Extension of exact-exchange density functional theory of solids to finite temperatures

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A general finite-temperature exact-exchange (EXX) formalism derived within the framework of finite-temperature density functional theory for grand canonical ensembles is presented. Based on this formalism a finite-temperature EXX method for solids using plane-wave basis sets is presented. The method is generally applicable, i.e., applicable to insulators, semiconductors, or metals and enables the investigation of temperature effects. More important, however, is that the finite-temperature EXX method enables an EXX treatment of metals by introducing a physically motivated Fermi broadening technique. We tested the method by applying it to sodium, magnesium, and aluminum and compare EXX and LDA (local density approximation) band structures as well as the density of states for the three metals. Differences between LDA and EXX band structures are negligible up to the Fermi level. Above the Fermi level, however, differences between LDA and EXX band structures of magnitudes of 1–2 eV start to build up for energetically higher bands. The magnitude of these differences is of the same order as that of the increases in EXX band gaps compared to LDA band gaps as they are reported for semiconductors and insulators.

I. INTRODUCTION

A basic shortcoming of conventional density functional methods, i.e., of Kohn-Sham (KS) methods relying on exchange-correlation functionals within the local density approximation (LDA) (Refs. [1–3]) or generalized gradient approximations (GGAs),[1–5] is the presence of unphysical Coulomb self-interactions. The Coulomb energy is defined as the energy of the classical electrostatic interaction of the electron density of an electronic system with itself. The Coulomb energy therefore contains unphysical contributions from the interaction of each electron with itself. Similarly, if the Coulomb potential, the classical electrostatic potential of the electron density, acts on an electron of the system then this electron is subject to an interaction with itself because the electron contributes to the electron density. This unphysical Coulomb self-interaction is cancelled by the exchange energy and potential, respectively. In conventional KS methods, however, the Coulomb energy and potential is calculated exactly while the exchange energy and potential is approximated. As a result the cancellation of unphysical Coulomb self-interactions is incomplete.

The presence of unphysical Coulomb self-interactions has severe consequences. Conventional exchange-correlation potentials are not attractive enough and, in finite systems, exhibit the wrong asymptotic behavior.[6–11] As consequence, the simplest system, the hydrogen atom, is not treated correctly, the additional electron in small anions often is erroneously unbound.[12–14] Moreover, the KS orbital and eigenvalue spectrum of conventional KS methods is qualitatively wrong.[1–3,12–15] In finite systems the energetical difference of

the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) is too small and no Rydberg series exist in eigenvalue spectra. In periodic solids band structures are affected. Conventional KS band gaps of semiconductors are much lower than experimental ones. In how far this is due to the principle difference between the KS band gap and the true quasiparticle band gap and in how far this is due to Coulomb self-interactions is an open question.[16–27] However, conventional KS band structures may even be qualitatively wrong exhibiting metallic instead of semiconductor characteristics, like, e.g., in the case of germanium.[28]

Exact-exchange (EXX) KS methods[28–60] solve this basic problem because they treat exactly the exchange energy and the local multiplicative KS exchange potential. The latter must not be confused with the nonlocal Hartree-Fock exchange potential. Hartree-Fock methods lead to occupied orbitals that are free of Coulomb self-interactions, but to unoccupied orbitals that are not. These unoccupied orbitals have little physical meaning. In EXX methods qualitatively correct orbital and eigenvalue spectra are obtained. In finite systems larger HOMO LUMO gaps emerge and Rydberg series are present. In solids qualitatively correct band structures are obtained.[28,35,37,49–51,59,60] In small and medium band gap semiconductors EXX band gaps are close to the experimental ones. Whether this agreement between KS and true quasiparticle band gaps would become worse if also the exact correlation potential could be employed is an open question.[16–27] In present EXX methods correlation is either neglected or treated via conventional LDA or GGA functionals. It turns out that the choice for the conventional correla-

tion potential or even its complete neglect has little effect on the KS eigenvalue spectra.

KS orbitals and eigenvalues are the starting point for methods like the GW method to calculate quasiparticle band structures[51,61–63] or for methods based on time-dependent density functional theory in the response regime to treat optical properties.[64,65] KS methods providing qualitatively correct band structures therefore are of importance. EXX methods are such methods.

Another advantage of EXX methods is that treating exchange energy and potential exactly represents a step in a systematical improvement of density functional methods. The exchange energy is the largest fraction of the exchange-correlation energy and in contrast to conventional KS methods no longer needs to be approximated. Conventional KS methods strongly rely on error cancellations between exchange and correlation.[1–5] Such error cancellations obviously are no longer present if exchange is treated exactly. However, such error cancellations, in any case, can only be exploited for exchange-correlation energies but not for exchange-correlation potentials. For example, the long-range behavior of the effective KS potential is determined exclusively by the exchange potential which exhibits a long-range $(-1/r)$-behavior with r denoting the distance from the electronic system. The LDA or GGA correlation potentials like the true correlation potential are short-ranged and also the LDA or GGA exchange potentials are short-ranged. Thus the correct long-range $(-1/r)$-behavior of the exchange potential can never occur due to error cancellations between conventional exchange and correlation potentials.

EXX methods have been introduced for atoms,[30] solids[28,35–37] as well as molecules.[40,41] EXX methods for molecules based on Gaussian basis sets are numerically demanding[40,43,45,66–68] and only recently a numerically stable method was introduced.[57] EXX methods for solids based on plane-wave basis sets,[28,36,37] on the other hand, turn out to be numerically stable provided the plane-wave cutoffs for the representation of the orbitals and of the exchange potential are well balanced. However, so far only EXX methods for the limit of zero temperature have been developed.

In this work we present a general finite-temperature EXX formalism within the framework of finite-temperature density functional theory for grand canonical ensembles.[69] The basic formalism is valid and applicable for finite as well as infinite systems. In this work we then focus on a finite-temperature EXX method for solids based on plane-wave basis sets and test it by applying it to simple metals. For the treatment of periodic solids we have to consider a fixed electron number in order to guarantee charge neutrality of the system, i.e., we cannot freely choose the chemical potential of the grand canonical ensemble but we have to set the chemical potential to a value leading to the required number of electrons. This means we effectively switch from a grand canonical ensemble to a canonical ensemble.

The motivation for this work is twofold. On the one hand, this opens the route to investigate temperature effects within an EXX framework. On the other hand, a finite-temperature approach may be used as technical procedure in the **k**-point sampling in a KS treatment of metals. In order to avoid the use of prohibitively large numbers of **k**-points "band broad-

ening" schemes are often used in the KS treatment of metals. In EXX methods the **k**-point sampling is especially critical because in the construction of the exact exchange potential the KS response function is required which contains terms with differences of occupied and unoccupied KS eigenvalues in the denominator. If KS eigenvalues of a **k** point at the Fermi level are degenerate this may lead to singularities. By using a "band broadening" scheme that has physical meaning such singularities are avoided.

This work is organized as follows. In Sec. II the EXX formalism is generalized to finite temperature by deriving an EXX formalism within the general framework of finite-temperature density functional theory for grand canonical ensembles.[69] In Sec. III the implementation and computational details are briefly described. In Sec. IV results of applying the new method to the metals sodium, magnesium, and aluminum are presented. Finally, Sec. V contains concluding remarks.

