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Exact treatment of exchange in Kohn-Sham band-structure schemes

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A Kohn-Sham (KS) scheme for solids treating exchange exactly is introduced. The scheme emerges from a recently introduced exact formal KS procedure [A. Görling and M. Levy, Phys. Rev. A **50**, 196 (1994)]. The exact density-functional exchange potential is obtained in terms of its Fourier components. The method can easily be implemented on the basis of existing Hartree-Fock schemes for solids employing plane waves as basis sets.

I. INTRODUCTION

The Kohn-Sham (KS) procedure of density-functional theory (DFT) (Refs. 1–4) is the most widely used method for the theoretical description of the electronic structure of solids. In this method the exchange and correlation interactions are treated via density functionals which are not known exactly. The necessary employment of approximate exchange and correlation density functionals introduces errors which inevitably limit the accuracy and reliability of results obtained with KS procedures. In this work a KS scheme is suggested which allows one to treat exchange interactions exactly, and therefore requires approximations only for the treatment of the electron correlation. The suggested scheme emerges from a recently introduced exact formal KS procedure which is based on perturbation theory.[5,6] The first-order terms of this procedure give access to the exact DFT exchange energy and potential, and thus to a KS scheme treating exchange exactly. Here this scheme is formulated within a basis set representation resting on plane waves. This allows its application in the calculation of electronic structures of solids. The implementation of the scheme on the basis of existing plane-wave Hartree-Fock (HF) computer codes, as it is described here, is possible without much programming effort, and its computational demands are similar to those of HF calculations for solids.

Note that the exchange energy in HF theory and in DFT are defined differently. Therefore the method introduced here and the HF method are different, although both, each in its own way, are exact exchange methods. However, the procedure, in contrast to the HF scheme leads to a local exchange potential. As a result the introduced exact exchange procedure should not suffer from undesirable features present in the HF method, like artificially increased band gaps.[7,8]

II. BASIC FORMALISM

The KS formalism of DFT is based on the calculation of the KS determinant $\Phi^{\mathrm{KS}}[\rho]$, a model system of noninteracting electrons with the same ground-state electron density as the real, physical interacting electron system.

The KS determinant $\Phi^{\mathrm{KS}}[\rho]$ is a Slater determinant constructed from the N energetically lowest KS orbitals ϕ_i.[1–4] Here N is the electron number of the considered system. The symbol ϕ_i includes the spin degree of freedom of the KS orbitals, i.e., the ϕ_i shall be two-dimensional spinors. Otherwise the form of the KS orbitals ϕ_i is not specified any further at this point. This means that the ϕ_i may be Block orbitals with periodic boundary conditions which are appropriate for the treatment of crystalline systems as well as KS orbitals vanishing exponentially at infinity as those connected with finite systems. Of course, in order to be describable by properly normalizable wave functions, the considered systems have to be finite. Therefore crystalline solids, as usual, are modeled here by systems with periodic boundary conditions which consist of a large but finite number of unit cells. The KS orbitals are eigenfunctions of the one-particle KS equations[1–4]

$$[(\tfrac{1}{2})\boldsymbol{\nabla}^2+v_s([\rho];\mathbf{r})]\phi_i=\epsilon_i\phi_i\,. \tag{1}$$

The effective or KS potential $v_s([\rho];\mathbf{r})$ is the sum of the external potential $v(\mathbf{r})$, the Coulomb potential $u([\rho];\mathbf{r})$, the exchange potential $v_x([\rho];\mathbf{r})$, and the correlation potential $v_c([\rho];\mathbf{r})$:

$$v_s([\rho];\mathbf{r}=v(\mathbf{r})+u([\rho];\mathbf{r})+v_x([\rho];\mathbf{r})+v_c([\rho];\mathbf{r}). \tag{2}$$

The potentials $u([\rho];\mathbf{r})$, $v_x([\rho];\mathbf{r})$, and $v_c([\rho];\mathbf{r})$ are the functional derivatives of the density functionals for the classical Coulomb energy $U[\rho]$, the exchange energy $E_x[\rho]$, and the correlation energy $E_c[\rho]$, respectively.[1–4]

The ground-state energy of the real physical system is given as functional of its ground-state density $\rho(\mathbf{r})$,[1–4]

$$E=T_s[\rho]+U[\rho]+E_x[\rho]+E_c[\rho]+\int d\mathbf{r}\;v(\mathbf{r})\rho(\mathbf{r}). \tag{3}$$

The noninteracting kinetic energy $T_s[\rho]$ in Eq. (3) is determined by the KS system according to

$$T_s[\rho]=\sum_i^{\mathrm{occ}}\int d\mathbf{r}\;\phi_i^*([\rho];\mathbf{r})(-\tfrac{1}{2}\boldsymbol{\nabla}^2)\phi_i([\rho];\mathbf{r}). \tag{4}$$

