

Implementation of the exact-exchange Kohn-Sham functional within the all-electron FLAPW method

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Abstract

The success of density-functional theory (DFT) relies on the availability of accurate approximations for the exchange-correlation (xc) functional. Standard xc functionals, such as the local-density and the generalized-gradient approximation, suffer from several shortcomings: an unphysical electronic self-interaction, no discontinuity of the xc potential at integral particle numbers, wrong asymptotic behavior etc.. Orbital-dependent functionals are a promising new generation of xc functionals. The simplest variant consistent with the Kohn-Sham theory requiring a local xc-potential is the exact-exchange (EXX) functional. It does not exhibit the above mentioned deficiencies. We implemented the EXX functional within the full-potential augmented-plane-wave (FLAPW) method as realized in the *FLEUR* code (www.flapw.de) using a specifically designed auxiliary basis set for the optimized effective potential (OEP) equation. We demonstrate that the auxiliary and FLAPW basis must be properly balanced to avoid spurious oscillations in the exact exchange potential and show results for prototype semiconductors and insulators.

Orbital-dependent functionals

Orbital-dependent xc functionals of DFT are indirect functionals of the density $E_{xc}[\varphi_{n\mathbf{k}}|V_s[n]]$, since the KS orbitals $\varphi_{n\mathbf{k}}$ are functionals of the effective KS potential V_s , which is a functional of the density [1]. In order to calculate the local xc potential for such a functional the chain rule for functional derivatives must be applied

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} = \sum_{n,\mathbf{k}} \iint d\mathbf{r}' d\mathbf{r}'' \left(\frac{\delta E_{xc}}{\delta \varphi_{n\mathbf{k}}(\mathbf{r}') \delta V_s(\mathbf{r}'')} + \text{c.c.} \right) \frac{\delta V_s(\mathbf{r}'')}{\delta n(\mathbf{r})}$$

We multiply with the density response function $\chi_s(\mathbf{r}, \mathbf{r}') = \delta n(\mathbf{r}) / \delta V_s(\mathbf{r}')$, use perturbation theory for the wavefunction response $\delta \varphi_{n\mathbf{k}}(\mathbf{r}) / \delta V_s(\mathbf{r}')$, and arrive at an integral equation for the local xc potential

$$\begin{aligned} & \int \chi_s(\mathbf{r}, \mathbf{r}') V_{xc}(\mathbf{r}') d\mathbf{r}' \\ &= \sum_{n,\mathbf{k}} \sum_{n' \neq n} \left[\left(\int \frac{\delta E_{xc}}{\delta \varphi_{n\mathbf{k}}(\mathbf{r}') \delta V_s(\mathbf{r}'')} \frac{\varphi_{n'\mathbf{k}}^*(\mathbf{r}) \varphi_{n\mathbf{k}}(\mathbf{r})}{\epsilon_{n\mathbf{k}} - \epsilon_{n'\mathbf{k}}} + \text{c.c.} \right) \right] \end{aligned}$$

So far, the formalism is valid for any orbital-dependent functional. Here, we employ the EXX functional

$$E_x = \sum_{n,\mathbf{k}} \iint \varphi_{n\mathbf{k}}^*(\mathbf{r}) V_x^{\text{NL}}(\mathbf{r}, \mathbf{r}') \varphi_{n\mathbf{k}}(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

with $V_x^{\text{NL}}(\mathbf{r}, \mathbf{r}') = - \sum_{n',\mathbf{q}}^{\text{occ.}} \frac{\varphi_{n'\mathbf{q}}(\mathbf{r}) \varphi_{n'\mathbf{q}}^*(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$. Then, the integral equation for the EXX potential becomes the OEP equation

$$\int \chi_s(\mathbf{r}, \mathbf{r}') V_x(\mathbf{r}') d\mathbf{r}' = \sum_{n\mathbf{k}} \sum_{n' \neq n}^{\text{occ.}, \text{unocc.}} \left[\frac{\langle \varphi_{n\mathbf{k}} | V_x^{\text{NL}} | \varphi_{n'\mathbf{k}} \rangle \varphi_{n'\mathbf{k}}^*(\mathbf{r}) \varphi_{n\mathbf{k}}(\mathbf{r})}{\epsilon_{n\mathbf{k}} - \epsilon_{n'\mathbf{k}}} + \text{c.c.} \right]$$