II. FINITE-TEMPERATURE EXX FORMALISM

A. Basic formalism and definition of energy functionals

An electronic system at finite temperature that can interchange electrons with its environment is described by the density matrix $\hat{\Gamma}_{v,T,\mu}$ if treated as grand canonical ensemble. The density matrix $\hat{\Gamma}_{v,T,\mu}$ among all density matrices $\hat{\Gamma}$ is the one that minimizes the grand potential $\Omega[\hat{\Gamma}]$ (Ref. 1)

$$\Omega[\hat{\Gamma}] = \mathrm{Tr}\,\hat{\Gamma}[\hat{H} + kT \ln \hat{\Gamma} - \mu \hat{N}] \tag{1}$$

according to

$$\Omega_{v,T,\mu} = \min_{\hat{\Gamma}} \Omega[\hat{\Gamma}] \tag{2}$$

for the Hamiltonian operator

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{v}, \tag{3}$$

the temperature T, and the chemical potential μ. In Eq. (3), $\hat{T}$ and $\hat{V}_{ee}$ designate the operators of the kinetic energy and the electron-electron interaction energy, respectively, while $\hat{v}$ denotes the operator corresponding to a local multiplicative external potential $v(\mathbf{r})$, usually the potential of the nuclei. In Eq. (1), $\hat{N}$ denotes the number operator and k the Boltzmann constant. The grand potentials $\hat{\Omega}[\hat{\Gamma}]$ are functionals of the density matrices $\hat{\Gamma}$, the minimum $\hat{\Omega}_{v,T,\mu}$ of the grand potential given in Eq. (2) corresponds to the minimizing density matrix $\hat{\Gamma}_{v,T,\mu}$, i.e.,

$$\Omega_{v,T,\mu} = \Omega[\hat{\Gamma}_{v,T,\mu}]. \tag{4}$$

The minimizing density matrix $\hat{\Gamma}_{v,T,\mu}$ is given by

$$\hat{\Gamma}_{v,T,\mu} = \sum_N \sum_n \frac{\exp[(-1/kT)(E_{N,n} - \mu N)]}{Z_{v,T,\mu}} |\Psi_{N,n}\rangle\langle\Psi_{N,n}| \tag{5}$$

with the grand partition function

$$Z_{v,T,\mu} = \sum_N \sum_n \exp[(-1/kT)(E_{N,n} - \mu N)]. \quad (6)$$

In Eqs. (5) and (6) $\Psi_{N,n}$ denotes the nth N-electron eigenstate of the Hamiltonian operator (3) and $E_{N,n}$ the corresponding energy eigenvalue. Strictly speaking, it is not correct to speak of one Hamiltonian operator (3) because for each particle number N there is a different Hamiltonian operator. Therefore, a reference to the Hamilton operator (3) shall always imply a reference to the appropriate N-electron Hamilton operators. This also holds true in formulas like those in Eqs. (1) and (2) where traces of Hamiltonian operators with density matrices containing contributions with different particle numbers occur.

Following the constrained-search formulation of density functional theory[1,70,71] we now rewrite the minimization (2),

$$\Omega_{v,T,\mu} = \min_{\rho} \{ \min_{\hat{\Gamma} \to \rho} \{ \mathrm{Tr}\, \hat{\Gamma}[\hat{H} + kT \ln \hat{\Gamma} - \mu \hat{N}] \} \}$$

$$= \min_{\rho} \left\{ \min_{\hat{\Gamma} \to \rho} \{ \mathrm{Tr}\, \hat{\Gamma}[\hat{T} + \hat{V}_{ee} + kT \ln \hat{\Gamma}] \} \right.$$

$$\left. + \int d\mathbf{r}[v(\mathbf{r}) - \mu]\rho(\mathbf{r}) \right\}$$

$$= \min_{\rho} \left\{ F[\rho,T] + \int d\mathbf{r}[v(\mathbf{r}) - \mu]\rho(\mathbf{r}) \right\} \quad (7)$$

with the Hohenberg-Kohn functional $F[\rho,T]$ as defined for grand canonical ensembles,[69] i.e., with

$$F[\rho,T] = \min_{\hat{\Gamma} \to \rho} \{ \mathrm{Tr}\, \hat{\Gamma}[\hat{T} + \hat{V}_{ee} + kT \ln \hat{\Gamma}] \}. \quad (8)$$

In the constrained-search formulation the original minimization in Eq. (2) is split into two minimizations, an inner one over all density matrices that yield a certain electron density ρ and an outer one over all electron densities ρ. Because the expectation values of the number operator $\hat{N}$ and operator $\hat{v}$ corresponding to the external potential depend exclusively on the electron density, the terms containing these two operators can be taken out of the inner minimization. The minimizing density matrix of the remaining inner minimization in Eq. (7), i.e., the minimizing density matrix of Eq. (8) defining the Hohenberg-Kohn functional depends on the electron density ρ, i.e., is a functional $\hat{\Gamma}[\rho,T]$ of ρ. The Hohenberg-Kohn functional $F[\rho,T]$ is given by

$$F[\rho,T] = \mathrm{Tr}\, \hat{\Gamma}[\rho,T][\hat{T} + \hat{V}_{ee} + kT \ln \hat{\Gamma}[\rho,T]] \quad (9)$$

in terms of the minimizing density matrices $\hat{\Gamma}[\rho,T]$, i.e., in terms of the functionals $\hat{\Gamma}[\rho,T]$. The electron density that minimizes the outer minimization in Eq. (7) shall be denoted $\rho_{v,T,\mu}$. The minimizing density matrix $\hat{\Gamma}_{v,T,\mu}$ is obtained as functional of the minimizing electron density $\rho_{v,T,\mu}$,

$$\hat{\Gamma}_{v,T,\mu} = \hat{\Gamma}[\rho_{v,T,\mu}, T]. \quad (10)$$

The Euler equation that corresponds to the outer minimization in Eq. (7) and that determines the minimizing electron density $\rho_{v,T,\mu}$ reads as

$$\left. \frac{\delta F[\rho,T]}{\delta\rho(\mathbf{r})} \right|_{\rho=\rho_{v,T,\mu}} = -v(\mathbf{r}) + \mu. \quad (11)$$

Next we introduce the KS system, a model system of fictitious noninteracting electrons with the same electron density as the real electron system. The KS Hamiltonian operator $\hat{H}^{KS}$ is given by

$$\hat{H}^{KS} = \hat{T} + \hat{v}_s. \quad (12)$$

Analogously to Eqs. (2) and (7)–(9) we introduce a minimal KS grand potential $\Omega_{v_s,T,\mu}^{KS}$ by the constrained-search minimization

$$\Omega_{v_s,T,\mu}^{KS} = \min_{\hat{\Gamma}} \mathrm{Tr}\, \hat{\Gamma}[\hat{H}^{KS} + kT \ln \hat{\Gamma} - \mu \hat{N}]$$

$$= \min_{\rho} \left\{ T_s[\rho] + \int d\mathbf{r}[v(\mathbf{r}) - \mu]\rho(\mathbf{r}) \right\} \quad (13)$$

with the functional $T_s[\rho,T]$ defined by

$$T_s[\rho,T] = \min_{\hat{\Gamma} \to \rho} \{ \mathrm{Tr}\, \hat{\Gamma}[\hat{T} + kT \ln \hat{\Gamma}] \}. \quad (14)$$

