

Exchange-correlation potentials with proper discontinuities for physically meaningful Kohn-Sham eigenvalues and band structures

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It is shown how to properly construct exchange-correlation (xc) potentials in the Kohn-Sham (KS) formalism of density-functional theory such that physically meaningful KS eigenvalues result. A potential adjustor Δ_{Hxc}^{N-} is derived which enables for any approximate functional for the xc energy the construction of a consistent xc potential leading to an eigenvalue of the energetically highest occupied KS orbital equal to the negative of the ionization potential. Together with a second potential adjustor Δ_{Hxc}^{N+} KS band structures can be converted in approximate quasiparticle band structures exhibiting the exact physical instead of the KS band gap. This represents an alternative route to the fundamental quasiparticle band gap, completely within the KS formalism without the need to resort to many-body perturbation theory approaches like the *GW* method. It is shown that, for any finite system, approximate xc potentials including those in the local density and generalized gradient approximations, in contrast to common belief, always exhibit consistent nonzero discontinuities at integer electron numbers, if constructed properly. Thus the discontinuity of xc potentials is identified as a derived quantity which emerges automatically by properly constructing xc potentials without the need to be specifically incorporated in approximate xc functionals. It is demonstrated that all relevant objects of the ensemble KS formalism, in particular functional derivatives and their discontinuities, can be expressed in terms of quantities readily available in the KS formalism of integer electron numbers within an approach named integer electron ensemble approach (IEEA). Attempts to specifically construct ensemble density functionals are shown to be needless. Taking the known asymptotic behavior of the electron density into account an internal consistency condition for xc potentials is presented which justifies tuning procedures of xc functionals and, furthermore, indicates how asymptotic corrections for xc potentials have to be properly employed.

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I. INTRODUCTION

The discontinuity [1–4] of the exchange-correlation (xc) potential, the functional derivative of the xc energy with respect to the electron density, at integer electron numbers is a key quantity in the Kohn-Sham (KS) formalism of density-functional theory (DFT) [5,6]. Discontinuities in the derivatives of components of the electronic energy are responsible for the fact that the Kohn-Sham band gap is not equal to the physical (quasiparticle) band gap, the difference between ionization potential and electron affinity. The band gap determines the electronic nature of periodic systems, e.g., metallic versus semiconducting behavior, but also of atoms and molecules. (In finite systems often the term hardness, being half the band gap, is used.) Because KS and quasiparticle band gaps are different, the latter are presently not accessible in KS methods and have to be calculated via many-body perturbation theory, in particular by *GW* methods [7–9]. *GW* methods are computationally expensive and typically carried out non-self-consistently based on KS band structures which is unsatisfying from a formal point of view. In this work the formal basis for a determination of the physical band gap, exclusively within the KS formalism, is presented which opens up an alternative route to the fundamental quasiparticle band gap and represents a long-standing goal in DFT.

The commonly employed approximate xc functionals are believed to lack derivative discontinuities [1–6,10,11]. Here

xc functionals within the generalized gradient approximation (GGA) [5,6] are considered as typical examples of standard density functionals. However, the results of this work are relevant for all approximate xc functionals and, furthermore, can be generalized [12] to the case of functionals occurring in generalized Kohn-Sham methods [13]. For an electronic system with integer electron number N the eigenvalue ε_N of the energetically highest occupied KS orbital equals the negative of the ionization potential IP_N provided the employed xc potential represents the correct limit of the corresponding ensemble xc potential from the electron deficiency side [1,14–18]. Standard GGA calculations yield eigenvalues ε_N which are not even close to the negative of the ionization potential.

In this work, a potential adjustor Δ_{Hxc}^{N-} is derived that gives access to the sum of the Hartree plus the xc (abbreviated as Hxc from now on) potential as it emerges in the ensemble KS formalism [5,6,19] using exclusively quantities readily available in the KS formalism of integer electron numbers. For any approximate functional of the xc energy the potential adjustor Δ_{Hxc}^{N-} leads to a corresponding Hxc potential with a proper absolute energy adjustment such that $\varepsilon_N = -IP_N$, in finite as well as periodic systems. Moreover, Hxc potentials obtained along these lines exhibit the proper consistent discontinuity at integer electron numbers. This demonstrates that the common wisdom [5,6,10,11] that standard xc functionals, e.g., within the GGA, suffer from the lack of derivative discontinuities is not true. *If GGA potentials as well as other approximate potentials are constructed properly then they do exhibit nonzero discontinuities, at least for finite electron systems.* Thus, the

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naive, straightforward use of GGA or other functionals as ensemble density functionals is identified as an approximation that leads to the lack of derivative discontinuities but not the GGA or other approximations themselves.

The energies of an electronic system at noninteger electron numbers form straight lines resulting from interpolating the energies of the system at the adjacent integer numbers [1]. Deviations from such straight lines in GGA calculations, termed localization and delocalization errors [10,11], again are manifestations of the fact that GGA functionals are not suitable approximations for ensemble functionals. However, it is shown here that the relevant objects occurring in the ensemble KS formalism can be expressed in terms of quantities readily available in the KS formalism of integer electron numbers and therefore there is no need for approximate ensemble xc functionals. Thus it is neither necessary to derive GGA ensemble functionals nor other specific ensemble density functionals. The approach towards the ensemble KS formalism which is advocated here and relies exclusively on density functionals for integer electron numbers represents an integer electron ensemble approach (IEEA) and shall be denoted by this name.

The potential adjustor Δ_{Hxc}^{N-} and an analogous potential adjustor Δ_{Hxc}^{N+} for the electron surplus side which emerge in the IEEA enable the conversion of KS band structures into approximate quasiparticle band structures exhibiting the physical instead of the KS band gap. As a result the fundamental physical band gap can be obtained entirely within the KS formalism and it is no longer necessary to resort to GW methods [7–9].