FLAPW method

In the FLAPW method space is partitioned into non-overlapping atom-centered muffin-tin (MT) spheres and the remaining interstitial region (IR). As basis functions we use the piecewise defined functions

$$\phi_{\mathbf{k}\mathbf{G}}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{\Omega}} \exp[i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}] & \text{if } \mathbf{r} \in \text{IR} \\ \sum_{lm} u_{lp}^a(\mathbf{k}, \mathbf{G}) A_{lmp}(\mathbf{k}, \mathbf{G}) u_{lp}^a(r) Y_{lm}(\hat{\mathbf{r}}) & \text{if } \mathbf{r} \in \text{MT}(a) \end{cases}$$

where the $A_{lmp}(\mathbf{k}, \mathbf{G})$ are defined such that the function matches to the plane wave in the IR in value and first radial derivative. The $u_{lp}^a(r)$ are the solutions of the radial scalar-relativistic Dirac equation with predefined energy parameters E_l , and the $u_{l1}(r)$ are their energy derivatives.

In order to increase the flexibility of the LAPW basis in the MT spheres, it can be augmented with local orbitals (LO), which are confined to the MT spheres

$$\phi_{\text{LO}}(\mathbf{r}) = \begin{cases} 0 & \text{if } \mathbf{r} \in \text{IR} \\ [a_{l0} u_{l0}^a(r) + b_{l0} u_{l1}^a(r) + c_{l0} u_{l2}^a(r)] Y_{lm}(\hat{\mathbf{r}}) & \text{if } \mathbf{r} \in \text{MT}(a) \end{cases}$$

The function $u_{l2}^a(r)$ solves the Dirac equation with another energy parameter. For an accurate representation of the unoccupied states we add local orbitals in each branch of the logarithmic derivative with the energy parameters chosen such that the solutions $u_{lp}^a(r)$, $p \geq 2$ fulfill the condition

$$\frac{d}{dr} \ln[u_{lp}^a(r)]|_{r=R_{\text{MT}}} = -(l+1)$$

at the MT sphere boundary $r = R_{\text{MT}}$.

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Implementation

In order to solve the OEP equation, we introduce a mixed product basis (MPB) $\{M_I(\mathbf{r})\}$ that reformulates the equation as a linear-algebra problem

$$\sum_J \chi_{s,IJ} V_{x,J} = t_I$$

with

$$\begin{aligned} \chi_{s,IJ} &= 2 \sum_{n,\mathbf{k}}^{\text{occ.}} \sum_{n',\mathbf{k}'}^{\text{unocc.}} \frac{\langle M_I \varphi_{n\mathbf{k}} | \varphi_{n'\mathbf{k}'} \rangle \langle \varphi_{n'\mathbf{k}'} | \varphi_{n\mathbf{k}} M_J \rangle}{\epsilon_{n\mathbf{k}} - \epsilon_{n'\mathbf{k}'}} \\ t_I &= 2 \sum_{n,\mathbf{k}}^{\text{occ.}} \sum_{n',\mathbf{k}'}^{\text{unocc.}} \frac{\langle \varphi_{n\mathbf{k}} | V_x^{\text{NL}} | \varphi_{n'\mathbf{k}'} \rangle \langle M_I \varphi_{n'\mathbf{k}'} | \varphi_{n\mathbf{k}} \rangle}{\epsilon_{n\mathbf{k}} - \epsilon_{n'\mathbf{k}'}} \end{aligned}$$