In contrast to the zero temperature case, the functional $T_s[\rho,T]$ not only contains a kinetic energy contribution, but in addition an entropy term, which we shall refer to as noninteracting entropy term. The minimizing density matrix obtained in the minimization (14) is a functional $\hat{\Gamma}^{KS}[\rho,T]$ of the electron density, similarly as the minimizing density matrix $\hat{\Gamma}[\rho,T]$ is a functional of ρ resulting from minimization (8). The functional $T_s[\rho,T]$ is given by

$$T_s[\rho,T] = \mathrm{Tr}\, \hat{\Gamma}^{KS}[\rho,T][\hat{T} + kT \ln \hat{\Gamma}^{KS}[\rho,T]] \quad (15)$$

in terms of the minimizing density matrices $\hat{\Gamma}^{KS}[\rho,T]$, i.e., in terms of the functionals $\hat{\Gamma}^{KS}[\rho,T]$. The minimizing density matrix corresponding to the first line of Eq. (13) shall be denoted as $\hat{\Gamma}_{v_s,T,\mu}^{KS}$, the minimizing KS electron density corresponding to the second line of Eq. (13) as $\rho_{v_s,T,\mu}^{KS}$. The former can be obtained as functional

$$\hat{\Gamma}_{v_s,T,\mu}^{KS} = \hat{\Gamma}^{KS}[\rho_{v_s,T,\mu}^{KS}, T] \quad (16)$$

of the minimizing electron density $\rho_{v_s,T,\mu}^{KS}$ in analogy to Eq. (10). Analogously to Eq. (11) the Euler equation that corresponds to the minimization of the second line of Eq. (13) and that determines the minimizing KS electron density $\rho_{v_s,T,\mu}^{KS}$ assumes the form

$$\left. \frac{\delta T_s[\rho,T]}{\delta\rho(\mathbf{r})} \right|_{\rho=\rho_{v_s,T,\mu}^{KS}} = -v_s(\mathbf{r}) + \mu. \quad (17)$$

A crucial property of the KS system is that, by definition, it has the same electron density as the real electron system, i.e.,

$$\rho^{KS}_{v_s,T,\mu} = \rho_{v,T,\mu} = \rho_0. \qquad (18)$$

For simplicity we omit the subscripts v, T, μ or v_s, T, μ and plainly write ρ_0 for the electron density of the real electron system and the KS electron system. If we now subtract the two Euler Eqs. (11) and (17) from each other, rearrange, and take into account Eq. (18) then we obtain an equation for the KS potential v_s

$$v_s(\mathbf{r}) = v(\mathbf{r}) + \left.\frac{\delta(F[\rho,T] - T_s[\rho,T])}{\delta\rho(\mathbf{r})}\right|_{\rho=\rho_0}. \qquad (19)$$

The difference $F[\rho,T] - T_s[\rho,T]$ contained in Eq. (19) is rewritten by adding and subtracting $\mathrm{Tr}\,\hat{\Gamma}^{KS}[\rho,T]\hat{V}_{ee}$

$$
\begin{aligned}
F[\rho,T] - T_s[\rho,T] &= \mathrm{Tr}\,\hat{\Gamma}^{KS}[\rho,T]\hat{V}_{ee} + (F[\rho,T] - T_s[\rho,T] \\
&\quad - \mathrm{Tr}\,\hat{\Gamma}^{KS}[\rho,T]\hat{V}_{ee}) \\
&= U[\rho] + E_x[\rho,T] + E_c[\rho,T] \qquad (20)
\end{aligned}
$$

with the sum of Coulomb and exchange energy given by

$$U[\rho] + E_x[\rho,T] = \mathrm{Tr}\,\hat{\Gamma}^{KS}[\rho,T]\hat{V}_{ee} \qquad (21)$$

and with the correlation energy given by

$$
\begin{aligned}
E_c[\rho,T] &= F[\rho,T] - T_s[\rho,T] - \mathrm{Tr}\,\hat{\Gamma}^{KS}[\rho,T]\hat{V}_{ee} \\
&= \mathrm{Tr}\,\hat{\Gamma}[\rho,T][\hat{T} + \hat{V}_{ee} + kT\ln\hat{\Gamma}[\rho,T]] \\
&\quad - \mathrm{Tr}\,\hat{\Gamma}^{KS}[\rho,T][\hat{T} + \hat{V}_{ee} + kT\ln\hat{\Gamma}^{KS}[\rho,T]].
\end{aligned}
\qquad (22)
$$

The sum of the Coulomb energy $U[\rho]$ and the exchange energy $E_x[\rho,T]$ according to Eq. (21) is defined as the electron-electron interaction energy the KS system would have if there were an electron-electron interaction in the KS system. Note that in addition to a kinetic and an electron-electron interaction contribution the correlation energy $E_c[\rho,T]$ also contains an entropy contribution that is absent in standard zero-temperature DFT. The corresponding Coulomb (Hartree), exchange and correlation potentials, v_H, v_x, and v_c are defined as the functional derivatives of the energy functionals with respect to the electron density, respectively. With these potentials the KS potential of Eq. (19) can be expressed in the usual form as

$$v_s(\mathbf{r}) = v(\mathbf{r}) + v_H([\rho_0];\mathbf{r}) + v_x([\rho_0,T];\mathbf{r}) + v_c([\rho_0,T];\mathbf{r}). \qquad (23)$$

Carrying out KS calculations within the framework of DFT for grand canonical ensembles requires either to approximate or to treat exactly the functionals for the Coulomb, exchange and correlation energies and potentials, as in standard DFT. In this work we present an approach to treat exchange energy and potential in addition to Coulomb energy and potential exactly while the correlation energy and potential is either neglected or treated via standard approxi-

mate correlation functionals. To this end we express the KS density matrix $\hat{\Gamma}^{KS}_{v_s,T,\mu}$ in analogy to Eq. (5) as

$$\hat{\Gamma}^{KS}_{v_s,T,\mu} = \sum_N \sum_n \frac{\exp[(-1/kT)(E^{KS}_{N,n} - \mu N)]}{Z^{KS}_{v_s,T,\mu}}|\Phi_{N,n}\rangle\langle\Phi_{N,n}| \qquad (24)$$

with the KS grand partition function

$$Z^{KS}_{v_s,T,\mu} = \sum_N \sum_n \exp[(-1/kT)(E^{KS}_{N,n} - \mu N)]. \qquad (25)$$

In Eqs. (24) and (25) $\Phi_{N,n}$ denotes the nth N-electron eigenstate of the KS Hamiltonian operator (12) and $E^{KS}_{N,n}$ the corresponding energy eigenvalue.

Because the KS Hamiltonian operator (12) is a simple sum of one-electron operators, its eigenstates $\Phi_{N,n}$ are Slater determinants constructed from KS orbitals ϕ_i, which obey the KS equation

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right]\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r}) \qquad (26)$$

with a KS potential v_s given by Eq. (23). The orbitals ϕ_i are spin orbitals, i.e., they shall be two-dimensional spinors representing either α- or β-spin orbitals. The energies $E^{KS}_{N,n}$ are the sum of the KS eigenvalues ε_i of the orbitals constructing the KS determinants $\Phi_{N,n}$, respectively. The exchange energy can be deduced from Eq. (21) by inserting the KS density matrix $\hat{\Gamma}^{KS}_{v_s,T,\mu}$. Before doing this we consider the simpler case of calculating the electron density ρ_0. It is given by

$$
\begin{aligned}
\rho_0(\mathbf{r}) = \rho_{v_s,T,\mu}(\mathbf{r}) &= \mathrm{Tr}\,\hat{\Gamma}^{KS}_{v_s,T,\mu}\hat{\rho}(\mathbf{r}) \\
&= \sum_N \sum_n \frac{\exp[(-1/kT)(E^{KS}_{N,n} - \mu N)]}{Z^{KS}_{v_s,T,\mu}}\langle\Phi_{N,n}|\hat{\rho}(\mathbf{r})|\Phi_{N,n}\rangle \\
&= \sum_i f_i\phi_i^\dagger(\mathbf{r})\phi_i(\mathbf{r}) \qquad (27)
\end{aligned}
$$

with the occupation numbers f_i of the KS orbitals given by

$$f_i = \frac{1}{1 + e^{(1/kT)(\varepsilon_i - \mu)}}, \qquad (28)$$

as derived in Ref. 72 and in the Appendix. The summation over the index i in Eq. (27) runs over all spin orbitals. For the last line of Eq. (27) we used that

$$\langle\Phi_{N,n}|\hat{\rho}(\mathbf{r})|\Phi_{N,n}\rangle = \sum_{i\in\Phi_{N,n}} \phi_i^\dagger(\mathbf{r})\phi_i(\mathbf{r}). \qquad (29)$$