The paper is organized as follows. In the next section the IEEA is introduced and it is shown how derivatives of energy functionals of the ensemble density-functional theory can be taken properly. Then a section follows which presents potential adjustors for arbitrary xc potentials including GGA ones to correctly fix the energetic position and to introduce discontinuities at integer electron numbers. Moreover, implications for strategies to develop new approximate xc functionals are discussed. This is followed by a section discussing implications for finite electron systems. In particular an internal consistency check for xc potentials is introduced and it is explained how asymptotic corrections for xc potentials should be applied. In the subsequent section the limit of infinite systems is analyzed. First, it is pointed out that, in contrast to common wisdom, a calculation of changes of total energies due to changes of particle numbers can be easily carried out for infinite systems. Then it is shown that for GGA functionals the previously introduced potential adjustors vanish in the limit of infinite systems and that GGA xc potentials do not exhibit discontinuities in this limit despite the fact that the energy correctly changes linearly with the particle number and therefore localization or delocalization errors do not occur. Orbital-dependent xc functionals, on the other hand, are shown to lead to xc potentials with discontinuities at integer electron numbers in the limit of infinite systems and to be well suited to determine fundamental quasiparticle band gaps within the IEEA and thus completely within DFT without invoking approaches from many-body perturbation theory like the GW method. Finally, in the last section, conclusions are given.

II. INTEGER ELECTRON ENSEMBLE APPROACH: DERIVATIVES OF ENERGY FUNCTIONALS

For a start, an important point to remember is that functional derivatives with respect to the electron density are defined only up to an additive constant in the KS formalism of integer electron numbers. This is because changes $\delta\rho(\mathbf{r})$ of the electron density ρ have to integrate to zero, i.e., $\int d\mathbf{r} \delta\rho(\mathbf{r}) = 0$, in order to not change the electron number to a noninteger value. The change δF of a functional $F[\rho]$ is given in terms of the functional derivative $f(\mathbf{r})$ of F and $\delta\rho(\mathbf{r})$ by $\delta F = \int d\mathbf{r} f(\mathbf{r})\delta\rho(\mathbf{r})$ but also by $\delta F = \int d\mathbf{r}[f(\mathbf{r}) + \nu]\delta\rho(\mathbf{r})$ with $\nu \in \mathcal{R}$ because $\int d\mathbf{r} \nu \delta\rho(\mathbf{r}) = 0$. This means in the KS formalism of integer electron numbers functional derivatives with respect to the electron density are always given by a set of functions whose members differ by the addition of a constant. Such a set of functions as well as an arbitrary member of such a set shall be denoted by a bar above the corresponding symbol, e.g., the set of functions $f(\mathbf{r}) + \nu$ is denoted by \bar{f} . The xc potential in the integer electron number KS formalism is given by the set of functions \bar{v}_{xc} and is undefined with respect to the addition of a constant. On the other hand, the commonly employed GGA xc potentials [5,6] are completely defined without the freedom of an additive constant. This is because the GGA expressions for the xc energy can be evaluated not only for electron densities yielding integer electron numbers but for arbitrary ones. A GGA xc potential obtained as naive, straightforward functional derivative of the GGA energy functional represents only one member of the set \bar{v}_{xc}^{GGA} of potentials. However, this member, in general, is not the one that equals the corresponding ensemble xc potential approaching the limit of the integer electron number of the considered electronic system from the electron deficiency side. Therefore, $\varepsilon_N \neq -IP_N$ in common GGA methods.

Within the ensemble KS formalism the Hohenberg-Kohn functional $F[\rho]$ is given by the constrained search $F[\rho] = \min_{\Gamma \rightarrow \rho} \{\text{Tr}[\Gamma(\hat{T} + \hat{V}_{ee})]\}$ searching among those density matrices $\Gamma = \sum_p c_p |\Psi_p\rangle\langle\Psi_p|$ with $\sum_p c_p = 1$ that yield the electron density $\rho(\mathbf{r})$ the one that minimizes the sum of the kinetic and the electron-electron interaction energy. By \hat{T} the kinetic energy operator is denoted and by \hat{V}_{ee} the operator of the electron-electron interaction. In the ensemble KS formalism the electron density ρ can integrate to noninteger electron numbers and the functional derivative $\delta F/\delta\rho(\mathbf{r})$ is completely defined without the freedom of adding a constant. The ground-state density matrix $\Gamma_0[\bar{v}, q]$ of an electronic system with the external potential v and an electron number q with $N-1 \leq q \leq N$ is given by $\Gamma_0[\bar{v}, q] = (N-q)|\Psi_0^{N-1}[\bar{v}]\rangle\langle\Psi_0^{N-1}[\bar{v}]| + (q-N+1)|\Psi_0^N[\bar{v}]\rangle\langle\Psi_0^N[\bar{v}]|$ with $\Psi_0^{N-1}[\bar{v}]$ and $\Psi_0^N[\bar{v}]$ being the ground-state wave functions of the corresponding electronic systems with $N-1$ and N electrons; see below for details. Changing the external potential v to $v + \nu$ by adding a constant ν does not change the eigenstates $\Psi_0^{N-1}[\bar{v}]$ and $\Psi_0^N[\bar{v}]$ or the density matrix $\Gamma_0[\bar{v}, q]$. Therefore $\Psi_0^{N-1}[\bar{v}]$, $\Psi_0^N[\bar{v}]$, and $\Gamma_0[\bar{v}, q]$ are considered as functionals not only of the actual external potential v but of the whole set \bar{v} . The ground-state electron density corresponding to the ground-state density matrix $\Gamma_0[\bar{v}, q]$ shall be denoted $\rho_0^q[\bar{v}]$. The Hohenberg-Kohn functional $F[\rho_0^q[\bar{v}]]$ is given by $F[\rho_0^q[\bar{v}]] = \text{Tr}\{\Gamma_0[\bar{v}, q](\hat{T} + \hat{V}_{ee})\}$. The ground-state electron

density $\rho_0^q[\bar{v}]$ obeys the Euler equation [5,6]

$$\left. \frac{\delta F}{\delta \rho(\mathbf{r})} \right|_{\rho=\rho_0^q[\bar{v}]} = -v(\mathbf{r}) + \mu^N[v] = -\bar{v}(\mathbf{r}) + \mu^N[\bar{v}] \quad (1)$$

with the chemical potential $\mu^N[v]$, equal to the negative of the ionization potential, given as the difference $\mu^N[v] = E_0^N[v] - E_0^{N-1}[v]$ of the ground-state energies $E_0^N[v]$ and $E_0^{N-1}[v]$ of the N - and $(N-1)$ -electron system with the external potential v . However, any potential \bar{v} obtained by adding a constant to v may enter the Euler equation (1) for the ground-state density $\rho_0^q[\bar{v}]$ as long as the consistent chemical potential $\mu^N[\bar{v}] = E_0^N[\bar{v}] - E_0^{N-1}[\bar{v}]$ corresponding to the potential \bar{v} occurs in Eq. (1). The right-hand sides of Eq. (1) are invariant with respect to the addition of a constant to the potentials v or \bar{v} because the addition of a constant ν changes the energies E_0^N and E_0^{N-1} by $N\nu$ and $(N-1)\nu$ and thus the difference $E_0^N - E_0^{N-1}$ by ν which cancels the shift $-\nu$ of $-v$ or $-\bar{v}$ upon addition of a constant ν .