The DFT exchange energy $E_x[\rho]$ is defined by the KS orbitals ϕ_i as

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$$E_x[\rho]=\frac{1}{2}\sum_i^{\text{occ}}\sum_j^{\text{occ}}\int d\mathbf{r}\int d\mathbf{r}'\times\frac{\phi_i^*([\rho];\mathbf{r}')\,\phi_j^*([\rho];\mathbf{r})\,\phi_j([\rho];\mathbf{r}')\,\phi_i([\rho];\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}. \tag{5}$$

The fact that the KS orbitals are functionals of the ground-state density $\rho(\mathbf{r})$ (Refs. 1–4) is expressed in Eqs. (4) and (5) by explicitly writing $\phi_i([\rho];\mathbf{r})$. The correlation energy $E_c[\rho]$ consists of all contributions to the total energy which are not contained in $T_s[\rho], U[\rho], E_x[\rho]$, and $\int d\mathbf{r}\, v(\mathbf{r})\rho(\mathbf{r})$. Whereas the latter energies can be calculated exactly from the KS orbitals ϕ_i, the correlation energy $E_c[\rho]$ has to be evaluated through an approximate density functional. Approximate density functionals also have to be employed for the exchange potential $v_x([\rho];\mathbf{r})$ and the correlation potential $v_c([\rho];\mathbf{r})$, which are required for the construction of the KS potential $v_s([\rho];\mathbf{r})$ of the KS equations (1) for the KS orbitals ϕ_i [see Eq. (2)]. Note that knowledge of the exchange energy $E_x[\rho]$ in terms of KS orbitals as provided by Eq. (5) does not mean that the form of its functional derivative with respect to the density, the exchange potential $v_x([\rho];\mathbf{r})$, is also known. The reason is that the form of the functional dependence of the orbitals on the density, like the form of the functional $E_x[\rho]$, is unknown.

In actual applications of the KS formalism, the exchange energy $E_x[\rho]$ [Eq. (5)] is usually also calculated via approximate exchange-density functionals despite the fact that it can be determined from the KS orbitals by using Eq. (5) without making further approximations. The reason is that the evaluation of the right side of Eq. (5) is computationally more demanding than all other steps of a KS scheme, and that so far approximate exchange functionals have to be employed in any case to provide the exchange potential. In this work, however, a procedure is discussed which allows one to generate the exchange potential without resorting to approximate functionals. The computational effort required by this procedure is about the same as the one necessary to handle the expression on the right-hand side of Eq. (5). Therefore, if one accepts this computational effort, which is of the same order of magnitude as the one required by HF procedures, one can treat the complete exchange interactions, as defined in DFT, exactly.

The exchange potential $v_x([\rho];\mathbf{r})$ is defined as the functional derivative of the exchange energy $E_x[\rho]$ with respect to the density $\rho(\mathbf{r})$,

$$v_x([\rho];\mathbf{r})=\frac{\delta E_x}{\delta\rho(\mathbf{r})}=\sum_i^{\text{occ}}\int d\mathbf{r}'\int d\mathbf{r}''\left[\frac{\delta E_x}{\delta\phi_i(\mathbf{r}'')}\,\frac{\delta\phi_i(\mathbf{r}'')}{\delta v_s(\mathbf{r}')}+\frac{\delta E_x}{\delta\phi_i^*(r'')}\,\frac{\delta\phi_i^*(\mathbf{r}'')}{\delta v_s(\mathbf{r}')}\right]\frac{\delta v_s(\mathbf{r}')}{\delta\rho(\mathbf{r})}. \tag{6}$$

The functional derivatives $\delta E/\delta\phi_i$ and $\delta E/\delta\phi_i^*$ occurring in Eq. (6) can be calculated directly from Eq. (5), whereas $\delta\phi_i/\delta v_s(\mathbf{r})$ and $\delta\phi_i^*/\delta v_s(\mathbf{r})$ are given by standard perturbation theory. As a result,[5,6] the exchange potential $v_x([\rho];\mathbf{r})$ is obtained as

$$v_x(\mathbf{r})=\int d\mathbf{r}'\left[\sum_i^{\text{occ}}\sum_s^{\text{unocc}}\langle\phi_i[\rho]|\hat{v}_x^{\text{NL}}[\rho]|\phi_s[\rho]\rangle\frac{\phi_s^*([\rho];\mathbf{r}')\,\phi_i([\rho];\mathbf{r}')}{\epsilon_i-\epsilon_s}+\text{c.c.}\right]\frac{\delta v_s(\mathbf{r}')}{\delta\rho(\mathbf{r})}. \tag{7}$$

The operator $\hat{v}_x^{\text{NL}}$ is a nonlocal exchange operator of the form of the HF exchange operator, though, constructed from KS orbitals. The functional derivative $\delta v_s(\mathbf{r}')/\delta\rho(\mathbf{r})$ occurring in Eqs. (6) and (7) determines changes $\delta v_s(\mathbf{r})$ of the effective potential $v_s(\mathbf{r})$ to given changes $\delta\rho(\mathbf{r})$ of the ground-state density $\rho(\mathbf{r})$. At this point the Hohenberg-Kohn theorem[1–4] is invoked. It establishes a one-to-one mapping between ground-state densities $\rho(\mathbf{r})$ and effective potentials $v_s(\mathbf{r})$ of a noninteracting KS system if additions of constants to the potential are disregarded. This allows one to consider the KS potential $v_s(\mathbf{r})$ as a functional of the density $\rho(\mathbf{r})$.