The summation $\sum_{i\in\Phi_{N,n}}$ shall run over all spin orbitals contained in the KS determinant $\Phi_{N,n}$. The sum of Coulomb and exchange energy, Eq. (21), leads to

$$U + E_x = \text{Tr } \hat{\Gamma}^{KS}_{v_s,T,\mu} \hat{V}_{ee}$$

$$= \sum_N \sum_n \frac{\exp[(-1/kT)(E^{KS}_{N,n} - \mu N)]}{Z^{KS}_{v_s,T,\mu}} \langle \Phi_{N,n} | \hat{V}_{ee} | \Phi_{N,n} \rangle. \tag{30}$$

Taking into account that

$$\langle \Phi_{N,n} | \hat{V}_{ee} | \Phi_{N,n} \rangle = (1/2) \sum_{i \in \Phi_{N,n}} \sum_{j \in \Phi_{N,n}} [\langle ij|ij \rangle - \langle ij|ji \rangle] \tag{31}$$

with $\langle ij|k\ell \rangle = \int d\mathbf{r} d\mathbf{r}'(\phi_i^\dagger(\mathbf{r}) \phi_j^\dagger(\mathbf{r}') \phi_k(\mathbf{r}) \phi_\ell(\mathbf{r}'))/|\mathbf{r} - \mathbf{r}'|$ we can express the sum of Coulomb and exchange energy in terms of KS orbitals and occupation numbers g_{ij} for pairs of orbitals as

$$U + E_x = (1/2) \sum_i \sum_j g_{ij}[\langle ij|ij \rangle - \langle ij|ji \rangle]. \tag{32}$$

The occurrence of occupation numbers g_{ij} for pairs of orbitals in Eq. (32) instead of the simple occupation numbers f_i is a consequence of the fact that the operator of the electron-electron interaction is a two-particle operator. For calculating the Coulomb and exchange energy with Eq. (32) we need an expression for occupation numbers g_{ij}. It turns out that the factors g_{ij} are simply given by the product of the factors f_i and f_j of the Fermi distribution (28), that is $g_{ij} = f_i f_j$. The relation between g_{ij} and f_i and f_j is derived in the Appendix for $i \neq j$. For g_{ii} an arbitrary value can be chosen because the difference $[\langle ij|ij \rangle - \langle ij|ji \rangle]$ equals zero for $i = j$. We choose $g_{ii} = f_i f_i$ and keep the term in the summation (32) because it enables us to define separable Coulomb and exchange energies U and E_x in Eqs. (A4)–(A6) later on.

Note that, as mentioned in the Introduction, electronic systems described in the framework of a grand canonical ensemble are characterized by the external potential v, the temperature T, and the chemical potential μ or alternatively, invoking the generalization of the Hohenberg-Kohn theorem to grand canonical ensembles, by the electron density ρ_0, the temperature T, and the chemical potential μ. The particle number is a function of v, T, and μ. In the treatment of periodic solids, however, usually the particle number is kept fixed in order to obey the requirement of charge neutrality of the solid. In this case the electronic system is characterized by v, T, and N and the chemical potential μ is a function of the latter quantities, i.e., the chemical potential has to assume a value such that the given particle number is obtained, that is the sum of all occupation numbers must equal the particle number N. In this case, the electronic system is characterized by the temperature T and the electron density ρ_0, invoking the finite-temperature generalization of the Hohenberg-Kohn theorem and using that the electron density ρ_0 determines the electron number N. By keeping the electron number fixed a canonical instead of a grand canonical ensemble is considered.

B. Coulomb and exchange potential

With expressions for the Coulomb and the exchange energy at hand that can be straightforwardly evaluated in a KS calculation we now consider the evaluation of the Coulomb potential and the exchange potential. The latter are defined as functional derivatives of the Coulomb and exchange energies with respect to the electron density. Taking this functional derivative is trivial for the Coulomb energy because it is given in terms of the electron density, see Eq. (A5) of the Appendix. The resulting Coulomb potential reads as

$$v_H(\mathbf{r}) = \int d\mathbf{r}' \frac{\rho_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{33}$$

and can be evaluated as in the zero-temperature KS formalism except that the occupation numbers f_i have to be taken into account in the construction of the electron density ρ_0, see Eq. (27).

The exchange potential is not directly accessible because the exchange energy is only known in terms of the KS orbitals and the occupation numbers but not explicitly in terms of the electron density. Because the KS orbitals and the occupation numbers are functionals of the electron density the exchange energy is implicitly a functional of the electron density. However, the dependence of the KS orbitals and the occupation numbers on the electron density is unknown and therefore taking the functional derivative of the exchange energy with respect to the electron density simply via the chain rule is not possible. Instead, we generalize the approach of the ground state EXX formalism,[15,30,33,34] and take the derivative of the exchange energy with respect to the effective KS potential v_s in two different ways:

$$\int d\mathbf{r}' \left[\frac{\delta E_x}{\delta \rho_0(\mathbf{r}')} \frac{\delta \rho_0(\mathbf{r}')}{\delta v_s(\mathbf{r})} \right]$$

$$= \sum_i \int d\mathbf{r}' \left[\frac{\delta E_x}{\delta \phi_i(\mathbf{r}')} \frac{\delta \phi_i(\mathbf{r}')}{\delta v_s(\mathbf{r})} + \text{c.c.} \right] + \sum_i \left[\frac{\delta E_x}{\delta f_i} \frac{\delta f_i}{\delta v_s(\mathbf{r})} \right]. \tag{34}$$

The derivative $\delta \rho_0(\mathbf{r}')/\delta v_s(\mathbf{r})$ of the electron density with respect to the KS potential is the KS response function $X_s(\mathbf{r}', \mathbf{r})$, i.e.,

$$X_s(\mathbf{r}, \mathbf{r}') = \frac{\delta \rho_0(\mathbf{r})}{\delta v_s(\mathbf{r}')}. \tag{35}$$

The functional derivative $\delta E_x/\delta \rho_0(\mathbf{r}')$ is the exchange potential $v_x(\mathbf{r}')$, the quantity we want to determine. The right-hand side of Eq. (34) shall be abbreviated by $t(\mathbf{r})$. If we furthermore use that the KS response function X_s is symmetric in its arguments, see Eqs. (37)–(46) below, then Eq. (34) assumes the form

$$\int d\mathbf{r}' X_s(\mathbf{r}, \mathbf{r}') v_x(\mathbf{r}') = t(\mathbf{r}). \tag{36}$$

known from the ground state EXX formalism.[28,37]