Next Eq. (1) is derived using only quantities readily available in the KS formalism of integer electron numbers. The approach to express the relevant objects of the ensemble KS formalism in terms of quantities from the KS formalism of integer electron numbers is the integer electron ensemble approach (IEEA) announced in the Introduction. By reducing objects of the ensemble KS formalism to those of the KS formalism of integer electron numbers the physical origin and the meaning of the former become clear and in applications additional approximations due to the ensemble formation are avoided such that only the common approximations required already in practical applications of the integer-electron-number KS formalism have to be invoked. As usual the electron density shall be ensemble v representable, i.e., it shall be the ensemble ground-state electron density ρ_0^q of an electronic system defined, besides the electron number $N-1 < q < N$, by some external potential v . The external potential v usually is the potential of the nuclei. For all known physical systems the ground-state energy is a convex function of the electron number consisting of straight lines connecting the ground-state energies $E_0^N[v]$ at integer electron numbers N [1]. The ground-state energy of the considered system with q electrons therefore is given by

$$\begin{aligned} E_0^q[v] &= (N-q)E_0^{N-1}[v] + (q-N+1)E_0^N[v] \\ &= (N-q)\langle \Psi_0^{N-1}[\bar{v}] | \hat{T} + \hat{V}_{ee} + \hat{v} | \Psi_0^{N-1}[\bar{v}] \rangle \\ &\quad + (q-N+1)\langle \Psi_0^N[\bar{v}] | \hat{T} + \hat{V}_{ee} + \hat{v} | \Psi_0^N[\bar{v}] \rangle \\ &= (N-q) \left[F[\rho_0^{N-1}] + \int d\mathbf{r} v(\mathbf{r}) \rho_0^{N-1}(\mathbf{r}) \right] \\ &\quad + (q-N+1) \left[F[\rho_0^N] + \int d\mathbf{r} v(\mathbf{r}) \rho_0^N(\mathbf{r}) \right] \\ &= (N-q)F[\rho_0^{N-1}] + (q-N+1)F[\rho_0^N] \\ &\quad + \int d\mathbf{r} v(\mathbf{r}) \rho_0^q(\mathbf{r}). \end{aligned} \quad (2)$$

In Eq. (2) it was used that the ground-state energy $E_0^N[v] = F[\rho_0^N] + \int d\mathbf{r} v(\mathbf{r}) \rho_0^N(\mathbf{r})$ and that $E_0^{N-1}[v] = F[\rho_0^{N-1}] + \int d\mathbf{r} v(\mathbf{r}) \rho_0^{N-1}(\mathbf{r})$ with the Hohenberg-Kohn functionals $F[\rho_0^N]$

and $F[\rho_0^{N-1}]$ of the ground-state electron densities ρ_0^N and ρ_0^{N-1} of the N - and $(N-1)$ -electron system, respectively. For the last line it was exploited that the ground-state electron density ρ_0^q of the ensemble with electron number $N-1 < q < N$ is given by $(N-q)\rho_0^{N-1} + (q-N+1)\rho_0^N$.

The ensemble ground-state electron density ρ_0^q behaves linear with q , like the ground-state energy $E_0^q[v]$, because the corresponding ground-state density matrix $\Gamma_0[v, q]$ behaves linear with q , i.e., as already stated above, is given by $\Gamma_0[v, q] = (N-q)|\Psi_0^{N-1}[v]\rangle\langle\Psi_0^{N-1}[v]| + (q-N+1)|\Psi_0^N[v]\rangle\langle\Psi_0^N[v]|$ with $\Psi_0^{N-1}[v]$ and $\Psi_0^N[v]$ being the ground-state wave functions of the corresponding electronic systems with $N-1$ and N electrons. The latter expression for $\Gamma_0[v, q]$ can be obtained by starting from the general ansatz $\Gamma_0[v, q] = \sum_M \sum_i c_i^M |\Psi_i^M[v]\rangle\langle\Psi_i^M[v]|$ with $\Psi_i^M[v]$ denoting the wave function of the i th eigenstate of the M -electron system with external potential v . Because the general ansatz for $\Gamma_0[v, q]$ is a linear form only ground states can contribute to the ensemble ground-state density matrix, that is only states with $i=0$. If an M -electron state with $i \neq 0$ contributed then the energy could be lowered by replacing it by the corresponding M -electron state with $i=0$. Thus the ansatz for $\Gamma_0[v, q]$ simplifies to $\Gamma_0[v, q] = \sum_M c_0^M |\Psi_0^M[v]\rangle\langle\Psi_0^M[v]|$. For all known physical systems the ionization energy is higher than the electron affinity for any given electron number M . Therefore only the ground states of the $(N-1)$ - and N -electron systems contribute to $\Gamma_0[v, q]$ for $N-1 < q < N$ and the above expression for $\Gamma_0[v, q]$ results. The ground-state energy $E_0^q[v] = \text{Tr}\{\Gamma_0[v, q](\hat{T} + \hat{V}_{ee} + \hat{v})\}$ and the electron density $\rho_0^q = \text{Tr}\{\Gamma_0[v, q]\hat{\rho}\}$ are given as simple traces of $\Gamma_0[v, q]$ with the Hamiltonian operator $\hat{T} + \hat{V}_{ee} + \hat{v}$ and the density operator $\hat{\rho}$, respectively, which implies that the linearity of $\Gamma_0[v, q]$ with q transfers to $E_0^q[v]$ and ρ_0^q ; see Ref. [1] for further discussions.

Subtraction of $\int d\mathbf{r} v(\mathbf{r}) \rho_0^q(\mathbf{r})$ from both sides of Eq. (2) yields the Hohenberg-Kohn functional

$$F[\rho_0^q] = (N-q)F[\rho_0^{N-1}] + (q-N+1)F[\rho_0^N] \quad (3)$$

for the electron density ρ_0^q . Here it is used that $E_0^q[v] = F[\rho_0^q] + \int d\mathbf{r} v(\mathbf{r}) \rho_0^q(\mathbf{r})$. Equation (3) shows that the Hohenberg-Kohn functional $F[\rho_0^q]$ for the electron density q , a quantity defined in the ensemble KS formalism, can be given by the linear interpolation between the Hohenberg-Kohn functionals $F[\rho_0^{N-1}]$ and $F[\rho_0^N]$ which are accessible in the KS formalism of integer electron numbers.

