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Density-functional theory for excited states

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A Kohn-Sham formalism for the treatment of excited states within the density-functional theory (DFT) is presented. DFT exchange and correlation energy functionals for excited states are defined. Explicit expressions for these functionals are derived by generalizing a recent DFT perturbation theory. A computational scheme for the treatment of excited states within the DFT is suggested. Differences of Kohn-Sham eigenvalues are shown to be well-defined approximations for excitation energies. Correction terms to these approximations are presented. Perturbation theory expansions for band gaps are discussed. [S1050-2947(96)06511-0]

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I. INTRODUCTION

Density-functional theory (DFT) usually, somewhat incorrectly, is labeled as a ground-state theory and with few exceptions [1–5] is employed exclusively for the treatment of electronic ground states and their properties. However, the Hohenberg-Kohn theorem [6], the basis of DFT, states that the ground-state density of an electronic system determines in addition to its electron number also its external potential and, therefore, its Hamiltonian operator. Because the Hamiltonian operator completely characterizes all states of the system, the excited states as well as the ground state are determined by the ground-state density. Nevertheless, the attitude of considering DFT as a ground-state theory has been justified because, so far, there exists no formalism, like the Kohn-Sham (KS) formalism for ground states [7], that exploits the formal dependence of excited states on the ground-state density and leads to a feasible procedure to treat excited states within DFT.

In this work, a KS formalism for the treatment of excited states within a DFT framework is introduced. DFT exchange and correlation energies for excited states are properly defined within the introduced formalism. The KS formalism for excited states is then combined with a recently presented DFT perturbation theory [8]. This combination results in a computational procedure to treat excited states within DFT that, in principle, is exact. The density functionals for the exchange and correlation energies of excited states are obtained as expressions of KS orbitals, KS eigenvalue differences, and certain parts of the exchange-correlation potential.

KS orbital eigenvalues, so far, are believed to have no physical meaning, except for the eigenvalue of the highest occupied KS orbital, which is the negative of the ionization energy. Here, differences of KS eigenvalues are identified as excitation energies and energy differences between excited states in zeroth order with respect to the electron-electron interaction. The corresponding higher-order correction terms are derived. Perturbation theory expansions for excitation energies are related to band gaps of solids.

Electronic systems of all types shall be considered here, atoms and molecules as well as crystalline solids. Their wave functions may exhibit an exponential decay far from the system or may have periodic boundary conditions but they must be finite in order to obtain normalizable wave function. The modeling of crystalline solids by a large but finite number of unit cells leads to the usual way of investigating them by explicitly treating one unit cell and by taking the repetition of the cell into account by a summation in **k** space. For the treatment of unbound states of atoms or molecules the system is placed in a large but finite box in order to obtained normalizable wave function. For simplicity only systems with a nondegenerate ground state are considered. However, the formalism derived here can easily be generalized to degenerate systems [9] within the framework of the symmetrized DFT presented in Ref. [10].

II. KS FORMALISM FOR EXCITED STATES

Electronic systems are characterized by their electron number N and by an external potential $v(\mathbf{r})$ determining their Hamiltonian operator $\hat{T}+\hat{V}_{ee}+\hat{v}$ that consists of the operators of the kinetic energy $\hat{T}$ and of the electron-electron repulsion $\hat{V}_{ee}$ besides the operator $\hat{v}$ corresponding to the external potential $v(\mathbf{r})$. The standard KS formalism for ground states is based on the noninteracting, N-electron Schrödinger equation

$$[\hat{T}+\hat{v}_s]\Phi_0=E_0^{\mathrm{KS}}\Phi_0, \tag{1}$$

the KS equation, with $\hat{v}_s$ being the N-electron operator corresponding to a local multiplicative potential $v_s(\mathbf{r})$ that as a consequence of the Hohenberg-Kohn theorem [6] is determined, up to an additive constant, by the requirement that the ground state of the KS Hamiltonian operator $\hat{T}+\hat{v}_s$, the KS wave function Φ_0, yields the same electron density $\rho_0(\mathbf{r})$ as the ground state of the corresponding interacting real system. For the nondegenerate systems considered here Φ_0 is a single Slater determinant consisting of N spin orbitals φ_i. The potential $v_s(\mathbf{r})$ is given as the sum