Similar as in the ground state EXX formalism[15,33,34] standard perturbation theory yields

$$X_s(\mathbf{r},\mathbf{r}') = \sum_i f_i \sum_{j \neq i} \left[\frac{\phi_i^\dagger(\mathbf{r})\phi_j(\mathbf{r})\phi_j^\dagger(\mathbf{r}')\phi_i(\mathbf{r}')}{\varepsilon_i - \varepsilon_j} + \text{c.c.} \right]$$
$$+ \sum_i \phi_i^\dagger(\mathbf{r})\phi_i(\mathbf{r})\frac{\delta f_i}{\delta v_s(\mathbf{r}')} \tag{37}$$

and

$$t(\mathbf{r}) = \sum_i f_i \sum_{j \neq i} \left[\frac{\langle\phi_i|\hat{v}_x^{\text{NL}}|\phi_j\rangle\phi_j^\dagger(\mathbf{r})\phi_i(\mathbf{r})}{\varepsilon_i - \varepsilon_j} + \text{c.c.} \right]$$
$$+ \sum_i \langle\phi_i|\hat{v}_x^{\text{NL}}|\phi_i\rangle\frac{\delta f_i}{\delta v_s(\mathbf{r})} \tag{38}$$

with the nonlocal exchange operator $\hat{v}_x^{\text{NL}}$ defined by its kernel

$$v_x^{\text{NL}}(\mathbf{r},\mathbf{r}') = -\sum_i f_i \frac{\phi_i(\mathbf{r})\phi_i^\dagger(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \tag{39}$$

Compared to the ground state EXX formalism additional terms occur in Eqs. (37) and (38), as well as Eq. (34), namely, those terms that contain derivatives $\delta f_i/\delta v_s(\mathbf{r})$ of the occupation numbers f_i with respect to the KS potential v_s. Taking into account Eq. (28), these derivatives are given by

$$\frac{\delta f_i}{\delta v_s(\mathbf{r})} = -\frac{e^{(\varepsilon_i-\mu)/kT}}{kT[e^{(\varepsilon_i-\mu)/kT}+1]^2}\left[\frac{\delta\varepsilon_i}{\delta v_s(\mathbf{r})} - \frac{\delta\mu}{\delta v_s(\mathbf{r})}\right]. \tag{40}$$

The second term in the square brackets of Eq. (40) arises because we consider the case of fixed particle number N. In order to calculate this term we use that the condition of a fixed particle number leads to the condition

$$\sum_i \frac{\delta f_i}{\delta v_s(\mathbf{r})} = 0 \tag{41}$$

for the derivatives of the occupation numbers with respect to the KS potential. Inserting Eq. (40) into Eq. (41) after some algebra leads to the expression

$$\frac{\delta\mu}{\delta v_s(\mathbf{r})} = \frac{\sum_i \frac{e^{(\varepsilon_i-\mu)/kT}}{[e^{(\varepsilon_i-\mu)/kT}+1]^2}\frac{\delta\varepsilon_i}{\delta v_s(\mathbf{r})}}{\sum_i \frac{e^{(\varepsilon_i-\mu)/kT}}{[e^{(\varepsilon_i-\mu)/kT}+1]^2}} \tag{42}$$

for the derivative of the chemical potential with respect to the KS potential.

The derivative $\delta\varepsilon_i/\delta v_s(\mathbf{r})$ according to standard perturbation theory is given by

$$\frac{\delta\epsilon_i}{\delta v_s(\mathbf{r})} = \phi_i^\dagger(\mathbf{r})\phi_i(\mathbf{r}). \tag{43}$$

Using furthermore

$$\frac{e^{(\varepsilon_i-\mu)/kT}}{[e^{(\varepsilon_i-\mu)/kT}+1]^2} = f_i(1-f_i) \tag{44}$$

we can express Eqs. (40) and (42) in the form

$$\frac{\delta f_i}{\delta v_s(\mathbf{r})} = -\frac{f_i(1-f_i)}{kT}\left[\phi_i^\dagger(\mathbf{r})\phi_i(\mathbf{r}) - \frac{\delta\mu}{\delta v_s(\mathbf{r})}\right] \tag{45}$$

and

$$\frac{\delta\mu}{\delta v_s(\mathbf{r})} = \frac{\sum_i f_i(1-f_i)\phi_i^\dagger(\mathbf{r})\phi_i(\mathbf{r})}{\sum_i f_i(1-f_i)}. \tag{46}$$

Based on Eq. (45) and (46) those terms in Eqs. (37) and (38) that are not present in the ground state EXX formalism, i.e., the terms arising due to finite temperature, can be evaluated. In the limit of zero temperature the products $f_i(1-f_i)$ vanish because the occupation numbers equal zero or one and the additional terms due to finite temperature vanish in Eqs. (37) and (38) and the ground state EXX formalism is recovered.

III. IMPLEMENTATION AND COMPUTATIONAL DETAILS

In this section, first, an overview of the implementation of the above finite-temperature EXX approach is presented and then computational details and parameters are listed. The EXX formalism for finite temperatures was implemented within an existing plane-wave Kohn-Sham code for periodic systems that contains a zero-temperature EXX option. The SCF (self-consistent field) cycle of the finite-temperature EXX implementation consists of the following steps, some of which are embedded in loops over the **k** points:

(i) From the effective KS potential $v_s(\mathbf{r})$, see Eq. (23), of the previous SCF cycle the KS Hamiltonian matrices are constructed and for each **k** point the corresponding eigenvectors and eigenvalues are determined.

(ii) From the eigenvalues, the number of electrons, and the chosen temperature the Fermi energy, i.e., the chemical potential μ and, subsequently, the occupation numbers f_i are determined by a bisection algorithm which is carried out until the sum over all occupation numbers equals the number of electrons roughly within machine precision. In this step, in principle, all eigenvalues have to be taken into account. However, for a reasonable plane-wave cutoff and temperature the vast majority of bands has occupation numbers close to zero. In order to save computational effort later on, a number of active bands is specified. The number of active bands has to comprise all bands with occupation numbers that differ from zero by a significant amount. For the simple metals considered here and the chosen temperature of 293 K about three to ten bands in addition to the bands that would be occupied at zero temperature were specified as active bands. The Fermi energy then is determined only with eigenvalues of the active bands and only for the latter fractional occupation numbers are determined. For the remaining "inactive" bands the occupation numbers are set to zero. In this procedure, if necessary, the number of active bands for a **k** point is increased such that degenerate or almost degenerate bands are all active if one of the degenerate bands initially turns out to be active. This step is crucial in order to guarantee that no symmetries of the system are destroyed.

TABLE I. Key calculational parameters for sodium, magnesium and aluminum: cutoff radii r_c (atomic units) of s-, p- and d-orbitals that were used for the construction of pseudopotentials and the used experimental lattice constants a (nm) (Ref. [75]).

Atom	r_c (a.u)			a (nm)
	s	p	d	
Na	3.3	4.0	4.0	0.42906
Mg	1.9	2.3	2.3	0.32094
Al	1.9	2.3	2.3	0.40496

(iii) From the occupation numbers, the eigenstates, and the eigenvalues the electron density ρ_0, given in Eq. (37), and the finite-temperature KS response function X_s of Eq. (37) are constructed.

(iv) From the electron density the Hartree potential v_H is determined. Additionally, conventional correlation potentials can be included and determined as well.

(v) Following Eqs. (38)–(46), in a double loop over the **k** points, the right hand side $t(\mathbf{r})$ is computed from the occupation numbers, the eigenstates, and the eigenvalues.

(vi) Solution of the Eq. (36), which contains the KS response function X_s and the right hand side t, yields the exact exchange potential v_x.

Furthermore, energies like the free energy, the total electronic energy, the noninteracting kinetic energy, as well as the Coulomb, the exchange, and the correlation energy are determined during each of the SCF cycles. The integrable singularities occurring in the calculation of the exchange energy were treated as described in Ref. [56].