Next changes $\delta\rho$ of the electron density ρ_0^q are considered. The changes $\delta\rho$ are decomposed according to

$$\delta\rho(\mathbf{r}) = \delta\rho^0(\mathbf{r}) + \delta q[\rho_0^N(\mathbf{r}) - \rho_0^{N-1}(\mathbf{r})] \quad (4)$$

with

$$\delta\rho^0(\mathbf{r}) = \delta\rho(\mathbf{r}) - \delta q[\rho_0^N(\mathbf{r}) - \rho_0^{N-1}(\mathbf{r})], \quad (5)$$

and

$$\delta q = \int d\mathbf{r}' \delta\rho(\mathbf{r}'). \quad (6)$$

By Eq. (4) an arbitrary change $\delta\rho$ of the electron density is decomposed into one part, $\delta\rho^0$, that does not change the particle number, i.e., for which $\int d\mathbf{r} \delta\rho^0(\mathbf{r}) = 0$ holds, and a second part that changes the electron number by the required

amount δq through the change $\delta q[\rho_0^N(\mathbf{r}) - \rho_0^{N-1}(\mathbf{r})]$ which equals the difference of the ground state N - and $(N-1)$ -electron densities scaled by δq .

In the KS formalism of integer electron numbers, here N or $N-1$, the functional derivatives of the Hohenberg-Kohn functionals $F[\rho_0^N]$ and $F[\rho_0^{N-1}]$ with respect to changes of the electron density, which then have to integrate to zero, are given by the set of functions $-\bar{v}$, i.e., by the negative of the external potential v plus an arbitrary additive constant. The change $\delta\rho^0(\mathbf{r})$ was constructed to integrate to zero. If we only consider changes δF of the Hohenberg-Kohn functional $F[\rho_0^q]$ that leave the electron number q unchanged,

$$\begin{aligned} \delta F &= - \int d\mathbf{r} \bar{v}(\mathbf{r}) \delta\rho^0(\mathbf{r}) + \delta q \{ F[\rho_0^N] - F[\rho_0^{N-1}] \} \\ &= - \int d\mathbf{r} \bar{v}(\mathbf{r}) [\delta\rho(\mathbf{r}) - \delta q [\rho^N(\mathbf{r}) - \rho^{N-1}(\mathbf{r})]] + \delta q \{ F[\rho_0^N] - F[\rho_0^{N-1}] \} \\ &= - \int d\mathbf{r} \bar{v}(\mathbf{r}) \delta\rho(\mathbf{r}) + \delta q \int d\mathbf{r} \bar{v}(\mathbf{r}) [\rho^N(\mathbf{r}) - \rho^{N-1}(\mathbf{r})] + \delta q \{ F[\rho_0^N] - F[\rho_0^{N-1}] \} \\ &= - \int d\mathbf{r} \bar{v}(\mathbf{r}) \delta\rho(\mathbf{r}) + \delta q \left\{ \left[F[\rho_0^N] + \int d\mathbf{r} \bar{v}(\mathbf{r}) \rho^N(\mathbf{r}) \right] - \left[F[\rho_0^{N-1}] + \int d\mathbf{r} \bar{v}(\mathbf{r}) \rho^{N-1}(\mathbf{r}) \right] \right\} \\ &= - \int d\mathbf{r} \bar{v}(\mathbf{r}) \delta\rho(\mathbf{r}) + \delta q \{ E_0^N[\bar{v}] - E_0^{N-1}[\bar{v}] \} = - \int d\mathbf{r} \bar{v}(\mathbf{r}) \delta\rho(\mathbf{r}) + \delta q \mu^N[\bar{v}] = \int d\mathbf{r} [-\bar{v}(\mathbf{r}) + \mu^N[\bar{v}]] \delta\rho(\mathbf{r}). \quad (7) \end{aligned}$$

In Eq. (7), among other things, Eqs. (5) and (6) were used. From Eq. (7) immediately Eq. (1) for the functional derivative of $F[\rho_0^q]$ follows. As desired, the derivation given here for Eq. (1), i.e., for the functional derivative of the Hohenberg-Kohn functional within the ensemble KS formalism, uses only quantities occurring in the KS formalism of integer electron numbers or quantities like $F[\rho_0^q]$ that can be expressed in terms of quantities from the KS formalism of integer electron numbers, in the case of $F[\rho_0^q]$ by Eq. (3).

The above considerations hold true equally well for model systems of noninteracting electrons, i.e., for KS systems. Equation (1) then turns into

$$\left. \frac{\delta T_s}{\delta\rho(\mathbf{r})} \right|_{\rho=\rho_{s,0}^q[\bar{v}_s]} = -\bar{v}_s(\mathbf{r}) + \varepsilon_N[\bar{v}_s], \quad (8)$$

a Euler equation for the derivative of the noninteracting kinetic energy T_s with a right-hand side consisting of the effective KS potential \bar{v}_s and the energetically highest occupied KS eigenvalue $\varepsilon_N[\bar{v}_s]$, which represents the difference in the energies of the N - and $(N-1)$ -electron KS systems, i.e., the chemical potential, of the KS system. Again the Euler equation holds for any member of the set \bar{v} provided the consistent eigenvalue $\varepsilon_N[\bar{v}_s]$ enters the Euler equation (8). As in the case of Eq. (1), the right-hand side of Eq. (8) only contains quantities of the KS formalism for integer electron numbers and the equation can be derived using only such quantities. This means that one not only can derive expressions for all required relevant objects of the ensemble KS formalism that contain only quantities of the KS formalism of integer electron numbers but furthermore the derivations of these expressions

i.e., changes by $\delta\rho^0(\mathbf{r})$, then the corresponding functional derivative of $F[\rho_0^q]$ again is $-\bar{v}$ and $\delta F = - \int d\mathbf{r} \bar{v} \delta\rho^0(\mathbf{r})$. Changes of the Hohenberg-Kohn functional $F[\rho_0^q]$ due to changes $\delta q[\rho_0^N(\mathbf{r}) - \rho_0^{N-1}(\mathbf{r})]$, on the other hand, are tantamount to changes of the electron density from ρ_0^q to $\rho_0^{q+\delta q}$ and the corresponding change δF of the Hohenberg-Kohn functional thus, according to Eq. (3), is given by $\delta F = \delta q \{ F[\rho_0^N] - F[\rho_0^{N-1}] \}$. If the changes $\delta F = - \int d\mathbf{r} \bar{v} \delta\rho^0(\mathbf{r})$ due to changes $\delta\rho^0(\mathbf{r})$ and the changes $\delta F = \delta q \{ F[\rho_0^N] - F[\rho_0^{N-1}] \}$ due to changes $\delta q[\rho_0^N(\mathbf{r}) - \rho_0^{N-1}(\mathbf{r})]$ are added then the change δF due to an arbitrary change $\delta\rho(\mathbf{r})$ of the electron density is obtained:

also require only quantities of the KS formalism of integer electron numbers.