The well-known static linear-response operator $\hat{X}$ for the noninteracting KS system relates changes $\delta\rho$ of the density with changes δv_s of the effective potential. In ordinary space this can be expressed as

$$\delta\rho(\mathbf{r})=\int d\mathbf{r}'\,X(\mathbf{r},\mathbf{r}')\,\delta v_s(\mathbf{r}'), \tag{8}$$

with

$$X(\mathbf{r},\mathbf{r}')=\sum_i^{\text{occ}}\sum_s^{\text{unocc}}\frac{\phi_i^*(\mathbf{r})\,\phi_s(\mathbf{r})\,\phi_s^*(\mathbf{r}')\,\phi_i(\mathbf{r}')}{\epsilon_i-\epsilon_s}+\text{c.c.} \tag{9}$$

The functional derivative $\delta\rho(\mathbf{r})/\delta v_s(\mathbf{r}')=X(\mathbf{r},\mathbf{r}')$ in some sense is the inverse of the functional derivative $\delta v_s(\mathbf{r})/\delta\rho(\mathbf{r}')$ of Eqs. (6) and (7). However, the problem arises that the linear-response operator $\hat{X}$ has no proper inverse. The reason is that constant functions are eigenfunctions of $\hat{X}$ with zero eigenvalues because the addition of a constant to a potential $v_s(\mathbf{r})$ leaves the orbitals and therefore the density constant. Furthermore, independently of the change $\delta v_s(\mathbf{r})$, the changes $\delta n(\mathbf{r})$ have to integrate to zero because the electron number is not affected by modifications of the effective potential $v_s(\mathbf{r})$. However, if constant functions are excluded from the space of the changes $\delta\rho$ and δv_s then the one-to-one mapping between potentials v_s and densities ρ established by the Hohenberg-Kohn theorem guarantees that the operator $\hat{X}$ is invertible on this restricted space. At this point, implicitly, the assumption of noninteracting v representability is made, i.e., it is assumed that to each density occurring here there exists an effective potential $v_s(\mathbf{r})$ which leads through the corresponding KS equation (1) to orbitals yielding that density. Note that this assumption underlies the KS formalism itself, and is not a specific requirement of the method developed here.

The representation of the inverse $\hat{X}^{-1}$ of $\hat{X}$ in ordinary space is not known. There is no simple way to exclude constant functions from ordinary space. However, if densities $\rho(\mathbf{r})$ and potentials $v_s(\mathbf{r})$, as well as their changes, are represented within a finite basis set, then the uniquely defined linear combination of basis functions corresponding to a constant function can easily be excluded from the basis set.[5] Within the resulting reduced basis set the representation of the inverse operator $\hat{X}^{-1}$ and therefore that of the functional derivative $\delta v_s(\mathbf{r})/\delta\rho(\mathbf{r}')$ is given by the inverse $\mathbf{X}^{-1}$ of the matrix $\mathbf{X}$ representing the operator $\hat{X}$ in the reduced basis set. Now all quantities appearing in Eq. (7) for the exchange potential $v_x([\rho];\mathbf{r})$ are accessible. This means that the exact exchange potential $v_x(r)$ in the form of its basis set representation is also accessible, and can be employed in a KS procedure.

The exchange potential as obtained by the procedure discussed above is defined only up to an additive constant. This, however, is not a shortfall of the procedure but reflects the fact that the exchange potential in DFT for integer electron numbers is defined only to within an additive constant because functional derivatives with respect to the density are defined only to within an additive constants if the electron number is fixed.

Acting with the operator $\int d\mathbf{r}''X(\mathbf{r},\mathbf{r}'')$ on both sides of Eq. (7) turns this equation into the basic relation for the exchange potential $v_x(\mathbf{r})$ within the optimized potential method (OPM).[9,10] The other way around the OPM relation for $v_x(\mathbf{r})$ is converted into Eq. (7) by applying $\int d\mathbf{r}''X^{-1}(\mathbf{r},\mathbf{r}'')$ on it. Both the OPM and the method discussed here are procedures to perform KS schemes treating exchange exactly. If correlation is neglected, both methods result in an exact exchange-only KS procedure. However, the OPM has the disadvantage that its basic equation is an integral equation which has to be solved numerically, That limits the applicability of the OPM to atomic systems. In order to treat solids with the OPM, one has to introduce additional approximations like the ones suggested by Krieger, Li, and Iafrate[11] resulting in an approximate scheme which was recently applied to solids by Bylander and Kleinman.[12] (An alternative approach to solve the OPM equations exactly by a transformation of the basic equation, as is discussed in Ref. 11(b), also leads to quite demanding integrodifferential equations.) The method discussed here, in contrast to the OPM, as a basis set method is not limited in its applicability to a certain type of systems. The introduction of the steps necessary for an implementation of this method which allows the treatment of solids is the main purpose of this work (see Sec. III).