After convergence of the SCF process band structures and density of states (DOS) were determined on the basis of the final effective potential v_s. The DOS $g(\varepsilon)$ for an energy ε was determined via[72]

$$g(\varepsilon) = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}} \sum_{i} \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(\varepsilon - \varepsilon_i)^2}{2\sigma^2}\right) \qquad (47)$$

with $N_{\mathbf{k}}$ denoting the number of **k** points used in the determination of the DOS and σ determining the half-width of the Gaussian broadening functions in Eq. (47). Suitable values for $N_{\mathbf{k}}$ and σ are listed below. The integral $\int_{-\infty}^{\mu} dE f(\varepsilon) g(E)$ with $f(\varepsilon) = 1/[\exp(\varepsilon - \mu) + 1]$ needs to yield the number of electrons per unit cell.

For all computations presented in this work, the convergence criterion for the SCF cycle was set to 10^{-8} a.u. for all relevant variables, i.e., for the local potential v_s, the electron density ρ_0, and the total and free energy of the system. The norm-conserving LDA and EXX pseudopotentials employed in this work were generated by a code of Engel[73] which is based on the Troullier-Martins scheme.[74] The cutoffs used for the construction of the pseudopotentials as well as the lattice constants of the crystals are listed in Table I. The plane-waves cutoff was set to 40 Ry for the eigenstates and to 20 Ry for the representation of the KS response function, the right-hand side of the EXX equation, and the exchange

potential. We used a regular grid of $6 \times 6 \times 6$ **k** points in the SCF cycles. In the sum over state expressions (34) and (35) for the response function and the right hand side of the EXX equation all orbitals were included in the summation over the indices. The effective KS potential and the band structures were fully converged with respect to the plane-wave cutoffs and the number of **k** points. Band structures obtained with somewhat lower cutoffs (30 Ry for eigenstates and 15 Ry for exchange potential) and somewhat less **k** points ($5 \times 5 \times 5$ **k** points) are indistinguishable on the scale of the figures of the band structures that are shown below.

For the LDA correlation functional complementing the LDA as well as the EXX exchange the parametrization of Vosko, Wilk, and Nusair (VWN) was used.[76] Note that the LDA functional in the standard form derived for zero temperature was used, however, it was evaluated for the finite-temperature electron density occurring in the calculations. All band structures and DOS presented later on were obtained from calculations at room temperature (293 K). In order to investigate the temperature dependence of the DOS we also carried out calculations at lower and higher temperatures. All presented band structures follow the classification of high symmetry **k**-points as described for instance in Ref. [77].

IV. APPLICATIONS: SODIUM, MAGNESIUM, AND ALUMINUM

In order to illustrate the application of the described finite-temperature EXX approach to metals we considered three selected metals: the alkali metal sodium (Na), the alkali earth metal magnesium (Mg), and aluminum (Al). We calculated band structures and density of states. For comparison, corresponding finite-temperature LDA calculations were performed. For each metal we considered the most common phases at room temperature at experimental lattice constants see Table I, i.e., for Na body-centered cubic (bcc), space group no. 229, $Im\bar{3}m$; for Mg hexagonal closest packing (hcp), space group no. 194, $P6_3/mmc$; and for Al face-centered cubic (fcc), space group no. 225, $Fm\bar{3}m$.

Figures 1–3 show comparisons of the EXX and LDA band structures for sodium, magnesium, and aluminum, respectively. Below and at the Fermi level, no significant differences between LDA and EXX band structures are observed. For aluminum the band repulsions below the Fermi level are slightly but not significantly larger (few meV) in the EXX than in the LDA band structure. LDA and EXX bands cross the Fermi level at almost exactly the same points in the Brillouin zone and all occupied LDA and EXX levels are qualitatively comparable, as expected. This similarity between LDA and EXX band structures is also observed for insulators.[28]

Above the Fermi level, in particular at higher energies, however, significant differences between the LDA and EXX band structures start to build up. These differences, in some cases, can have magnitudes of 0.5 up to 2.0 eV. For instance, consider the EXX eigenvalues close to 8 eV for the **k**-point H in sodium (see Fig. 1) and for the **k**-point M of magnesium (see Fig. 2). These EXX eigenvalues are higher by
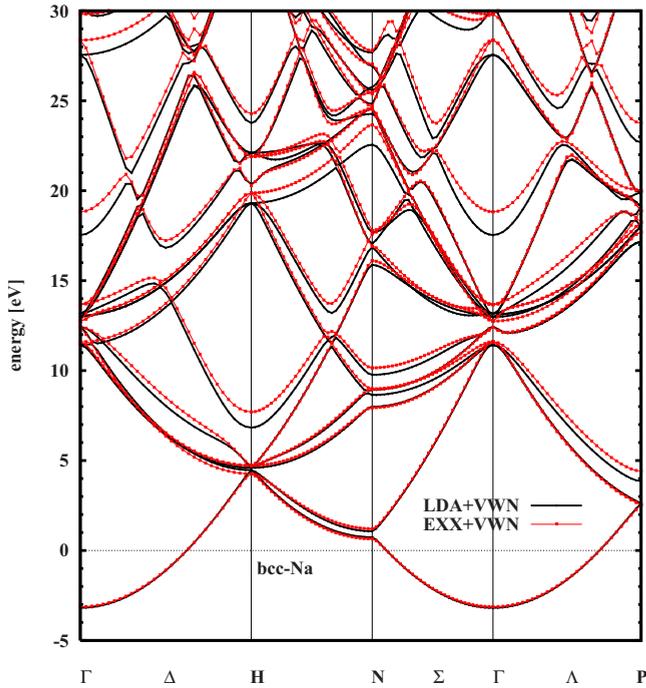
FIG. 1. (Color online) Comparison of LDA and EXX band structures (evaluated at room temperature) for sodium. The zero energy level corresponds the Fermi level.

more than 1 eV compared to their LDA counterparts. At higher energies the differences can occasionally increase up to almost 2.0 eV, e.g., at the Γ point of sodium (see Fig. 1). We emphasize that these shifts in the energies of unoccupied bands are of the same order as the band gap shifts observed in semiconductors and insulators.[28] We observe also that
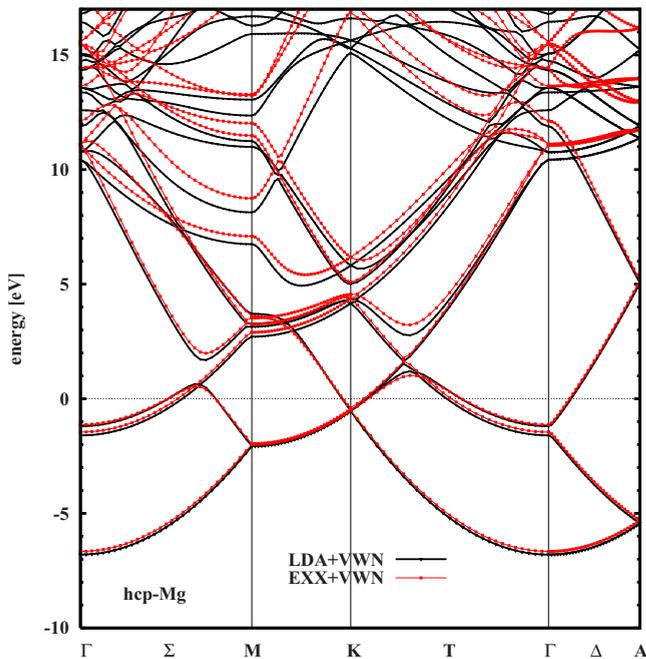
FIG. 2. (Color online) Comparison of LDA and EXX band structures (evaluated at room temperature) for magnesium. The zero energy level corresponds the Fermi level.
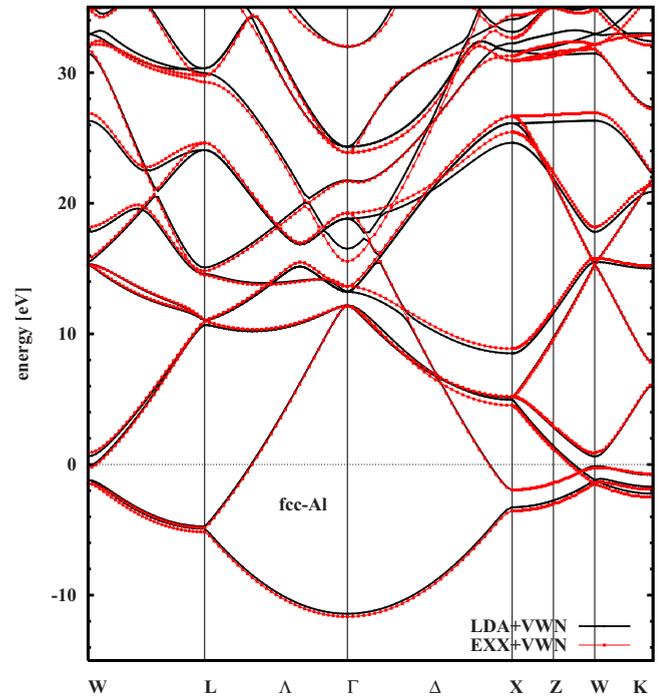
FIG. 3. (Color online) Comparison of LDA and EXX band structures (evaluated at room temperature) for aluminum. The zero energy level corresponds the Fermi level.