III. POTENTIAL ADJUSTORS FOR EXCHANGE-CORRELATION POTENTIALS LEADING TO CONSISTENT DISCONTINUITIES

The KS system associated with a given real electron system is the one that has the same ground-state electron density, that is the KS system with the ground-state density $\rho_{s,0}^q[\bar{v}_s] = \rho_0^q[\bar{v}]$. For this electron density ρ_0^q the difference between the Hohenberg-Kohn functional $F[\rho_0^q]$ and the noninteracting kinetic energy $T_s[\rho_0^q]$ defines the Hxc energy $E_{Hxc}[\rho_0^q]$. Taking the difference between the Euler equations (1) and (8) and the limit $q \rightarrow N_-$ leads to

$$\lim_{q \rightarrow N_-} \left. \frac{\delta E_{Hxc}}{\delta\rho(\mathbf{r})} \right|_{\rho=\rho_0^q} = v_{Hxc}^{N-}(\mathbf{r}) = \bar{v}_{Hxc}(\mathbf{r}) + \Delta_{Hxc}^{N-}[\bar{v}_{Hxc}] \quad (9)$$

with the potential adjustor

$$\begin{aligned} \Delta_{Hxc}^{N-}[\bar{v}_{Hxc}] &= \mu_N[\bar{v}] - \varepsilon_N[\bar{v} + \bar{v}_{Hxc}] \\ &= E_0^N[\bar{v}] - E_0^{N-1}[\bar{v}] - \varepsilon_N[\bar{v} + \bar{v}_{Hxc}]. \quad (10) \end{aligned}$$

The potential adjustor $\Delta_{Hxc}^{N-}[\bar{v}_{Hxc}]$ shifts an arbitrary member of the set of Hxc potential $\bar{v}_{Hxc} = \bar{v}_s(\mathbf{r}) - \bar{v}(\mathbf{r})$ of the KS formalism of integer electron number N to the one Hxc potential v_{Hxc}^{N-} which emerges in the ensemble KS formalism in the limit of approaching the electron number N from the electron deficiency side [20,21]. The potential v_{Hxc}^{N-} is the one that needs to be used in a KS calculation in order to obtain an energetically highest occupied KS orbital with an eigenvalue equal to the negative of the ionization energy.

The Hxc potential used in actual KS calculations is one out of the set \bar{v}_{Hxc} but, in general, not v_{Hxc}^{N-} and, hence, the corresponding eigenvalue of the energetically highest occupied KS orbital, in general, is not related to the ionization energy. Equations (9) and (10) are valid for arbitrary members of the sets of potentials \bar{v} and \bar{v}_s ; the only requirement is consistency, i.e., that the chemical potential $\mu_N[\bar{v}] = E_0^N[\bar{v}] - E_0^{N-1}[\bar{v}]$ refers to \bar{v} and that the eigenvalue $\varepsilon_N[\bar{v} + \bar{v}_{Hxc}]$ belongs to the KS one-electron equation with the corresponding KS potential $\bar{v}_s = \bar{v} + \bar{v}_{Hxc}$. Equations (9) and (10) are key equations of this work. Their value is that they relate the Hxc potential v_{Hxc}^{N-} from the ensemble KS formalism to quantities of the KS formalism of integer electron numbers N and $N - 1$ which are easily accessible in actual calculations.

For any given approximation of the xc energy Eqs. (9) and (10) enable the construction of the corresponding Hxc potential v_{Hxc}^{N-} . This is demonstrated for the GGA for the xc energy. If the actual external potential v is chosen from the set \bar{v} then Eq. (9) reads as

$${}^{GGA}v_{Hxc}^{N-}(\mathbf{r}) = {}^{GGA}\bar{v}_{Hxc}(\mathbf{r}) + {}^{GGA}\Delta_{Hxc}^{N-}[{}^{GGA}\bar{v}_{Hxc}] \quad (11)$$

with

$$\begin{aligned} & {}^{GGA}\Delta_{Hxc}^{N-}[{}^{GGA}\bar{v}_{Hxc}] \\ &= {}^{GGA}E_0^N[v] - {}^{GGA}E_0^{N-1}[v] - \varepsilon_N^{GGA}[v + \bar{v}_{Hxc}]. \end{aligned} \quad (12)$$

On the right-hand side of Eq. (11) any member of the set ${}^{GGA}\bar{v}_{Hxc}$ can enter but usually it would be the one obtained as straightforward functional derivative of the GGA xc energy. The calculation of the potential adjutor ${}^{GGA}\Delta_{Hxc}^{N-}[{}^{GGA}\bar{v}_{Hxc}]$ via Eq. (12) requires just a second self-consistent GGA calculation for the $(N - 1)$ -electron system to obtain ${}^{GGA}E_0^{N-1}[v]$ besides the N -electron GGA calculation yielding ${}^{GGA}\bar{v}_{Hxc}$, $\varepsilon_N^{GGA}[v + {}^{GGA}\bar{v}_{Hxc}]$, and ${}^{GGA}E_0^N[v]$. Note that the energies ${}^{GGA}E_0^N[v]$ and ${}^{GGA}E_0^{N-1}[v]$ do not depend on which potential of the set ${}^{GGA}\bar{v}_{Hxc}$ is chosen and that the effect of an additive constant in ${}^{GGA}\bar{v}_{Hxc}$ is canceled in Eq. (11) by the corresponding shift of $\varepsilon_N^{GGA}[v + {}^{GGA}\bar{v}_{Hxc}]$ changing ${}^{GGA}\Delta_{Hxc}^{N-}[{}^{GGA}\bar{v}_{Hxc}]$ in the opposite direction. If the adjutor ${}^{GGA}\Delta_{Hxc}^{N-}[{}^{GGA}\bar{v}_{Hxc}]$ is added to the commonly employed Hxc GGA potential ${}^{GGA}\bar{v}_{Hxc}$ in order to obtain ${}^{GGA}v_{Hxc}^{N-}$ then all KS eigenvalues are shifted by ${}^{GGA}\Delta_{Hxc}^{N-}[{}^{GGA}\bar{v}_{Hxc}]$. The energetically highest occupied KS eigenvalue $\varepsilon_N^{GGA}[v + {}^{GGA}\bar{v}_{Hxc}]$ turns into $\varepsilon_N^{GGA}[v + {}^{GGA}\bar{v}_{Hxc}] + {}^{GGA}\Delta_{Hxc}^{N-}[{}^{GGA}\bar{v}_{Hxc}] = {}^{GGA}E_0^N[v] - {}^{GGA}E_0^{N-1}[v] = \mu_N^{GGA}[v] = \varepsilon_N^{GGA}[v + {}^{GGA}v_{Hxc}^{N-}]$, i.e., the highest occupied KS eigenvalue $\varepsilon_N^{GGA}[v + {}^{GGA}v_{Hxc}^{N-}]$ then equals the GGA chemical potential $\mu_N^{GGA}[v]$ or the negative of the GGA ionization potential ${}^{GGA}E_0^N[v] - {}^{GGA}E_0^{N-1}[v]$ as it would emerge from a GGA Δ SCF (difference self-consistent field) calculation.