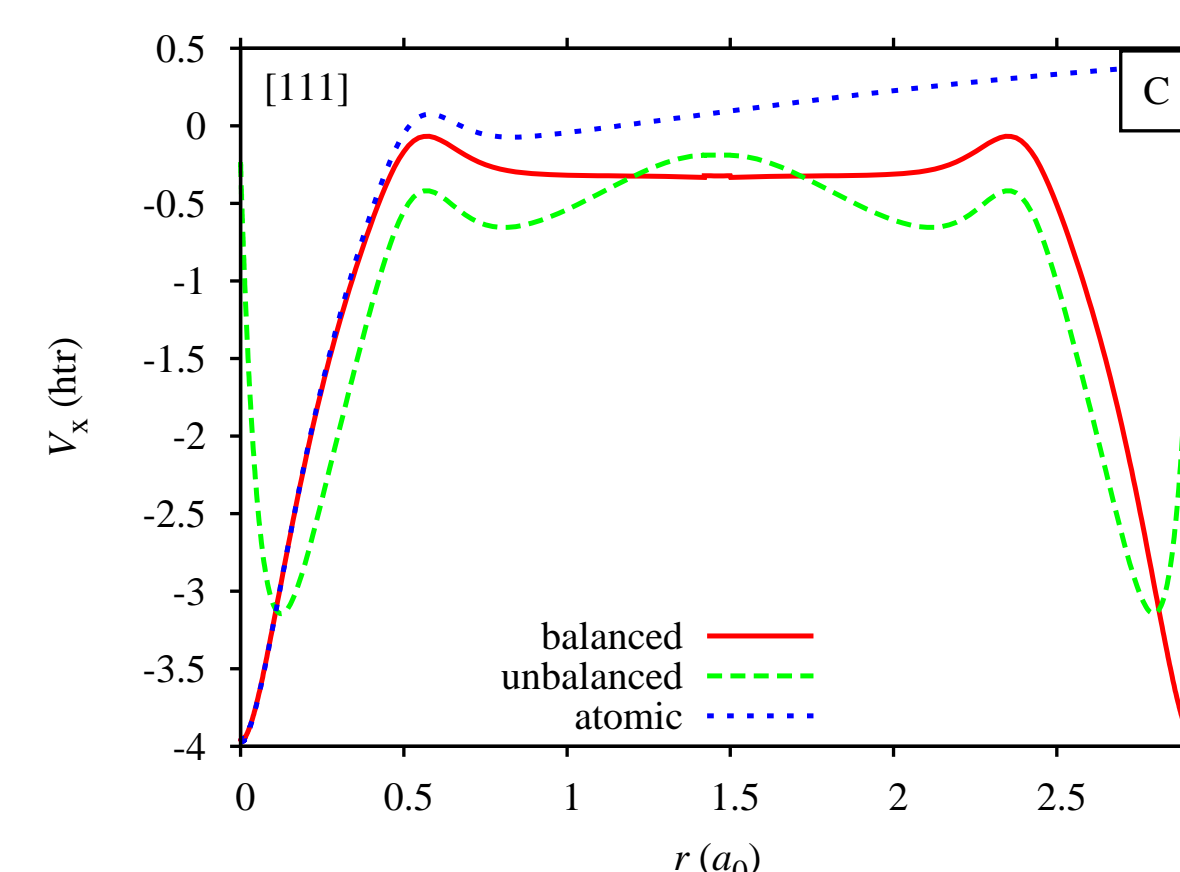
After elimination of the constant function, this equation can be solved by matrix inversion of χ_s .

The MPB $\{M_I(\mathbf{r})\}$ is constructed from products of LAPW basis functions, which yields interstitial plane-waves (IPWs) in the IR and MT functions of the form $U_{LP}(r) Y_{LM}(\mathbf{r})$ in the spheres [2, 3]. We remove near linear dependencies in the set of MT functions $U_{LP}(r)$ leading to a smaller and more efficient basis. Furthermore, we add the atomic exact exchange potential to the set $U_{(L=0),P}$. In analogy to the LAPW basis set, two radial MT functions for each lm channel are used to augment the IPWs, while the remaining functions are combined to form local orbitals.