$$v_s(\mathbf{r})=v(\mathbf{r})+u([\rho_0];\mathbf{r})+v_x([\rho_0];\mathbf{r})+v_c([\rho_0];\mathbf{r}) \tag{2}$$

of the external potential $v(\mathbf{r})$ and the Coulomb potential $u([\rho_0];\mathbf{r})$, the exchange potential $v_x([\rho_0];\mathbf{r})$, and the correlation potential $v_c([\rho_0];\mathbf{r})$, which are functionals of the ground-state density $\rho_0(\mathbf{r})$. After Eqs. (1) and (2) have been solved self-consistently the ground-state energy E_0^1 (the meaning of the superscript 1 is explained below) of the interacting system is obtained as

$$E_0^1=\langle\Phi_0|\hat{T}|\Phi_0\rangle+U[\rho_0]+E_x[\rho_0]+E_c[\rho_0]+\int d\mathbf{r}\;\rho_0(\mathbf{r})v(\mathbf{r}) \tag{3}$$

with $U[\rho_0]$, $E_x[\rho_0]$, and $E_c[\rho_0]$ being the Coulomb, the exchange, and the correlation energy, respectively.

Note that it is not necessary to know the exchange and correlation potentials and energies as explicit functionals of the density to carry out the standard Kohn-Sham procedure. It is sufficient to know the exchange and correlation potentials and energies as functionals $v_x([\{\varphi_i,\varepsilon_i-\varepsilon_{i'}\}];\mathbf{r})$, $v_c([\{\varphi_i,\varepsilon_i-\varepsilon_{i'}\}];\mathbf{r})$, $E_x[\{\varphi_i,\varepsilon_i-\varepsilon_{i'}\}]$, and $E_c[\{\varphi_i,\varepsilon_i-\varepsilon_{i'}\}]$ of the KS orbitals φ_i and differences $\varepsilon_i-\varepsilon_{i'}$ of their eigenvalues ε_i. Because the KS orbitals and their eigenvalue differences are functionals of the ground-state density $\rho_0(\mathbf{r})$ any functional of them also is a functional of $\rho_0(\mathbf{r})$. The explicit expressions for the density functionals for the exchange and correlation energies of excited states derived later on depend on KS orbitals and their eigenvalue differences.

The adiabatic connection or coupling constant path [11] characterized by the Schrödinger equation

$$[\hat{T}+\alpha\hat{V}_{ee}+\hat{v}^{\alpha}]\Psi_n^{\alpha}=E_n^{\alpha}\Psi_n^{\alpha} \tag{4}$$

represents a continuous connection between a noninteracting model system, the KS system, and the real physical system. In this work not only the ground state Ψ_0^{α} but also the nth eigenstate Ψ_n^{α} of the coupling constant Hamiltonian operator $\hat{T}+\alpha\hat{V}_{ee}+\hat{v}^{\alpha}$ is considered. The coupling constant α, or to be precise, its square root, can be interpreted as a factor scaling the elementary charge of the electron. The potential $v^{\alpha}(\mathbf{r})$ leading to the N-electron operator $\hat{v}^{\alpha}$ in Eq. (4) through the Hohenberg-Kohn theorem [6] is defined by the requirement that the ground state Ψ_0^{α} yields the density $\rho_0(\mathbf{r})$ independently of the value of the coupling constant α and therefore is a functional $v^{\alpha}([\rho_0];\mathbf{r})$ of $\rho_0(\mathbf{r})$. This defines $v^{\alpha}([\rho_0];\mathbf{r})$ only up to an α-dependent additive constant for $\alpha\neq 1$. For $\alpha=1$, the additional requirement that $v^{\alpha}([\rho_0];\mathbf{r})$ equals the external potential $v(\mathbf{r})$, i.e., $v^1([\rho_0];\mathbf{r})=v(\mathbf{r})$, leaves no freedom for an additive constant. For $\alpha=1$ Eq. (4) turns into the Schrödinger equation of the real physical system whereas for $\alpha=0$ the corresponding KS equation results, $v_s(\mathbf{r})=v^0([\rho_0];\mathbf{r})$. Therefore the eigenstates of the KS Hamiltonian operator $\hat{T}+\hat{v}_s$, the KS states Φ_n, and their energies E_n^{KS} alternatively may be denoted as Ψ_n^0 and E_n^0, i.e., $\Psi_n^0=\Phi_n$ and $E_n^0=E_n^{\mathrm{KS}}$.