All the above arguments can be repeated for an electronic system with a fractional occupation number q with $N \leq q \leq N + 1$ and the limit $q \rightarrow N_+$ can be taken. Equation (9) for v_{Hxc}^{N-} then turns into the equation

$$v_{Hxc}^{N+}(\mathbf{r}) = \bar{v}_{Hxc}(\mathbf{r}) + \Delta_{Hxc}^{N+}[\bar{v}_{Hxc}] \quad (13)$$

for v_{Hxc}^{N+} , i.e., the Hxc potential obtained in the ensemble KS formalism by approaching the integer electron number N from

the electron surplus side. The Hxc potential v_{Hxc}^{N+} obtained by adding the potential adjutor

$$\Delta_{Hxc}^{N+}[\bar{v}_{Hxc}] = E_0^{N+1}[\bar{v}] - E_0^N[\bar{v}] - \varepsilon_{N+1}[\bar{v} + \bar{v}_{Hxc}] \quad (14)$$

to a member of the set of potentials $\bar{v}_{Hxc}(\mathbf{r})$ leads to a one-electron KS equation with the effective KS potential $\bar{v} + v_{Hxc}^{N+}$ which yields an eigenvalue $\varepsilon_{N+1}[\bar{v} + v_{Hxc}^{N+}(\mathbf{r})]$ being equal to the negative of the ionization energy of the $N + 1$ electron system.

The difference between $v_{Hxc}^{N+}(\mathbf{r})$ and $v_{Hxc}^{N-}(\mathbf{r})$ is the derivative discontinuity Δ_{Hxc}^N of the Hxc energy at the integer electron number N . From Eqs. (9) and (13) together with Eqs. (10) and (14) one obtains

$$\begin{aligned} \Delta_{Hxc}^N &= \Delta_{Hxc}^{N+}[\bar{v}_{Hxc}] - \Delta_{Hxc}^{N-}[\bar{v}_{Hxc}] \\ &= E_0^{N+1}[\bar{v}] + E_0^{N-1}[\bar{v}] - 2E_0^N[\bar{v}] \\ &\quad - \varepsilon_{N+1}[\bar{v} + \bar{v}_{Hxc}] + \varepsilon_N[\bar{v} + \bar{v}_{Hxc}] \end{aligned} \quad (15)$$

for the derivative discontinuity. While the individual quantities on the right-hand side of Eq. (15) depend on which members of the sets \bar{v} and \bar{v}_{Hxc} are chosen, the derivative discontinuity Δ_{Hxc}^N is invariant with respect to this choice, i.e., additions of constants to the potentials \bar{v} and \bar{v}_{Hxc} cancel.

Eqs. (9), (10), and (13)–(15) enable the calculation of the potentials v_{Hxc}^{N-} , v_{Hxc}^{N+} , and of the derivative discontinuity Δ_{Hxc}^N for any given approximation of the xc energy. By using v_{Hxc}^{N-} in the one-electron KS equation the resulting KS eigenvalue $\varepsilon_N[v + v_{Hxc}^{N-}]$ equals the negative of the ionization potential as it emerges from a corresponding Δ SCF calculation, i.e., the difference of the corresponding N and $(N - 1)$ -electron KS calculations. The sum of the KS band gap plus the discontinuity Δ_{Hxc}^N of the xc potential, for all approximate xc energy functionals including GGA functionals, yields the physical band gap as it emerges from a Δ SCF calculation. For finite systems, Δ_{Hxc}^N is always nonzero for any approximate xc functional. The potentials v_{Hxc}^{N-} , v_{Hxc}^{N+} , and the derivative discontinuity Δ_{Hxc}^N only depend on the xc energy functional for integer electron numbers. This means they are derived quantities which need and should not be approximated by any extra measures. If an approximate xc energy functional yields good ionization energies and electron affinities in Δ SCF calculations it automatically yields good fundamental band gaps; see later on for the implications in the case of semiconductors.

The reason why GGA functionals are commonly erroneously believed [5,6,10,11] to not exhibit a derivative discontinuity is that GGA expressions not only are considered as approximate xc energy functionals in the KS formalism of integer electron numbers but also in a naive, straightforward way as approximate ensemble density functionals. The step to consider GGA functionals as ensemble density functionals, however, represents a second severe and poor approximation. As shown here, this second step is not necessary because all required objects from ensemble DFT are easily accessible from quantities readily available in the KS formalism of integer electron numbers. This includes energies of ensembles with noninteger electron numbers q which can be obtained straightforwardly [1] by linear interpolation of the energies

of the electron systems with the integer electron numbers bracketing q . Localization or delocalization errors reported in Refs. [10, 11] for GGA functionals only occur if GGA functionals are used straightforwardly as ensemble functionals. This as well as attempts to construct specific approximations for ensemble xc functionals do not make much sense from the perspective of this work. The consequence for future strategies to develop new functionals in DFT is that efforts should concentrate on the improvement of xc *energy* functionals for *integer* electron numbers.