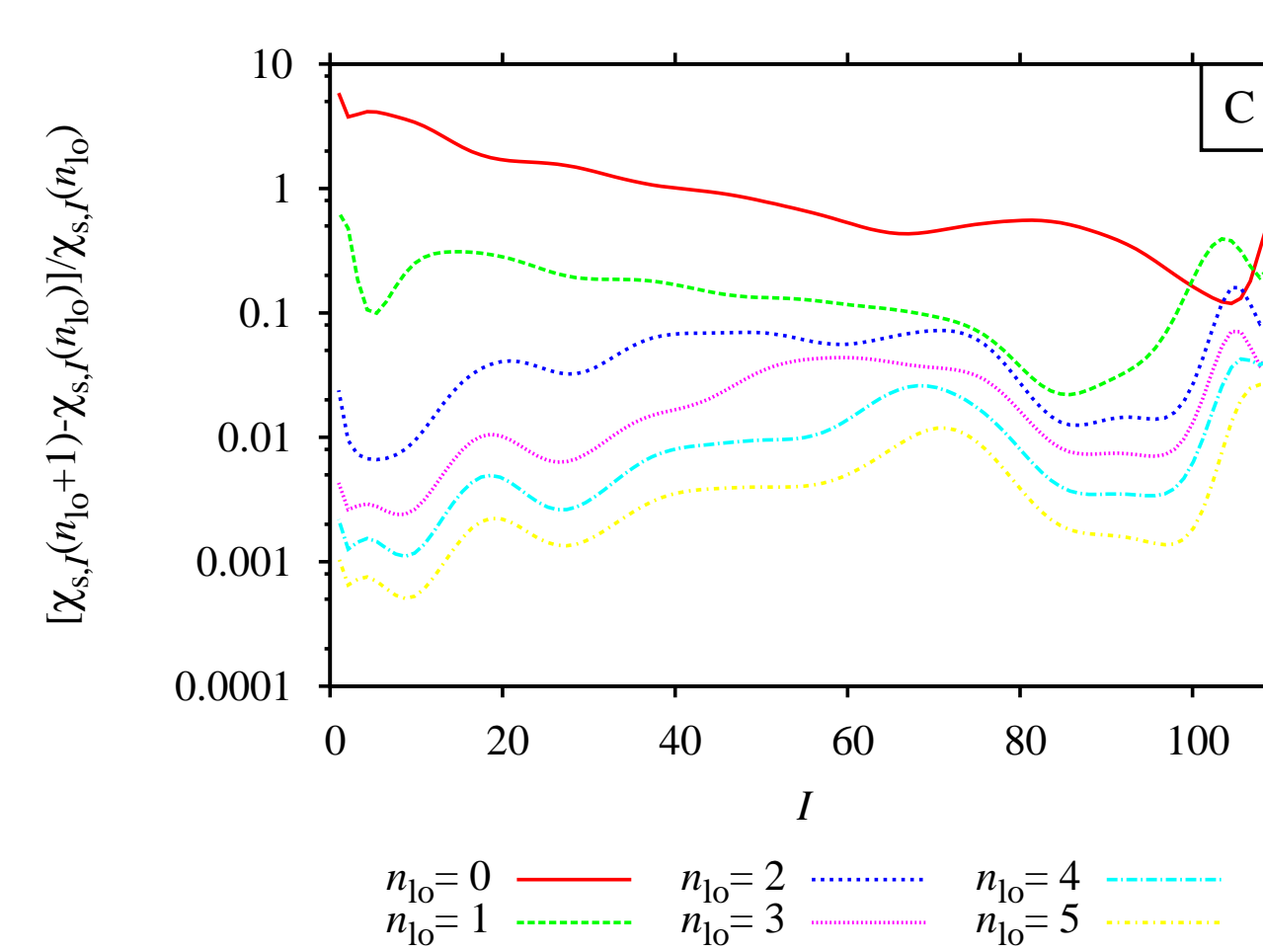
Balance of basis sets

We demonstrate for the case of diamond that a smooth and physical local EXX potential requires a balance of the LAPW and MPB.