Now the additional assumption is made that the energetic order of eigenstates Ψ_n^{α} of the same symmetry is preserved along the adiabatic connection, i.e., when going from the noninteracting system $\alpha=0$ to the interacting system $\alpha=1$. Under this assumption, *the coupling constant path defined by the Hamiltonian operator* $\hat{T}+\alpha\hat{V}_{ee}+\hat{v}^{\alpha}$ *establishes a continuous connection between the nth eigenstates of the KS Hamiltonian operator and of the interacting physical Hamiltonian operator*. This finding, as simple as it is, is the basis of the KS formalism for excited states introduced here.

In order to define DFT exchange and correlation energies for excited states the nth eigenvalue $E_n^{\alpha}=\langle\Psi_n^{\alpha}[\rho_0]|\hat{T}+\alpha\hat{V}_{ee}+\hat{v}^{\alpha}[\rho_0]|\Psi_n^{\alpha}[\rho_0]\rangle$ of the coupling constant Hamiltonian, Eq. (4), is decomposed. The noninteracting kinetic energy $T_{s,n}[\rho_0]$, the DFT exchange energy $E_{x,n}[\rho_0]$, and the DFT correlation energy $E_{c,n}^{\alpha}[\rho_0]$ for the nth eigenstate Ψ_n^{α} are defined as

$$T_{s,n}[\rho_0]=\langle\Phi_n[\rho_0]|\hat{T}|\Phi_n[\rho_0]\rangle, \tag{5}$$

$$E_{x,n}[\rho_0]=\langle\Phi_n[\rho_0]|\hat{V}_{ee}|\Phi_n[\rho_0]\rangle-U_n[\rho_0], \tag{6}$$

$$E_{c,n}^{\alpha}[\rho_0]=\langle\Psi_n^{\alpha}[\rho_0]|\hat{T}+\alpha\hat{V}_{ee}+\hat{v}^{\alpha}|\Psi_n^{\alpha}[\rho_0]\rangle-\langle\Phi_n[\rho_0]|\hat{T}+\alpha\hat{V}_{ee}+\hat{v}^{\alpha}|\Phi_n[\rho_0]\rangle. \tag{7}$$

Here $U_n[\rho_0]$ is the classical Coulomb interaction of the electron density $\rho_n^0(\mathbf{r})$ of the nth KS state $\Phi_n=\Psi_n^0$. For $n\neq 0$ the correlation energy contains Coulomb and potential energy contributions as a consequence of the fact that the electron density $\rho_n^{\alpha}(\mathbf{r})$ of the states Ψ_n^{α} for $n\neq 0$ varies with α in contrast to the ground-state density $\rho_0^{\alpha}(\mathbf{r})=\rho_0(\mathbf{r})$. Of course, for $n=0$ the standard ground-state functionals result. Because the potential $v^{\alpha}([\rho_0];\mathbf{r})$ that determines the eigenstates Ψ_n^{α} for a given α is a functional of the ground-state density $\rho_0(\mathbf{r})$, the eigenstates $\Psi_n^{\alpha}[\rho_0]$, their electron density $\rho_n^{\alpha}([\rho_0];\mathbf{r})$, and therefore also $T_{s,n}[\rho_0]$, $U_n[\rho_0]$, $E_{x,n}[\rho_0]$, and $E_{c,n}^{\alpha}[\rho_0]$ *are functionals of the ground-state electron density* $\rho_0(\mathbf{r})$. The sum of the functionals $T_{s,n}[\rho_0]$, $U_n[\rho_0]$, $E_{x,n}[\rho_0]$, and $E_{c,n}^{\alpha}[\rho_0]$ can be identified as a generalization $F_n^{\alpha}[\rho_0]$ of the well-known Hohenberg-Kohn functional for excited states and for varying coupling strength α. With these definitions the energy E_n^{α} reads