If the self-consistent total energies $E_0^{N-1}[\bar{v}]$ and $E_0^{N+1}[\bar{v}]$ in Eqs. (10), (14), and (15) for the potential adjustors $\Delta_{Hxc}^{N-}[\bar{v}_{Hxc}]$ and $\Delta_{Hxc}^{N+}[\bar{v}_{Hxc}]$ and the derivative discontinuity Δ_{Hxc}^N are replaced by non-self-consistent energies obtained by evaluating the total energy of the $(N-1)$ - and the $(N+1)$ -electron system with the KS orbitals of the N -electron system, then an approximate adjustment of potentials as suggested in Refs. [22] and [23] is obtained. An evaluation of all required energies with the orbitals of the N -electron system means that relaxation effects upon ionization or upon addition of an electron are neglected.

IV. AN INTERNAL CONSISTENCY RELATION FOR FINITE SYSTEMS AND ASYMPTOTIC CORRECTIONS FOR XC POTENTIALS

If the Hxc potential v_{Hxc}^{N-} obtained by properly adjusting a Hxc potential \bar{v}_{Hxc} by $\Delta_{Hxc}^{N-}[{}^{GGA}\bar{v}_{Hxc}]$ is employed in the KS equations then it was shown that the eigenvalue of the highest occupied KS orbital obeys the equation

$$\varepsilon_N[v + v_{Hxc}^{N-}] = -IP_N \quad (16)$$

with IP_N denoting the ionization potential of a *finite* N -electron system. The electron density of finite electronic systems was shown to decay according to $\rho(\mathbf{r}) \rightarrow e^{-2\alpha r}$ with $\alpha = [2(IP)]^{1/2}$ if the external potential $v(\mathbf{r})$ is a Coulombic potential approaching zero for $\mathbf{r} \rightarrow \infty$ like, e.g., the potential generated by the nuclei of a molecule [18, 24]. Similarly, the electron density of a finite KS system, a model system consisting of hypothetical noninteracting electrons, decays like $\rho(\mathbf{r}) \rightarrow e^{-2\alpha r}$ with $\alpha = (-2\{\varepsilon_N[\bar{v}_s] - \bar{v}_s(\infty)\})^{1/2}$ and with $\bar{v}_s(\infty)$ being the asymptotic value of the effective KS potential \bar{v}_s for $r \rightarrow \infty$. By construction the KS model system and the physical electron system have the same electron density. Therefore

$$-\varepsilon_N[\bar{v}_s] + \bar{v}_s(\infty) = IP_N. \quad (17)$$

If $v + v_{Hxc}^{N-}$ is chosen for the effective KS potential \bar{v}_s in Eq. (17), Eq. (16) is considered, and the fact is taken into account that v vanishes for $\mathbf{r} \rightarrow \infty$, then the equation

$$v_{Hxc}^{N-}(\infty) = \bar{v}_{Hxc}(\infty) + \Delta_{Hxc}^{N-}[\bar{v}_{Hxc}] = 0 \quad (18)$$

follows in agreement with Refs. [18, 24]. Here $v_{Hxc}^{N-}(\infty)$ is the asymptotic value v_{Hxc}^{N-} for $r \rightarrow \infty$. Equation (18) represents an internal consistency check. If the potential adjustor $\Delta_{Hxc}^{N-}[\bar{v}_{Hxc}]$ is added to a member of a set of approximate Hxc potentials \bar{v}_{Hxc} then the resulting Hxc potential v_{Hxc}^{N-} has to approach zero for $r \rightarrow \infty$. The other way around,

for that member of the set of approximate Hxc potentials \bar{v}_{Hxc} that approaches zero for $r \rightarrow \infty$ the potential adjustor $\Delta_{Hxc}^{N-}[\bar{v}_{Hxc}]$ has to be zero, i.e., this member of the set is v_{Hxc}^{N-} and the eigenvalue of the highest occupied KS orbital obtained with it has to equal $E_0^N[v] - E_0^{N-1}[v]$ determined by the corresponding Δ SCF calculation. GGA functionals do not meet this internal consistency condition for finite systems.

It is common to compare the eigenvalue of the highest occupied KS orbital with the negative of the experimental ionization potential for KS calculations with Hxc potentials approaching zero for $r \rightarrow \infty$ like, e.g., GGA Hxc potentials obtained as straightforward functional derivatives of the GGA Hxc energy. This represents a check against an external quantity, the experimental ionization potential. Whether the adjusted Hxc potential $\bar{v}_{Hxc} + \Delta_{Hxc}^{N-}[\bar{v}_{Hxc}]$, for a given approximate xc functional, approaches zero for $\mathbf{r} \rightarrow \infty$ represents an internal check. Alternatively, it can be checked whether the potential adjustor $\Delta_{Hxc}^{N-}[\bar{v}_{Hxc}]$ is zero if, for a given approximate xc functional, that Hxc potential is chosen from the set \bar{v}_{Hxc} that approaches zero for $\mathbf{r} \rightarrow \infty$. GGA functionals will neither meet the check against the experimental IP nor the internal check. The internal check can be used for a system-dependent optimization or tuning of xc functionals. Suppose we make an ansatz for a xc functional containing adjustable parameters that, due to its form, leads to xc potentials approaching zero for $r \rightarrow \infty$. Then the parameters can be tuned in a way that the internal check is met, i.e., that the eigenvalue of the highest occupied KS orbital equals $E_0^N[v] - E_0^{N-1}[v]$ calculated by the corresponding Δ SCF calculations. Such a tuning has been proposed in the framework of generalized KS methods [13] to improve response properties, in particular, excitation energies in Refs. [25–27]. Here an additional justification for such a tuning is given because it can be interpreted as a measure to obey the above internal consistency condition. Assuming that the results of this work are also valid [12] for generalized KS methods, this might be considered as a stronger justification than arguing that the eigenvalue of the highest occupied KS orbital should equal the experimental IP_N which is then approximated by a Δ SCF calculation.

A further implication from the results of this work is that asymptotic corrections for approximate xc potentials [28, 29] should be added after adding the potential adjustor Δ_{Hxc}^{N-} . Energetic shifts of asymptotic corrections in order to not change the original xc potential in the uncorrected region do not make sense because the energetic position of the original xc potential prior to adding the potential adjustor has little physical meaning.