The step from Eq. (7) to the OPM relation for the exchange potential, and vice versa, is not trivial, because for its justification the Hohenberg-Kohn theorem has to be invoked and this requires the exclusion of constant functions from the space of the changes of potentials and densities. Furthermore, the derivation of Eq. (7) as given in Refs. 5 and 6 and as discussed here is based solely on the fundamental principles of DFT and does not use stationarity properties of the total energy with respect to an effective potential, as the usual derivation[9,10] of the OPM relation for $v_x(\mathbf{r})$ does. Also note that Eq. (7) represents the first-order step in a more general formalism leading to an exact KS scheme which is described in Refs. 5 and 6.

III. KS SCHEME FOR SOLIDS TREATING EXCHANGE EXACTLY

The exposition given so far was not restricted to specific systems. Now this work concentrates on periodic systems, i.e., crystalline solids. Furthermore, the systems considered shall exhibit inversional symmetry. The latter is by no means a necessary condition for the computational scheme introduced here; however, it simplifies the notation. Besides densities and potentials also the KS orbitals shall be developed into a basis set. The canonical KS orbitals for periodic systems are Bloch orbitals $\phi_{n,k}(\mathbf{r})$ characterized by a band index n and a vector $\mathbf{k}$ lying in the first Brillouin zone. The basis sets $\{\chi_{\mathbf{k},\mathbf{G}}\}$ for the KS orbitals shall consist of M_χ plane waves,

$$\chi_{\mathbf{k},\mathbf{G}}(\mathbf{r})=\frac{1}{\sqrt{\Omega}}e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}, \tag{10}$$

with Ω being the unit-cell volume and $\mathbf{G}$ being a reciprocal-lattice vector. [In the orbital basis set the inversional symmetry is not exploited here. The volume Ω can alternatively be identified with the crystal volume. Then integrations in ordinary space have to be performed over the whole crystal instead of over one unit cell, and the averaging over the Brillouin zone in Eqs. (19) and (22) has to be replaced by a summation.]

The basis set $\{g_{\mathbf{Q}}\}$ used to represent densities and potentials shall contain M_g real symmetric linear combinations of plane waves,

$$g_{\mathbf{Q}}(\mathbf{r})=\frac{1}{\sqrt{2\Omega}}[e^{i\mathbf{Q}\cdot\mathbf{r}}+e^{-i\mathbf{Q}\cdot\mathbf{r}}], \tag{11}$$

with $\mathbf{Q}$ being a reciprocal-lattice vector which may not be equal to the zero vector in order to exclude constant functions from $\{g_{\mathbf{Q}}\}$. Densities and potentials exhibit the full translational symmetry of the system, and therefore only basis functions with this symmetry need to be included in $\{g_{\mathbf{Q}}\}$, i.e., $\{g_{\mathbf{Q}}\}$ contains only basis functions with a $\mathbf{k}$ vector being the zero vector. The exchange potential $v_x(\mathbf{r})$, for example, shall be expanded according to

$$v_x(\mathbf{r})=\sum_{\mathbf{Q}} a_{\mathbf{Q}}g_{\mathbf{Q}}(\mathbf{r}). \tag{12}$$

The fact that $g_{\mathbf{Q}}(\mathbf{r})=g_{-\mathbf{Q}}(\mathbf{r})$ is taken into account by requiring that one component of $\mathbf{Q}$, e.g., $\mathbf{Q}_x$, shall be positive.

The maximal size M_g of the basis set $\{g_{\mathbf{Q}}\}$ is determined by the requirement that it shall be complete with respect to given orbital basis sets $\{\chi_{k,\mathbf{G}}\}$. The size M_χ of the latter usually is determined by the condition that the magnitudes $|\mathbf{G}|$ of the reciprocal-lattice vectors $\mathbf{G}$ defining the basis functions $\chi_{\mathbf{k},\mathbf{g}}$ are smaller than a chosen threshold $G_{\max}$. The corresponding maximal threshold $Q_{\max}$ for the reciprocal-lattice vectors $\mathbf{Q}$ of the basis functions $g_{\mathbf{Q}}(\mathbf{r})$ has to be set equal to twice the value of $G_{\max}$, i.e., $Q_{\max}=2G_{\max}$, in order to obtain a basis set $\{g_{\mathbf{Q}}\}$ which is complete with respect to the basis sets $\{\chi_{\mathbf{k},\mathbf{G}}\}$. In practice, it might be sufficient to use a threshold $Q_{\max}$ which is much smaller than $2G_{\max}$.[13] Indeed this may be necessary to obtain a numerically stable procedure.[13] For systems with higher symmetry, e.g., cubic symmetry, the fact that the density and all potentials are totally symmetric allows one to include only totally symmetric basis functions $g_{\mathbf{Q}}(\mathbf{r})$ in the basis set $\{g_{\mathbf{Q}}\}$. This can drastically reduce the size of $\{g_{\mathbf{Q}}\}$.