$$E_n^{\alpha}=\langle\Phi_n[\rho_0]|\hat{T}|\Phi_n[\rho_0]\rangle+U_n[\rho_0]+E_{x,n}[\rho_0]+E_{c,n}^{\alpha}[\rho_0]+\int d\mathbf{r}\;\rho_n^0(\mathbf{r})v^{\alpha}(\mathbf{r}). \tag{8}$$

As in the ground-state formalism, the correlation energy $E_{c,n}^{\alpha}[\rho_0]$ contains all parts of the energy E_n^{α} that cannot be obtained from the corresponding KS wave function $\Phi_n=\Psi_n^0$. The energy E_n^{α} depends on the choice of the additive constant to the potential $v^{\alpha}(\mathbf{r})$ for all values of α except for $\alpha=1$ where $v^{\alpha}(\mathbf{r})$ is completely determined by the requirement $v^1(\mathbf{r})=v(\mathbf{r})$. However, the functionals $T_{s,n}[\rho_0]$, $U_n[\rho_0]$, $E_{x,n}[\rho_0]$, and $E_{c,n}^{\alpha}[\rho_0]$ are *independent* of the choice of the additive constant. For $T_{s,n}[\rho_0]$, $U_n[\rho_0]$, and $E_{x,n}[\rho_0]$ this follows from the fact that they are determined exclusively by the KS wave function Φ_n that is not affected by an addition of a constant to $v^{\alpha}(\mathbf{r})$. Because the contributions in the expectation values of Eq. (7) resulting from a constant added to $v^{\alpha}(\mathbf{r})$ cancel each other and because Ψ_n^{α}, like Φ_n, is not affected by such an additive constant the correlation energy $E_{c,n}^{\alpha}[\rho_0]$ is also independent of an additional constant.

In order to treat excited states of an electronic system within a KS formalism, first, a standard KS procedure has to be carried out to obtain the ground-state density $\rho_0(\mathbf{r})$ and the KS wave functions $\Phi_n[\rho_0]$. The KS wave functions $\Phi_n[\rho_0]$ then yield the energies $T_{s,n}[\rho_0]$, $U_n[\rho_0]$, $E_{x,n}[\rho_0]$, and $\int d\mathbf{r}\,\rho_n^0(\mathbf{r})v^{\alpha}(\mathbf{r})$ by employing Eqs. (5) and (6). The correlation energies of the excited states can be obtained by evaluating the density functionals $E_{c,n}^1[\rho_0]$. Addition of all energy terms results in the energies E_n^1 of the excited states. As in the ground state formalism, the exchange energy may alternatively be determined by evaluating the density functionals $E_{x,n}[\rho_0]$. This concludes the introduction of the basic KS formalism for excited states.