band repulsions are stronger in the EXX band structures far above the Fermi level. For instance, in aluminum, the singly degenerated bands at the Γ point between 16 and 20 eV in the EXX case exhibit a band repulsion about 0.5 eV larger than in the LDA case. Furthermore the positions of several band crossings are shifted in some cases to the left and/or to the right in the EXX band structures compared to the LDA band structures, due to larger band repulsion in the EXX band structures. This finding also is observed in semiconductor band structures, e.g., for germanium.[28] We emphasize, however, that the described local variations in LDA and EXX band energies do not affect the general shape and appearance of the band structures of Na, Mg, and Al, i.e., band ordering remains the same in LDA and EXX.

The corresponding DOS are shown in Fig. 4 for the LDA and the EXX case of the three considered metals. Convergence of the DOS with respect to $N_{\mathbf{k}}$ was accomplished for each of the metals with $25 \times 25 \times 25$ **k** points and for Na with a halfwidth of $\sigma_{Na} = 0.74$ eV, for Mg with $\sigma_{Mg} = 1.04$ eV and for Al with $\sigma_{Al} = 0.64$ eV, respectively [see Eq. (47)]. Up to 1.0–2.0 eV below Fermi level, the LDA and EXX case do not show any significant differences as expected from the corresponding band structures. Around the Fermi level and above, small differences build up due to the exact treatment of the unoccupied states in EXX formalism. Hereby, the EXX DOS can differ up to 3% to 5% from the LDA DOS, consider for instance the deviation in sodium at 3 eV or in aluminum at 4 eV. In order to investigate the temperature dependence of the DOS we did LDA and EXX calculations for Al and Na at 100 K and at a temperature close to the melting point (i.e., at 800 K for Al and at 350 K for Na). As expected, the resulting DOS did not change signifi-
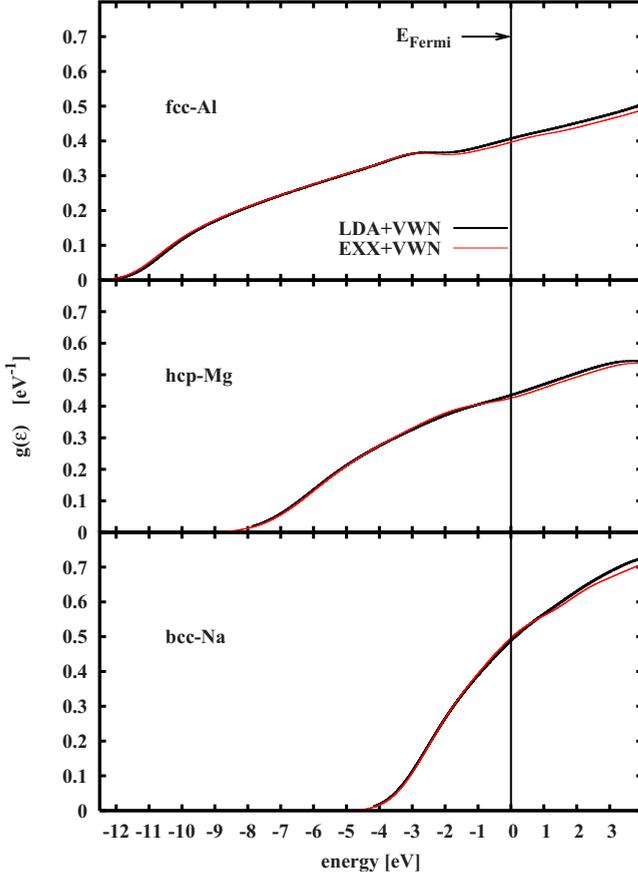
FIG. 4. (Color online) Comparison of the density of states per unit cell between sodium, magnesium and aluminum (evaluated at room temperature for $N_k = 25 \times 25 \times 25$ and $\sigma_{Na} = 0.74$ eV, $\sigma_{Mg} = 1.04$ eV and $\sigma_{Al} = 0.64$ eV). Results for LDA and EXX are presented in each case. The zero energy level corresponds the Fermi level.

cantly from the DOS at room temperature, i.e., changes never exceeded 2×10^{-4} eV.

We conclude this section by emphasizing that the effect of the presented EXX method, compared to the LDA method clearly *does not* correspond to that of a "scissors" operator. More precisely, the observed stronger band repulsions and the band shifts locally modify the band structures, especially high above the Fermi level.

V. CONCLUDING REMARKS

Now having at hand a finite-temperature EXX method for solids and, in particular, for metals it seems interesting to investigate with the new method metals that are insufficiently described by conventional LDA or GGA method. For example, metals having d electron shells, such as copper or iron, so as to determine exchange effects on the copper d bandwidth. Another example may be f-shell metals such as any of the lanthanoids.

In a next step the finite-temperature EXX approach presented here can be combined with the magnetization-current density functional theory of Refs. 78 and 79 in order to take

into account spin-orbit effects, noncollinear spin, and magnetic effects in metals.

APPENDIX: OCCUPATION NUMBERS

At first, we here briefly reconsider a derivation of expression (28) for the occupation numbers f_i of KS orbitals in the case of a grand canonical ensemble[72] and then generalize this derivation to the case of the occupation numbers g_{ij} of pairs of KS orbitals. The occupation numbers f_i are given by

$$
\begin{aligned}
f_i &= \sum_{N=1}^{\infty} \sum_{\substack{n \\ i \in \Phi_{N,n}}} \frac{\exp[(-1/kT)(E_{N,n}^{KS} - \mu N)]}{Z_{v_s,T,\mu}^{KS}} \\
&= 1 - \sum_{N=1}^{\infty} \sum_{\substack{n \\ i \notin \Phi_{N,n}}} \frac{\exp[(-1/kT)(E_{N,n}^{KS} - \mu N)]}{Z_{v_s,T,\mu}^{KS}} \\
&= 1 - e^{(1/kT)(\varepsilon_i - \mu)} \sum_{N=1}^{\infty} \\
&\quad \times \sum_{\substack{n \\ i \in \Phi_{N+1,n}}} \frac{\exp[(-1/kT)(E_{N+1,n}^{KS} - \mu(N+1))]}{Z_{v_s,T,\mu}^{KS}} \\
&= 1 - e^{(1/kT)(\varepsilon_i - \mu)} \sum_{N=2}^{\infty} \sum_{\substack{n \\ i \in \Phi_{N,n}}} \frac{\exp[(-1/kT)(E_{N,n}^{KS} - \mu N)]}{Z_{v_s,T,\mu}^{KS}} \\
&\approx 1 - e^{(1/kT)(\varepsilon_i - \mu)} \sum_{N=1}^{\infty} \sum_{\substack{n \\ i \in \Phi_{N,n}}} \frac{\exp[(-1/kT)(E_{N,n}^{KS} - \mu N)]}{Z_{v_s,T,\mu}^{KS}} \\
&= 1 - e^{(1/kT)(\varepsilon_i - \mu)} f_i. \qquad (A1)
\end{aligned}
$$