The choice of plane waves as basis functions for all involved basis sets and the determination of the size M_g of the basis set $\{g_{\mathbf{Q}}\}$ as a function of the size M_χ of the basis sets $\{\chi_{\mathbf{k},\mathbf{G}}\}$ leads to basis sets for the KS orbitals, and for the densities and potentials which are perfectly balanced. This means that the expansion of the exchange potential into plane waves does not introduce additional basis set errors because the basis set $\{g_{\mathbf{Q}}\}$ is complete, or for $Q_{\max}<2G_{\max}$ *de facto* complete, with respect to the basis set $\{\chi_{\mathbf{k},\mathbf{G}}\}$. In other words, the only inaccuracy in the Fourier components of the DFT exchange potential as obtained by the scheme suggested here should be due to the inevitable incompleteness of the basis set $\{\chi_{\mathbf{k},\mathbf{G}}\}$ for the KS orbitals. Furthermore, for the balanced basis sets used here, one does not expect to encounter any problems originating from the fact that the Hohenberg-Kohn theorem can be violated if one employs unbalanced basis sets (see Ref. 14 for a discussion of this point).

The expansion of the KS orbital $\phi_{n,\mathbf{k}}(\mathbf{r})$ in the basis functions $\chi_{\mathbf{k},\mathbf{g}}$ turns the KS equations (1) into matrix equations

$$\mathbf{H}_{\mathbf{k}}^{\mathrm{KS}}\mathbf{c}_{n,\mathbf{k}}=\epsilon_{n,\mathbf{k}}\mathbf{c}_{n,\mathbf{k}}, \tag{13}$$

with vectors $\mathbf{c}_{n,\mathbf{k}}$ representing the orbitals $\phi_{n,\mathbf{k}}(\mathbf{r})$ in the basis sets $\{\chi_{\mathbf{k},\mathbf{G}}\}$ and with the $\epsilon_{n,\mathbf{k}}$ being the corresponding KS eigenvalues. The Hamiltonian matrix $\mathbf{H}_{\mathbf{k}}^{\mathrm{KS}}$can be decomposed into contributions $\mathbf{H}_{T,\mathbf{k}}$,$\mathbf{H}_v$,$\mathbf{H}_C$,$\mathbf{H}_x$, and $\mathbf{H}_c$ belonging to the operator of the kinetic energy and the operators of the external, the Coulomb, the exchange, and the correlation potentials, respectively,

$$\mathbf{H}_{\mathbf{k}}^{\mathrm{KS}}=\mathbf{H}_{T,\mathbf{k}}+\mathbf{H}_v+\mathbf{H}_C+\mathbf{H}_x+\mathbf{H}_c. \tag{14}$$

With the exception of $\mathbf{H}_x$ all contributions to the Hamiltonian matrix $\mathbf{H}_{\mathbf{k}}^{\mathrm{KS}}$ are treated here as usual in KS plane-wave methods for solids (or as in HF plane-wave methods), and therefore need not be discussed any further (see, for example, Refs. 7 and 15 for further information). The matrix elements $\langle\chi_{\mathbf{k},\mathbf{G}}|\hat{v}_x|\chi_{\mathbf{k},\mathbf{G}'}\rangle$ of the exchange contribution $\mathbf{H}_x$ to $\mathbf{H}^{\mathrm{KS}}$, which are independent of the vector $\mathbf{k}$, are here not evaluated by employing an approximate exchange functional as in standard KS procedures, but in another way by exploiting Eq. (7).

With respect to the basis set $\{g_{\mathbf{Q}}\}$, the exchange potential $v_x(\mathbf{r})$ is represented by the vector $\mathbf{a}$, collecting the expansion coefficients $a_{\mathbf{Q}}$ of Eq. (12). The $\mathbf{k}$-independent exchange contribution $\mathbf{H}_x$ to the Hamiltonian matrix $\mathbf{H}_{\mathbf{k}}^{\mathrm{KS}}$ is then obtained by

$$\mathbf{H}_x=\sum_{\mathbf{Q}} a_{\mathbf{Q}}\mathbf{H}^{\mathbf{Q}}, \tag{15}$$

with the matrix elements $H^{\mathbf{Q}}_{\mathbf{GG}'}=\langle\chi_{\mathbf{k},\mathbf{G}}|g_{\mathbf{Q}}|\chi_{\mathbf{k},\mathbf{G}'}\rangle$ of the matrices $\mathbf{H}^{\mathbf{Q}}$ being given by

$$H^{Q}_{\mathbf{GG}'}=(2\Omega)^{-1/2}\delta(\mathbf{Q}+\mathbf{G}-\mathbf{G}')+(2\Omega)^{-1/2}\delta(\mathbf{Q}-\mathbf{G}+\mathbf{G}'). \tag{16}$$