III. DFT PERTURBATION THEORY FOR EXCITED STATES

After having derived the basic KS formalism for excited states the problem of determining the density functionals $E_{x,n}[\rho_0]$ and $E^1_{c,n}[\rho_0]$ remains. In order to address this problem and to get further insight into the formalism a recently introduced DFT perturbation theory is employed [8]. The DFT perturbation theory is based on the Taylor series of $v^\alpha([\rho_0];\mathbf{r})$, $v^\alpha([\rho_0];\mathbf{r})=\Sigma_{k=0}^{\infty}\alpha^k\,{}^kv([\rho_0];\mathbf{r})$, and E^α_0 with respect to α. In this work the excited-state energies E^α_n are also developed in Taylor series: $E^\alpha_n=\Sigma_{k=0}^{\infty}\alpha^k\,{}^kE_n$. The zeroth-order term ${}^0v([\rho_0];\mathbf{r})$ equals the KS potential $v_s(\mathbf{r})$, i.e., ${}^0v([\rho_0];\mathbf{r})=v_s(\mathbf{r})=v^{\alpha=0}([\rho_0];\mathbf{r})$. The higher-order terms are related to Coulomb, exchange, and correlation potentials. Because $v^\alpha([\rho_0];\mathbf{r})$ is defined only up to an α-dependent constant, each of the potentials ${}^kv([\rho_0];\mathbf{r})$ contains an undefined constant. The choice of this constant is only restricted by the additional requirement that the sum of all ${}^kv([\rho_0];\mathbf{r})$ yields $v(\mathbf{r})=v^{\alpha=1}([\rho_0];\mathbf{r})$. If the zeroth-order potential, i.e., the KS potential, is determined through Eq. (2) then this constraint is always obeyed.

In Ref. [8] it was shown that the requirement that the ground-state density $\rho_0(\mathbf{r})$ is invariant along the coupling constant path allows one to calculate up to an additive constant the potentials ${}^kv(\mathbf{r})$ for $k\geqslant 1$ as functionals ${}^kv([\{\varphi_i\},\{\varepsilon_i-\varepsilon_{i'}\},{}^1v(\mathbf{r}),\ldots,{}^{k-1}v(\mathbf{r})];\mathbf{r})$ of the KS orbitals, KS eigenvalue differences, and the lower-order potentials ${}^lv(\mathbf{r})$ excluding the KS potential ${}^0v(\mathbf{r})$, i.e., $1\leqslant l\leqslant k-1$. This means for any given KS potential, i.e., for any local multiplicative potential, all the potentials ${}^kv(\mathbf{r})$ and therefore the full exchange-correlation potential can be calculated exactly by order to order recursion. This allows one, in principle, to perform an exact KS procedure by self-consistently solving Eqs. (1) and (2) using exchange-correlation potentials obtained from the ${}^kv(\mathbf{r})$ [8]. Of course, in practice only potentials ${}^kv(\mathbf{r})$ up to a limited order k can be treated.

The terms ${}^kE_n$ of the Taylor series for ground as well as excited-state energies E^α_n are now obtained using perturbation theory once more:

$$
{}^kE_n={}^kF_n[\{\varphi_i\},\{\varepsilon_i-\varepsilon_{i'}\},{}^1v(\mathbf{r}),\ldots,{}^{k-1}v(\mathbf{r})] + \int d\mathbf{r}\;\rho^0_n(\mathbf{r})\;{}^kv(\mathbf{r}). \tag{9}
$$

The contributions ${}^kF_n[\{\varphi_i\},\{\varepsilon_i-\varepsilon_{i'}\},{}^1v(\mathbf{r}),\ldots,{}^{k-1}v(\mathbf{r})]$, like the potentials ${}^kv(\mathbf{r})$, consist of KS orbitals, KS eigenvalue differences, and the lower-order potentials ${}^lv(\mathbf{r})$ with $1\leqslant l\leqslant k-1$ and are independent with respect to the addition of constants to the potentials ${}^kv(\mathbf{r})$. This follows from the change of the energy E^α_n as well as of the term $\alpha^k\int d\mathbf{r}\,\rho^0_n(\mathbf{r}){}^kv(\mathbf{r})$ by α^kNc_k upon addition of the constant c_k to ${}^kv(\mathbf{r})$. For $\alpha=1$, the physically relevant value of α, the terms $\int d\mathbf{r}\,\rho^0_n(\mathbf{r}){}^kv(\mathbf{r})$ can be added up to give $\int d\mathbf{r}\,\rho^0_n(\mathbf{r})v(\mathbf{r})$ because $\Sigma_{k=0}^{\infty}\,{}^kv([\rho_0];\mathbf{r})=v(\mathbf{r})$ if the KS potential $v_s(\mathbf{r})={}^0v(\mathbf{r})$ is determined in a self-consistent procedure according to Eq. (2). The energy E^1_n then is given by