If we only use the conventional LAPW basis, the potential (green dashed line) shows an over-pronounced intershell-hump and tends to an unphysical positive value close to the atomic nucleus. Here, the basis sets are unbalanced. In order to converge the EXX potential to the red solid line we had to add no less than six local orbitals per lm channel with $l = 0, \dots, 5$ and $m \leq |l|$ leading to a LAPW basis that is five times as large as that required for conventional local functionals.

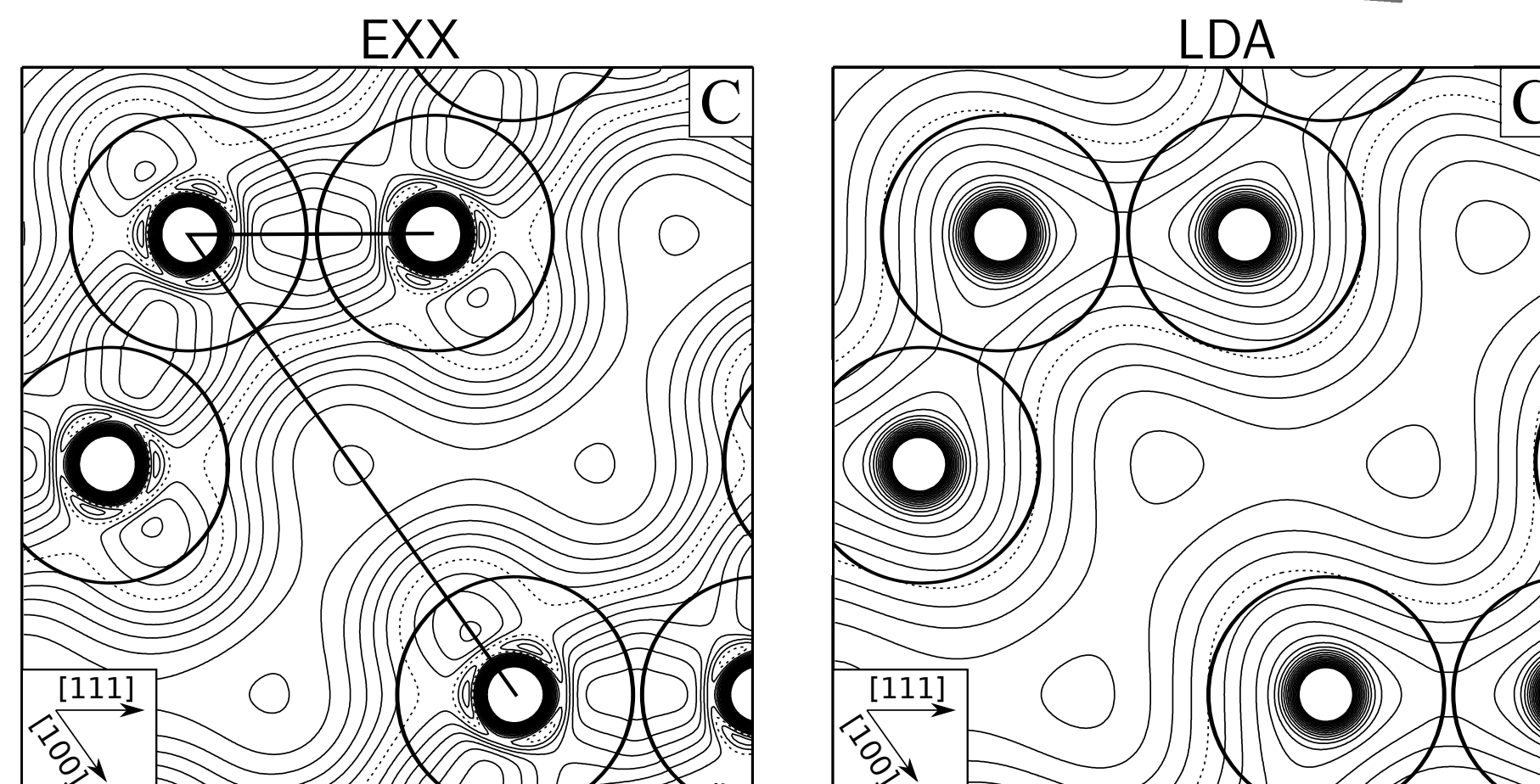


We have traced back the spurious oscillations in the unbalanced case to an insufficiently converged response function. If the LAPW basis, which parametrizes the electron density, is not flexible enough, the electron density cannot follow the changes of the effective potential that are described by the MPB. This becomes evident in the convergence of the relative change of the eigenvalues of the density response function χ_s with respect to the LAPW basis. We add $2l+1$ additional local orbitals per l quantum number ($l = 0, \dots, 5$) in each step.



Full-potential treatment I

The EXX (left) and LDA (right) exchange potentials on the (011) plane of diamond are shown as a contour plot. The non-sphericity of the EXX potential is considerably more pronounced than in LDA, which stresses the importance a full-potential treatment.