In order to determine the vector $\mathbf{a}$ which characterizes the exchange contribution $\mathbf{H}_x$ to the Hamiltonian matrix $\mathbf{H}_{\mathbf{k}}^{\mathrm{KS}}$, one has to calculate the matrix representations X and $\mathbf{X}^{-1}$ of the static linear-response operator $\hat{X}$ and its effective inverse $\hat{X}^{-1}$, respectively, for changes of the KS potential and the KS density which exhibit the translational symmetry of the system.[16] In order to do this, one constructs auxiliary $(M_\chi-N_{\mathbf{k}})\times N_{\mathbf{k}}$ matrices $\mathbf{A}_{\mathbf{Q},\mathbf{k}}$, with $N_{\mathbf{k}}$ being the number of occupied KS bands for the vector $\mathbf{k}$. The matrix elements of $\mathbf{A}_{\mathbf{Q},\mathbf{k}}$ are given by the matrix elements $\langle\phi_{s,\mathbf{k}}|g_{\mathbf{Q}}|\phi_{i,\mathbf{k}}\rangle$ of basis functions $g_{\mathbf{Q}}(\mathbf{r})$ between unoccupied and occupied KS orbitals $\phi_{s,\mathbf{k}}$ and $\phi_{i,\mathbf{k}}$, respectively. The matrices $\mathbf{A}_{\mathbf{Q},\mathbf{k}}$ can be obtained through simple similarity transformations of the corresponding matrices $\mathbf{H}_{\mathbf{Q}}$ by matrices $\mathbf{C}_{\mathbf{k}}$ which shall consist of columns given by the vectors $\mathbf{c}_{n,\mathbf{k}}$ representing the KS orbitals $\phi_{n,\mathbf{k}}(\mathbf{r})$ in the basis set $\{\chi_{\mathbf{k},\mathbf{G}}\}$:

$$\tilde{\mathbf{A}}_{\mathbf{Q},\mathbf{k}}=\mathbf{C}_{\mathbf{k}}^{\dagger}\mathbf{H}_{\mathbf{Q}}\mathbf{C}_{\mathbf{k}}. \tag{17}$$

The parts of the $M_\chi\times M_\chi$ matrices $\tilde{\mathbf{A}}_{\mathbf{Q},\mathbf{k}}$ given by the last $(M_\chi-N_{\mathbf{k}})$ elements of the first $N_{\mathbf{k}}$ rows constitute the matrices $\mathbf{A}_{\mathbf{Q},\mathbf{k}}$. Of course, in practice only those latter matrix elements of $\tilde{\mathbf{A}}_{\mathbf{Q},\mathbf{k}}$ which contribute to $\mathbf{A}_{\mathbf{Q},\mathbf{k}}$ have to be calculated. Also, note that the specific form of the matrices $\mathbf{H}_{\mathbf{Q}}$ [Eq. (16)] simplifies the similarity transformation (17).

Next, a second set of auxiliary matrices, the matrices $\mathbf{B}_{\mathbf{Q},\mathbf{k}}$, are determined from the matrices $\mathbf{A}_{\mathbf{Q},\mathbf{k}}$ by simply dividing each matrix element $\langle\phi_{s,\mathbf{k}}|g_{\mathbf{Q}}|\phi_{i,\mathbf{k}}\rangle$ of $\mathbf{A}_{\mathbf{Q},\mathbf{k}}$ by differences of the corresponding KS eigenvalues $\epsilon_{i,\mathbf{k}}-\epsilon_{s,\mathbf{k}}$. The matrices $\mathbf{A}_{\mathbf{Q},\mathbf{k}}$ and $\mathbf{B}_{\mathbf{Q},\mathbf{k}}$ are then used to calculate the matrix elements $X_{\mathbf{k},\mathbf{QQ}'}$ of contributions $X_{\mathbf{k}}$ to the static linear-response matrix $\mathbf{X}$ according to

$$X_{\mathbf{k},\mathbf{QQ}'}=\mathrm{Tr}[\mathbf{A}_{\mathbf{Q},\mathbf{k}}^{\dagger}\mathbf{B}_{\mathbf{Q}',\mathbf{k}}]+\mathrm{c.c.} \tag{18}$$

In Eq. (18), Tr stands for the taking of the trace of a matrix. Averaging over the vectors $\mathbf{k}$ of the first Brillouin zone results in the matrix representation $\mathbf{X}$ of the static linear-response operator $\hat{X}$,

$$\mathbf{X}=\frac{1}{N}\sum_{k}\mathbf{X}_{\mathbf{k}}, \tag{19}$$

Here N shall be the number of vectors $\mathbf{k}$ in the first Brillouin zone. Of course, in practice Eq. (19) would be performed through a special $\mathbf{k}$-point integration.[17] The inverse $\mathbf{X}^{-1}$ of the matrix $\mathbf{X}$ represents the operator $\hat{X}^{-1}$ in the basis set $\{g_{\mathbf{Q}}\}$.