$$
E^1_n=\sum_{k=1}^{\infty}{}^kF_n[\{\varphi_i\},\{\varepsilon_i-\varepsilon_{i'}\},{}^1v(\mathbf{r}),\ldots,{}^{k-1}v(\mathbf{r})] + \int d\mathbf{r}\;\rho^0_n(\mathbf{r})v(\mathbf{r}). \tag{10}
$$

This allows one to treat, at least in principle, excited states exactly within DFT, by first performing an exact KS procedure to determine the densities $\rho^0_n(\mathbf{r})$, the potentials ${}^kv(\mathbf{r})$, and the KS orbitals φ_i and eigenvalues ε_i. Subsequently Eq. (10) is used to determine the energies E_n. If other properties besides the energy shall be investigated then also the wave functions Ψ^1_n can be obtained through perturbation theory in form of their Taylor series.

The zeroth-order term ${}^0F_n[\rho_0]$ equals $T_{s,n}[\rho_0]$, i.e., ${}^0F_n[\rho_0]=\langle\Phi_n[\rho_0]|\hat{T}|\Phi_n[\rho_0]\rangle$, the first-order term ${}^1F_n[\rho_0]$ equals $E_{x,n}[\rho_0]$ plus $U_n[\rho_0]$, i.e., ${}^1F_n[\rho_0]=\langle\Phi_n[\rho_0]|\hat{V}_{ee}|\Phi_n[\rho_0]\rangle$, and the higher-order terms sum up to $E^1_{c,n}[\rho_0]$. The second-order term ${}^2F_n[\rho_0]$ is given by

$$
{}^2F_n[\rho_0]=\sum_{j\neq n}\frac{\langle\Phi_n[\rho_0]|\hat{V}_{ee}-\hat{u}[\rho_0]-\hat{v}_x[\rho_0]|\Phi_j[\rho_0]\rangle\langle\Phi_j[\rho_0]|\hat{V}_{ee}-\hat{u}[\rho_0]-\hat{v}_x[\rho_0]|\Phi_n[\rho_0]\rangle}{E^{\mathrm{KS}}_n-E^{\mathrm{KS}}_j}. \tag{11}
$$

Perturbation theory yields the functionals ${}^kF_n[\rho_0]$ in terms of ground state and excited KS wave functions Φ_n and KS energies E^{KS}_n. However, these consist of KS orbitals and eigenvalues and therefore the functionals ${}^kF_n[\rho_0]$ also can be expressed in terms of the latter.

As an example the zero- and first-order energies for an excited state corresponding to a singly excited KS state are considered. The KS ground state of a nondegenerate system is a single Slater determinant with $N/2$ doubly occupied spatial orbitals ϕ_i. Promotion of one electron from an occupied orbital ϕ_i into an unoccupied orbital ϕ_ν gives rise to four excited KS determinants that have the same KS energies E^{KS}_n but are distinguished by the spin components of the involved orbitals ϕ_i and ϕ_ν. The four excited KS determinants can be combined to a singlet and threefold degenerate triplet state in the usual way. The zeroth-order contributions ${}^0\Delta E(S,i\rightarrow\nu)$ and ${}^0\Delta E(T,i\rightarrow\nu)$ of the excitation energies between the ground state of the interacting physical system and the excited states that are adiabatically connected to the two KS states obtained by promoting an electron from ϕ_i into ϕ_ν equal the KS eigenvalue difference $\varepsilon_\nu-\varepsilon_i$,

$$
{}^0\Delta E(S,i\rightarrow\nu)={}^0\Delta E(T,i\rightarrow\nu)=\varepsilon_\nu-\varepsilon_i. \tag{12}
$$