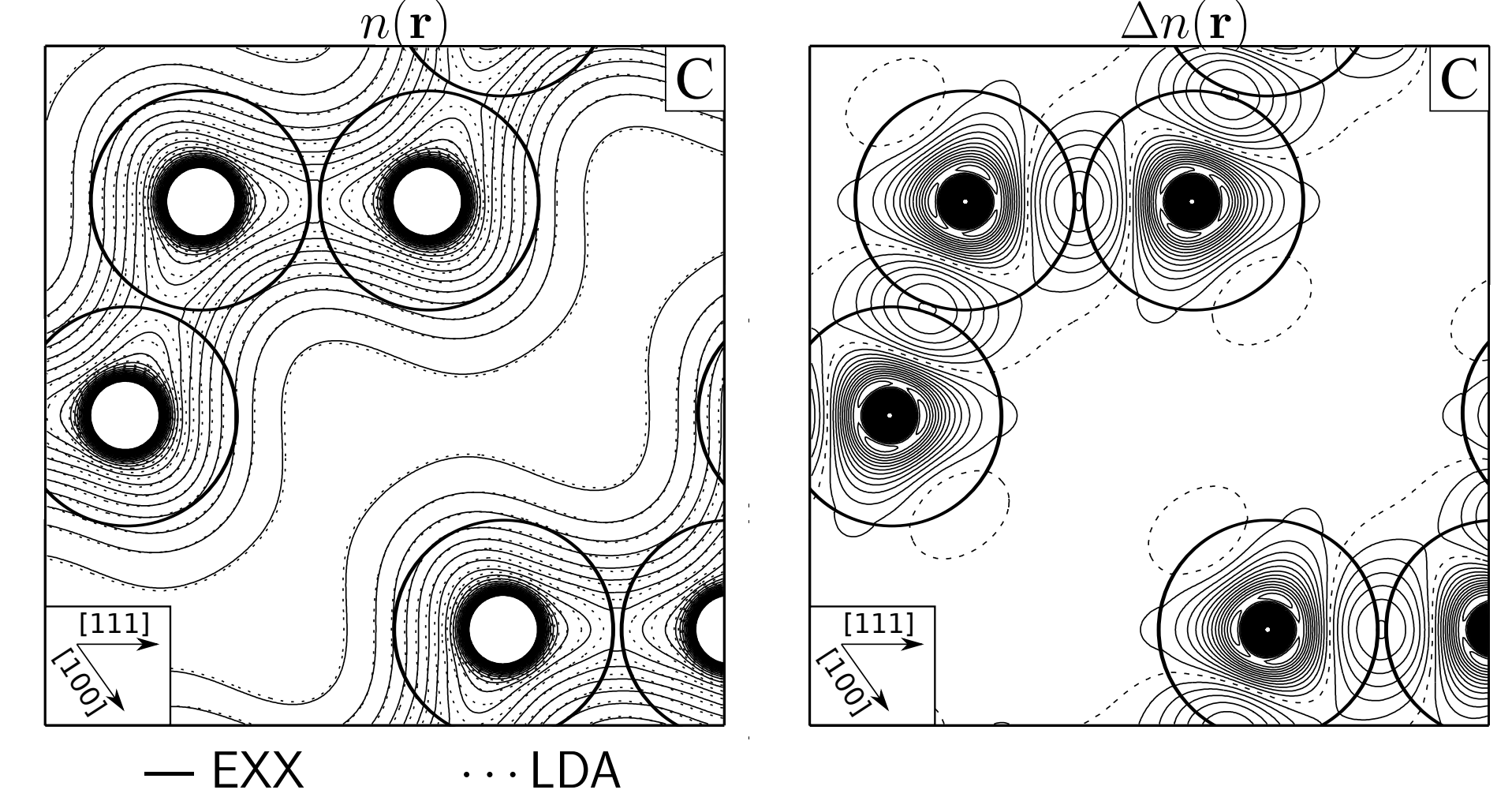


The contour lines have an interval of 0.05 htr and the dotted lines correspond to $V_x = 0.00$ htr. The MT sphere boundaries are indicated. (We have defined $\int V_x(\mathbf{r}) d^3\mathbf{r} = 0$.)

The self-consistent total electron densities show corresponding variations, which are particularly apparent in the density difference $\Delta n(\mathbf{r}) = n_{\text{EXX}}(\mathbf{r}) - n_{\text{LDA}}(\mathbf{r})$.

Full-potential treatment II

Due to the self-interaction correction the EXX wave functions and, hence, the electron density are less delocalized. As can be seen, charge also accumulates in the bonds.



For the density (density difference) plot the contour levels have a spacing of $0.03 a_0^{-3}$ ($0.003 a_0^{-3}$). The dotted lines correspond to $\Delta n = 0 a_0^{-3}$.

Results

		This work			Plane-wave PP		Expt.
		LDA	EXX	EXXc	EXX	EXXc	
C	$\Gamma \rightarrow \Gamma$	5.56	6.21	6.26	6.19 ^a , 6.21 ^b	6.28 ^c	7.3 ^e
	$\Gamma \rightarrow \text{L}$	8.43	9.09	9.16	9.15 ^b	9.18 ^c	
	$\Gamma \rightarrow \text{X}$	4.71	5.20	5.33	5.34 ^b	5.43 ^c	