Next the term in the square brackets on the right-hand side of Eq. (6) has to be calculated. The matrix $\mathbf{H}_{x,\mathbf{k}}^{\mathrm{HF}}$ shall be the matrix representing, in a basis set of plane waves, a nonlocal exchange operator for orbitals characterized by the vector $\mathbf{k}$. The nonlocal exchange operator has the form of the Hartree-Fock exchange operator, but is generated by KS orbitals in the scheme presented here. The technique of calculating the matrices $\mathbf{H}_{x,\mathbf{k}}^{\mathrm{HF}}$, including the treatment of the occurring integrable singularities, is known from Hartree-Fock methods, and needs no further discussion here (see, for example, Ref. 7).

Transformations of the matrices $\mathbf{H}_{x,\mathbf{k}}^{\mathrm{HF}}$ into the basis of the KS orbitals lead to matrices $\tilde{\mathbf{R}}_{\mathbf{k}}$,

$$\tilde{\mathbf{R}}_{\mathbf{k}}=\mathbf{C}_{\mathbf{k}}^{\dagger}\mathbf{H}_{x,\mathbf{k}}^{\mathrm{HF}}\mathbf{C}_{\mathbf{k}} \tag{20}$$

Auxiliary matrices $\mathbf{R}_{\mathbf{k}}$ are obtained as the parts of the $M_{\chi}\times M_{\chi}$ matrices $\tilde{\mathbf{R}}_{k}$ given by the $(M_{\chi}-N_{k})$ last elements of the first N_{k} rows. [The steps from the matrices $\mathbf{H}_{\mathbf{x},k}^{\mathrm{HF}}$ to the matrices $\mathbf{R}_{\mathbf{k}}$, Eq. (20), are the same as those from the matrices $\mathbf{H}_{Q}$ to the matrices $\mathbf{A}_{\mathbf{Q},\mathbf{k}}$, Eq. (17).] Next the elements $a_{\mathbf{k},\mathbf{Q}}$ of vectors $\mathbf{a}_{\mathbf{k}}$ are determined according to

$$a_{\mathbf{k},\mathbf{Q}}=[\mathbf{R}_{\mathbf{k}}^{\dagger}\mathbf{B}_{\mathbf{Q},\mathbf{k}}]+\mathrm{c.c.} \tag{21}$$

Finally, averaging of the vectors $\mathbf{a}_{\mathbf{k}}$ in $\mathbf{k}$ space leads to the term in the square brackets on the right-hand side of Eq. (7), and multiplication by $\mathbf{X}^{-1}$ results in the vector $\mathbf{a}$ characterizing through Eq. (15) the matrix representation $\mathbf{H}_{x}$ of the KS exchange potential:

$$\mathbf{H}_{x}=\mathbf{X}^{-1}\left[\frac{1}{N}\sum_{k}\mathbf{a}_{\mathbf{k}}\right], \tag{22}$$

Note that $\mathbf{H}_{x}$ does not depend on $\mathbf{k}$, i.e., the Hamiltonian matrices $\mathbf{H}_{\mathbf{k}}^{\mathrm{KS}}$, independently of $\mathbf{k}$, all contain the same exchange contribution. The reason is that the exchange potential in the KS formalism is a local, multiplicative potential, in contrast to the one of the HF procedure.

The above-suggested KS scheme, which treats exchange exactly, now can easily be implemented on the basis of existing[7] plane-wave HF computer codes for solids. An iteration cycle of the resulting scheme consists of the following steps:

(i) Construct the HF Hamiltonian operator from the orbitals of the previous cycle.

(ii) Determine the static linear response operator and its effective inverse [Eqs. (17)–(19)].

(iii) Calculate the KS exchange operator and use it to replace the HF exchange operator of the Hamiltonian operator of step (i) [Eqs. (20)–(22)].

(iv) Solve the one-particle equations in order to generate new orbitals.

Steps (ii) and (iii) have to be added to a standard plane-wave HF scheme consisting of steps (i) and (iv) in order to convert the HF scheme into a KS procedure treating exchange exactly. Of course, the orbitals generated by the suggested scheme are KS orbitals. Therefore, the Hamiltonian operator constructed in step (i) and modified in step (iii) is not really a HF Hamiltonian operator, but a Hamiltonian operator which depends on the KS orbitals in the same way as the HF Hamiltonian operator depends on HF orbitals.