The first-order terms are given by

$$^1\Delta E(T,i\rightarrow\nu)=\langle\phi_\nu|\hat{v}_x^{\mathrm{NL}}-\hat{v}_x[n_0]|\phi_\nu\rangle -\langle\phi_i|\hat{v}_x^{\mathrm{NL}}-\hat{v}_x[n_0]|\phi_i\rangle-\langle\nu i|\nu i\rangle, \tag{13a}$$

$$^1\Delta E(S,i\rightarrow\nu)=\langle\phi_\nu|\hat{v}_x^{\mathrm{NL}}-\hat{v}_x[n_0]|\phi_\nu\rangle -\langle\phi_i|\hat{v}_x^{\mathrm{NL}}-\hat{v}_x[n_0]|\phi_i\rangle -\langle\nu i|\nu i\rangle+2\langle\nu i|i\nu\rangle \tag{13b}$$

with $\langle ij|st\rangle=\int d\mathbf{r}\,d\mathbf{r}'\ \phi_i^*(\mathbf{r})\ \phi_j^*(\mathbf{r}')\ \phi_s(\mathbf{r})\ \phi_t(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$ and with $\hat{v}_x^{\mathrm{NL}}$ being a nonlocal exchange operator of the form of the Hartree-Fock exchange operator, however, constructed from the $N/2$ occupied KS orbitals. Equation (12) demonstrates that KS *orbital eigenvalues are not just auxiliary quantities without physical meaning; their difference is a well-defined approximation to excitation energies* of zeroth order in the electron-electron interaction [12]. The first-order correction terms (13a) and (13b) *take the symmetry of the final states into account*. It is a general advantage of the orbital-dependent energy functionals defined here that they incorporate symmetry in a natural straightforward manner. The approximate energy functionals currently employed in standard KS calculations that explicitly depend on the electron density do not directly account for the symmetry. As a result, singlet triplet splittings can be estimated only indirectly from the energies of a triplet KS determinant and a KS determinant that is a mixture of a singlet and a triplet state [13]. Other KS orbital differences, like $\varepsilon_\nu+\varepsilon_\mu-\varepsilon_i-\varepsilon_j$ or $\varepsilon_\nu-\varepsilon_i-\varepsilon_\mu+\varepsilon_j$, also can be identified with zero-order approximations of excitation energies or energy differences between excited states of the physical interacting system (i,j and ν,μ denote KS orbitals being occupied and unoccupied, respectively).

In crystalline solids the lowest excitation energy is equal to the band gap. For the energetically lowest excitation characterized by $i=N/2$ and $\nu=N/2+1$ the perturbation theory expansion for the excitation energy therefore constitutes an expansion of the band gap. This expansion for $i=N/2$ and $\nu=N/2+1$ indeed is identical to a perturbation expansion for the band gap that was derived recently [14] by other means except for terms that vanish for systems with periodic boundary conditions in the limit of an infinite number of unit cells [in Eqs. (13a) and (13b) the terms $\langle\nu i|\nu i\rangle$ and $\langle\nu i|i\nu\rangle$ vanish in this limit]. The derivation of perturbation expansions for band gaps via excitation energies given in this work has the advantage that it is not restricted to the fundamental band gap.

In conclusion, the formalism introduced here opens the way to treat excited states within DFT both on a formal level and in practical calculations. The exact KS orbital- and eigenvalue-dependent functionals introduced here not only can be directly used in practical procedures but also may serve as a starting point to derive new approximate energy functionals for ground as well as excited states that also may account for symmetry.

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