Si	$\Gamma \rightarrow \Gamma$	2.53	3.13	3.21	3.12 ^b	3.26 ^c	3.4 ^e
	$\Gamma \rightarrow \text{L}$	1.42	2.21	2.28	2.21 ^b	2.35 ^c	2.4 ^e
	$\Gamma \rightarrow \text{X}$	0.61	1.30	1.44	1.25 ^b	1.50 ^c	
SiC	$\Gamma \rightarrow \Gamma$	6.27	7.18	7.24		7.37 ^c	
	$\Gamma \rightarrow \text{L}$	5.38	6.14	6.21		6.30 ^c	
	$\Gamma \rightarrow \text{X}$	1.32	2.29	2.44		2.52 ^c	2.42 ^e
Ge	$\Gamma \rightarrow \Gamma$	-0.14	1.24	1.21		1.28 ^c	1.0 ^e
	$\Gamma \rightarrow \text{L}$	0.06	0.89	0.94		1.01 ^c	0.7 ^e
	$\Gamma \rightarrow \text{X}$	0.66	1.15	1.28		1.34 ^c	1.3 ^e
GaAs	$\Gamma \rightarrow \Gamma$	0.29	1.72	1.74		1.82 ^c	1.63 ^e
	$\Gamma \rightarrow \text{L}$	0.85	1.79	1.86		1.93 ^c	
	$\Gamma \rightarrow \text{X}$	1.35	1.95	2.12		2.15 ^c	2.18 ^e
Ne	$\Gamma \rightarrow \Gamma$	11.43	14.79	15.46	14.15 ^d	14.76 ^d	21.51 ^f
	$\Gamma \rightarrow \text{L}$	16.97	20.49	21.16			
	$\Gamma \rightarrow \text{X}$	18.27	21.85	22.56			
Ar	$\Gamma \rightarrow \Gamma$	8.19	9.65	10.09	9.61 ^d	9.95 ^d	14.15 ^f
	$\Gamma \rightarrow \text{L}$	11.06	12.22	12.60			
	$\Gamma \rightarrow \text{X}$	10.86	12.08	12.49			

