expression

$$E_g(r_c) = E_g(0) + \alpha r_c^{\beta}, \tag{6}$$

with $\beta=9/2$. Figure 2 shows this function with the coefficients $E_g(0)$ and α determined by the numerical values for the LDA gap at $r_c=0.35$ and 0.45 bohr. The gap of 4.106 eV obtained with $r_c=0.15$ bohr differs only marginally from the extrapolated true value of 4.102 eV resulting from Eq. (6). Both numbers are in excellent agreement with the full-potential LAPW value of 4.11 eV (Ref. 15) (obtained with the same LDA functional).

Figure 2 also shows that E_g^{LDA} is much more sensitive to r_c than the EXX gap. In the case of the LDA the cusp of the $1s$ orbital directly enters v_x, while the EXX potential is determined by integrals involving this orbital. The available data for the EXX gap are accurately reproduced by the function (6) if $\beta=4$ is chosen. The corresponding fit with $E_g(0)$ and α determined by the values for the EXX gap at $r_c=0.35$ and 0.45 bohr is included in Fig. 2. The extrapolated value for the true gap is 4.60 eV, which is only 0.03 eV lower than the E_g of 4.63 eV found for $r_c=0.35$ bohr. For this reason the subsequent discussion of the AE-EXX bands will be based on the results obtained with $r_c=0.35$ bohr, in order to avoid extrapolation of the complete band structure.

As $v_x(\boldsymbol{r})$ is much smoother than the nuclear potential, an energy cutoff $X_{\text{cut}} < E_{\text{cut}}$ is sufficient for the representation of v_x on the reciprocal lattice.[5,16] The reduced cutoff energy in Eq. (1) has the advantage that both χ_s [Eq. (2)] and Λ_x [Eq. (3)] need not be evaluated for energies beyond X_{cut}, which limits the number of conduction bands to be included (as the bands beyond X_{cut} are dominated by $\boldsymbol{G}$ vectors larger than $\sqrt{2mX_{\text{cut}}}$). Nevertheless, $X_{\text{cut}}=E_{\text{cut}}$ has been applied in the actual PP calculations. The AE calculations, on the other hand, relied on $X_{\text{cut}}=130$ Ry for Li (requiring the inclusion

TABLE I. Fundamental band gap E_g and band gap at Γ point $E_g(\Gamma)$ of diamond: PP- versus AE-EXX results and experimental data [for the experimental $E_g(\Gamma)$ one also finds 6.5 ± 1.0 (Ref. 17) and 7.3 (Ref. 18)—all energies are in eV].

	EXX only			EXX+LDA			
	AE		PP	AE	PP		
	Ref. 11	pw	pw	Ref. 19	Ref. 4	pw	Expt.
E_g	5.1	4.60	4.67	4.58	5.06	4.79	5.48[a]
$E_g(\Gamma)$	6.67	6.19	6.24	5.87	6.28	6.30	6.0 ± 0.2 [b]

[a] Reference 20.
[b] Reference 21.

of 3800 bands) and $X_{\mathrm{cut}}=220$ Ry for diamond (4300 bands). The valence- and lowest conduction-band energies obtained with these X_{cut} differ by no more than 1 meV from the values, which are found with X_{cut} reduced by 20 Ry for both lithium and diamond. When going from 220 to 270 Ry, the maximum difference between the energies of all valence and lowest conduction bands of diamond is below 5 meV and the energies of the 1*s* states differ by 15 meV. Moreover, the fundamental gap of diamond shrinks by only 0.5 meV—if X_{cut} is reduced to 200 Ry—and increases by only 1.5 meV, if X_{cut} is enlarged to 270 Ry. The sensitivity of E_{g} to X_{cut} is an order of magnitude lower than that to r_{c}.

Taking all sources of uncertainty together, the softened AE valence- and conduction-band energies agree with their exact counterparts within 0.01 eV for lithium and 0.07 eV for diamond. The resulting band structures are shown in Figs. 3 and 4. PP and AE results cannot be distinguished for most bands. One only notices a tiny shift of some unoccupied *s* bands of Li. This shift can be eliminated by using the *s*-PP as a local component of the PP, at the price of introducing a slight shift of the *p* bands. The deviation of the PP bands originates from the high polarizability of the Li core and is in no way related to the exact exchange. This statement is verified in Fig. 5, which shows the same comparison as Fig. 3 for the case of the LDA (all technical parameters are chosen as for the EXX). In fact, the deviations between AE and PP bands are clearly larger in the case of the LDA.

The agreement of PP with AE bands is particularly impressive in the case of diamond. The corresponding fundamental band gaps as well as the band gap at the Γ point are listed in Table I. As to be expected from Fig. 4, one finds good agreement of PP and AE data. The present AE gaps are about 0.5 eV smaller than the LAPW results.[11] This difference is a factor of 5–10 larger than the inaccuracy of our AE gaps (as discussed earlier). Moreover, after the inclusion of LDA correlation our PP gaps are close to the corresponding results of Ref. 4.

As already indicated by the agreement of PP and AE results for diatomic molecules,[13] the core-valence interaction appears to be of limited importance in the case of the exact exchange, at least for first row elements. This conclusion is also supported by the good agreement of the PP and AE gaps of the CO and BeO molecules, demonstrated in the preceding paper.[22]

I would like thank D. Ködderitzsch for very helpful discussions and S. Sharma for making the EXX data of Ref. 11 available for me. The calculations for this work have been performed in the computer cluster of the Center for Scientific Computing of J.W. Goethe-Universität Frankfurt.

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