The computationally most expensive task that has to be performed in the additional steps (ii) and (iii) is the part of the construction of the linear-response operator $\mathbf{X}$ described by Eqs. (17) and (18). The necessary computation time to carry out Eqs. (17) and (18) scales with the number of special $\mathbf{k}$ points times the number of occupied bands times the third power of the number of plane waves. For this estimate it is used that the number of basis functions in the basis sets $\{\chi_{\mathbf{k},\mathbf{G}}\}$ and $\{g_{\mathbf{Q}}\}$ are proportional. The computationally most expensive step in a standard plane-wave HF scheme for solids is the generation of the HF exchange operator. It requires one more summation (integration) in $\mathbf{k}$ space than the generation of the linear-response operator $\mathbf{X}$. Furthermore, the problem of singularities is only present in the construction of the HF exchange operator. Also, the generation of $\mathbf{X}$ consists mostly of standard linear algebra operations which can be performed highly efficiently on modern computers. Therefore the exact exchange KS scheme for solids introduced here seems to be feasible.

IV. CONCLUDING REMARKS

If the KS scheme introduced here is carried out by modifying an existing HF computer code, as described in Sec. III, then it treats exchange exactly but neglects correlation. However, correlation, of course, can be taken into account as usual in KS schemes by approximate correlation functionals.

The construction of the exact DFT exchange potential as described here is not only of interest for applications of the KS formalism, but is also very helpful for further formal and methodical developments in DFT. So far exchange potentials from approximate density functionals could be compared with the exact exchange potentials only for atoms within the framework of the optimized potential method.[18] Now this is also possible for solids. To have the exact exchange potential at hand is also helpful for further investigations of the question of the magnitude of the difference between the exact KS band gap and the physical band gap of semiconductors. In the KS scheme introduced here the error in the KS band gap arises solely from the approximate treatment of the electron correlation but not from the way exchange is taken into account. Because the introduced KS scheme allows us to perform an exact exchange-only procedure, it is also possible to check the accuracy of an approximate exchange-only schemes[11] based on the optimized potential method which recently has been implemented for solids.[12]

If the KS exchange energy is replaced by a screened exchange energy,[19,20] then the procedure developed here can be used to generate the exact screened exchange potential. In other words, the generalization of the scheme of this work to treat screened exchange interactions is straightforward.

The effective inverse of the static linear-response operator described here can also be used to obtain the exact KS band structure to a given electron density by the method described in Refs. 14 and 21. This method is tantamount to determining the KS band structure by a constrained search directly from a given density. This is of practical as well as formal interest.[14,21]

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[1] R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, Oxford, 1989).

[2] R. M. Dreizler and E. K. U. Gross, *Density Functional Theory* (Springer, Berlin, 1990).

[3] R. O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989).

[4] Adv. Quantum Chem. **21** (1990) [special issue on *Density Functional Theory of Many-Fermion Systems*, edited by S. B. Trickey].

[5] A. Görling and M. Levy, Phys. Rev. A **50**, 196 (1994).

[6] A. Görling and M. Levy, Int. J. Quantum Chem. **S29**, 93 (1995).

[7] F. Gygi and A. Baldereschi, Phys. Rev. B **34**, 4405 (1986).

[8] P. Fulde, *Electron Correlation in Molecules and Solids* (Springer, Berlin, 1991).

[9] R. T. Sharp and G. K. Horton, Phys. Rev. **90**, 317 (1953).

[10] J. D. Talman and W. F. Shadwick, Phys. Rev. A **14**, 36 (1976).

[11] (a) J. B. Krieger, Y. Li, and G. J. Iafrate, Phys. Rev. A **45**, 101 (1992); (b) Y. Li, J. B. Krieger, and G. J. Iafrate, in *Density Functional Theory,* Vol. 337 of *NATO Advanced Study Institute, Series B: Physics*, edited by E. K. U. Gross and R. M. Dreizler (Plenum, New York, 1995).

[12] D. M. Bylander and L. Kleinman, Phys. Rev. Lett. **74**, 3660 (1995).

[13] A. Görling, M. Städele, and P. Vogl (unpublished).

[14] A. Görling and M. Ernzerhof, Phys. Rev. A **51**, 4501 (1995).

[15] J. R. Chelikowsky and M. L. Cohen, in *Basic Properties of Semiconductors*, edited by P. T. Landsberg, Handbook of Semiconductors Vol. 1 (North-Holland, Amsterdam, 1992), and references therein.

[16] M. S. Hybertsen and S. G. Louie, Phys. Rev. B **35**, 5585 (1987).

[17] See, for example, R. A. Evarestov and V. P. Smirnov, Phys. Status Solidi **119**, 9 (1983).

[18] Y. Lin, J. B. Krieger, and G. J. Iafrate, Phys. Rev. A **47**, 165 (1993); E. Engel and S. H. Vosko, *ibid.* **47**, 2800 (1993).

[19] D. M. Bylander and L. Kleinman, Phys. Rev. B **41**, 7868 (1990).

[20] A. Seidl, A. Görling, P. Vogl, J. A. Majewski, and M. Levy, Phys. Rev. B **53**, 3764 (1996).

[21] A. Görling, Phys. Rev. A **46**, 3753 (1992).