^aReference [4] ^bReference [5] ^cReference [6]

^dReference [7] ^eReference [8] ^fReference [9]

We obtain transition energies in very good agreement with plane-wave pseudopotential calculations (Ne is an exception). This is at variance with the findings of Ref. 10.

Outlook: IBS treatment

The OEP equation contains the response function $\delta \varphi_{n\mathbf{k}}(\mathbf{r}) / \delta V_s(\mathbf{r}')$. As the LAPW basis functions $\phi_{\mathbf{k}\mathbf{G}}(\mathbf{r})$ depend explicitly on the potential, an additional term beyond the 'standard' perturbation theory result arises

$$\begin{aligned} \frac{\delta \varphi_{n\mathbf{k}}(\mathbf{r})}{\delta V_s(\mathbf{r}')} &= \sum_{n' \neq n} \frac{\varphi_{n'\mathbf{k}}^*(\mathbf{r}') \varphi_{n\mathbf{k}}(\mathbf{r}')}{\epsilon_{n\mathbf{k}} - \epsilon_{n'\mathbf{k}'}} \varphi_{n'\mathbf{k}'}(\mathbf{r}) \\ &+ \int d^3r'' \left[\delta(\mathbf{r} - \mathbf{r}'') - \sum_{n'} \phi_{n'\mathbf{k}}(\mathbf{r}) \phi_{n'\mathbf{k}}^*(\mathbf{r}'') \right] \sum_{\mathbf{G}} z_{\mathbf{G}}(n\mathbf{k}) \frac{\delta \phi_{\mathbf{k}\mathbf{G}}(\mathbf{r}'')}{\delta V_s(\mathbf{r}')} \end{aligned}$$

with the KS wavefunction $\varphi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} z_{\mathbf{G}}(n\mathbf{k}) \phi_{\mathbf{k}\mathbf{G}}(\mathbf{r})$. This additional term vanishes in the limit of a complete basis corresponding to an LAPW basis with many LOs. We currently seek to treat this incomplete-basis-set (IBS) term explicitly. We hope that this will reduce the demand on the LAPW basis.

Conclusions

- We have presented an implementation of the exact-exchange functional within the all-electron FLAPW method based on the mixed product basis.
- For the case of diamond, we have demonstrated that the LAPW and mixed product basis are not independent. They must be properly balanced to obtain a smooth and physical EXX potential.
- We have shown for the case of diamond that the local EXX potential is spatially strongly corrugated, which makes a full-potential treatment even more important than in conventional LDA or GGA calculations.
- We find that with properly balanced basis sets the transition energies for a variety of semiconductors and insulators are in very good agreement with plane-wave pseudopotential results from the literature. This confirms the adequacy of the pseudopotential approximation in the context of the EXX-OEP formalism and clarifies a previous contradiction between FLAPW and pseudopotential results [10].

Acknowledgments

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