In the first line of Eq. (A1) we sum up the probability weights of all KS determinants that contain the KS orbital ϕ_i. To obtain the second line of Eq. (A1) we use that its sum is the same as one minus the sum of the probability weights of all KS determinants that do *not* contain the KS orbital ϕ_i. For the third line we exploit that a summation over all N-electron KS determinants that do not contain the KS orbital ϕ_i equals a summation over all $N+1$-electron KS determinants that do contain the KS orbital ϕ_i because the addition of an electron in the orbital ϕ_i to an N-electron KS determinant not containing ϕ_i leads to an $(N+1)$-electron KS determinant containing orbital

ϕ_i and because vice versa the removal of an electron in the orbital ϕ_i from an $(N+1)$-electron KS determinant containing ϕ_i leads to an N-electron KS determinant not containing orbital ϕ_i. Furthermore the energy of the considered pairs of N- and $(N+1)$-electron determinants differs by the eigenvalues ε_i of the orbital ϕ_i. The forth line of Eq. (A1) follows from a simple change of the summation variable. The forth and the fifth line differ by the summation term for $N=1$ only. This term equals $1/Z^{KS}_{v_s,T,\mu}$, the inverse of the

grand partition function (6), and approaches zero for a large average electron number N as it occurs in the treatment of a solid if a large enough number of **k** points and/or a large enough unit cell is taken into account and the chemical potential μ is adjusted such that the solid is neutral. Rearrangement of Eq. (A1) leads to expression (28) for the occupation numbers f_i.

The occupation numbers g_{ij} of pairs of KS orbitals are given by

$$
\begin{aligned}
g_{ij} &= \sum_{N=2}^{\infty} \sum_{\substack{n \\ i \in \Phi_{N,n} \\ j \in \Phi_{N,n}}} \frac{\exp[(-1/kT)(E^{KS}_{N,n} - \mu N)]}{Z^{KS}_{v_s,T,\mu}} \\
&= 1 - \sum_{N=1}^{\infty} \sum_{\substack{n \\ i \notin \Phi_{N,n}}} \frac{\exp[(-1/kT)(E^{KS}_{N,n} - \mu N)]}{Z^{KS}_{v_s,T,\mu}} - \sum_{N=1}^{\infty} \sum_{\substack{n \\ j \notin \Phi_{N,n}}} \frac{\exp[(-1/kT)(E^{KS}_{N,n} - \mu N)]}{Z^{KS}_{v_s,T,\mu}} + \sum_{N=1}^{\infty} \sum_{\substack{n \\ i \notin \Phi_{N,n} \\ j \notin \Phi_{N,n}}} \frac{\exp[(-1/kT)(E^{KS}_{N,n} - \mu N)]}{Z^{KS}_{v_s,T,\mu}} \\
&= f_i + f_j - 1 + \sum_{N=1}^{\infty} \sum_{\substack{n \\ i \notin \Phi_{N,n} \\ j \notin \Phi_{N,n}}} \frac{\exp[(-1/kT)(E^{KS}_{N,n} - \mu N)]}{Z^{KS}_{v_s,T,\mu}} \\
&= f_i + f_j - 1 + e^{(1/kT)(\varepsilon_i + \varepsilon_i - \mu - \mu)} \sum_{N=1}^{\infty} \sum_{\substack{n \\ i \in \Phi_{N+2,n} \\ j \in \Phi_{N+2,n}}} \frac{\exp[(-1/kT)(E^{KS}_{N+2,n} - \mu(N+2))]}{Z^{KS}_{v_s,T,\mu}} \\
&= f_i + f_j - 1 + e^{(1/kT)(\varepsilon_i + \varepsilon_i - \mu - \mu)} \sum_{N=3}^{\infty} \sum_{\substack{n \\ i \in \Phi_{N,n} \\ j \in \Phi_{N,n}}} \frac{\exp[(-1/kT)(E^{KS}_{N,n} - \mu N)]}{Z^{KS}_{v_s,T,\mu}} \\
&\approx f_i + f_j - 1 + e^{(1/kT)(\varepsilon_i + \varepsilon_i - \mu - \mu)} \sum_{N=2}^{\infty} \sum_{\substack{n \\ i \in \Phi_{N,n} \\ j \in \Phi_{N,n}}} \frac{\exp[(-1/kT)(E^{KS}_{N,n} - \mu N)]}{Z^{KS}_{v_s,T,\mu}} = f_i + f_j - 1 + e^{(1/kT)(\varepsilon_i + \varepsilon_i - \mu - \mu)} g_{ij}. \quad \text{(A2)}
\end{aligned}
$$

In the step from the second to the third line of Eq. (A2) we add and subtract one and use the third line of Eq. (A1). The fifth and sixth line of Eq. (A2) differ by the summation term for $N=2$ that again equals $1/Z^{KS}_{v_s,T,\mu}$, the inverse of the grand partition function (6) and approaches zero for large enough electron numbers as they are encountered in the treatment of solids.

Rearrangement of Eq. (A2) leads to

$$
g_{ij} = \frac{f_i + f_j - 1}{1 - e^{(1/kT)(\varepsilon_i + \varepsilon_i - \mu - \mu)}} = f_i f_j. \quad \text{(A3)}
$$

The occupation numbers g_{ij} of pairs of KS orbitals thus are just given by the product of the occupation numbers f_i and f_j of the KS orbitals i and j.

With Eq. (A3) expression (32) for the sum of Coulomb and exchange energy assumes the form

$$
\begin{aligned}
U + E_x &= (1/2) \sum_i \sum_j f_i f_j [\langle ij|ij \rangle - \langle ij|ji \rangle] \\
&= (1/2) \int d\mathbf{r} d\mathbf{r}' \frac{\rho_0(\mathbf{r})\rho_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - (1/2) \sum_i \sum_j f_i f_j \langle ij|ji \rangle,
\end{aligned}
$$
$$\text{(A4)}$$

which suggests to define the Coulomb and exchange energies individually as

$$U = (1/2) \int d\mathbf{r} d\mathbf{r}' \frac{\rho_0(\mathbf{r})\rho_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{A5}$$

and

$$E_x = (-1/2) \sum_i \sum_j f_i f_j \langle ij | ji \rangle, \tag{A6}$$

respectively. The evaluation of the Coulomb and exchange energy via Eqs. (A5) and (A6) is straightforward and just requires a simple generalization of whatever procedure is used to calculate Coulomb and exchange energy in a ground state EXX approach.

The expressions for the occupation numbers g_{ij} and for the Coulomb and exchange energy given in Eqs. (A3), (A5), and (A6) are those that are suggested by naive guess. However, it seems preferable to give the expressions a firm formal basis by deriving them starting from the basic finite-temperature KS formalism.

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