V. POTENTIAL ADJUSTORS AND DISCONTINUITIES OF XC FUNCTIONALS IN THE LIMIT OF INFINITE SYSTEMS

The results of this work are valid both for finite, i.e., atomic or molecular, systems as well as for periodic systems. For periodic systems in the limit of infinite size, in practice for large numbers M of \mathbf{k} points, a calculation of total-energy differences $E_0^N[\bar{v}] - E_0^{N-1}[\bar{v}]$ or $E_0^{N+1}[\bar{v}] - E_0^N[\bar{v}]$ might seem to be not feasible at first sight. Clearly the change of the total energy per unit cell vanishes for $M \rightarrow \infty$ if a single electron is added or removed from a system with M \mathbf{k} points, which corresponds to an arrangement of M unit

cells. However, it is straightforward to carry out total-energy calculations with one single electron added or removed. In a semiconductor, e.g., the one-electron state at the bottom of the conduction band or at the top of the valence band becomes occupied or unoccupied, respectively. Indeed such calculations are simpler than in the case of finite systems because in the limit $M \rightarrow \infty$ an addition or removal of a single electron does not change the KS orbitals. Therefore the total energy of the $(N - 1)$ - and the $(N + 1)$ -electron systems can be evaluated with the one-electron states obtained in the KS calculation for the N -electron system, without additional SCF calculations for the $(N - 1)$ or $(N + 1)$ system; see below for details.

By adding the potential adjustor Δ_{Hxc}^{N-} to the valence band of a semiconductor and Δ_{Hxc}^{N+} to the conduction bands, the KS band structure turns into an approximate quasiparticle band structure with the physical instead of the KS band gap. This means that the KS formalism itself yields access to the exact fundamental quasiparticle band gap by transforming a regular KS band structure with the help of the potential adjustors Δ_{Hxc}^{N-} and Δ_{Hxc}^{N+} into a KS quasiparticle band structure. While such a KS quasiparticle band structure yields the exact fundamental band gap, it is only an approximation to a full quasiparticle band structure at points other than the fundamental band gap, however, an approximation that can be assumed to be much better than the regular, i.e., not adjusted, KS band structure. In the special case of GGA functionals and related functionals it turns out, see below, that ${}^{GGA}E_0^N[v] - {}^{GGA}E_0^{N-1}[v] = \varepsilon_N^{GGA}$ and ${}^{GGA}E_0^{N+1}[v] - {}^{GGA}E_0^N[v] = \varepsilon_{N+1}^{GGA}$ if from the set of Hxc potentials \tilde{v}_{Hxc} the one resulting from straightforward differentiation of the energy functional is used. As a consequence, see later on, potential adjustors and the derivative discontinuity vanish in the limit of infinite systems in the case of GGAs and of approximations of a related form. This, however, is a specific shortcoming of the GGA. For orbital-dependent functionals [30], e.g., on the basis of the random-phase approximation [31–34], the potential adjustors do not vanish and yield finite band gaps [35]. The calculation of band gaps via orbital-dependent density-functional methods represents an alternative to GW methods with many opportunities to be explored in the future.

Now the IEEA for xc functional shall be considered in more detail for the case of infinite systems. To that end a system consisting of $\ell \times m \times n = M$ unit cells in periodic boundary conditions, i.e., Born von Karman boundary conditions, shall be considered. This system shall be treated by a GGA calculation with a regular grid of $\ell \times m \times n = M$ \mathbf{k} points. The complete system consisting of M unit cells shall have N electrons. Its GGA ground state energy ${}^{GGA}E_0^N[v]$ is given by

$${}^{GGA}E_0^N[v] = \sum_{i\mathbf{k}} \langle \phi_{i\mathbf{k}} | \hat{T} | \phi_{i\mathbf{k}} \rangle + \int_{\Omega} d\mathbf{r} v(\mathbf{r}) \rho_0^N(\mathbf{r}) + E_{Hxc}^{GGA}[\rho_0^N] \quad (19)$$

with the Hxc energy

$$E_{Hxc}^{GGA}[\rho_0^N] = \int_{\Omega} d\mathbf{r} \epsilon_{Hxc}^{GGA}(\mathbf{r}) \rho_0^N(\mathbf{r}) \quad (20)$$

and the ground state N -electron density

$$\rho_0^N(\mathbf{r}) = \sum_{i\mathbf{k}} \phi_{i\mathbf{k}}^*(\mathbf{r}) \phi_{i\mathbf{k}}(\mathbf{r}). \quad (21)$$

In Eqs. (19)–(21) $\hat{T} = (-1/2)\nabla^2$ is the operator of the kinetic energy and $\epsilon_{Hxc}^{GGA}(\mathbf{r})$ is the GGA Hxc energy density [5,6]. The summation $\sum_{i\mathbf{k}}$ runs over all M \mathbf{k} points and for a given \mathbf{k} point over the index i of all occupied bands. The integration volume Ω is the crystal volume, the volume of the complete systems consisting of all M unit cells, that is M times the unit-cell volume V , i.e., $\Omega = MV$. In a KS calculation usually the total energy per unit cell is calculated, which is obtained from ${}^{GGA}E_0^N[v]$ of Eq. (19) by division by M . The KS orbitals $\phi_{i\mathbf{k}}$ are normalized with respect to the crystal volume Ω , i.e., $\int_{\Omega} d\mathbf{r} \phi_{i\mathbf{k}}^*(\mathbf{r}) \phi_{i\mathbf{k}}(\mathbf{r}) = 1$. In an actual calculation the integrations $\int_{\Omega} d\mathbf{r} v(\mathbf{r}) \rho_0^N(\mathbf{r})$ and $\int_{\Omega} d\mathbf{r} \epsilon_{Hxc}^{GGA}(\mathbf{r}) \rho_0^N(\mathbf{r})$ can be replaced by corresponding integration $\int_V d\mathbf{r} v(\mathbf{r}) \rho_0^N(\mathbf{r})$ and $\int_V d\mathbf{r} \epsilon_{Hxc}^{GGA}(\mathbf{r}) \rho_0^N(\mathbf{r})$ over one unit cell instead of the crystal volume to directly obtain the corresponding energy contributions per unit cell.

The energy ${}^{GGA}E_0^{N-1}[v]$ of the complete system consisting of M unit cells with one single electron removed is given by

$$\begin{aligned} {}^{GGA}E_0^{N-1}[v] &= \sum_{i\mathbf{k}} \langle \phi_{n\mathbf{k}} | \hat{T} | \phi_{n\mathbf{k}} \rangle \\ &+ \int_{\Omega} d\mathbf{r} v(\mathbf{r}) \rho_0^{N-1}(\mathbf{r}) + E_{Hxc}^{GGA}[\rho_0^{N-1} - \rho^{\phi_N}] \\ &- \langle \phi_N | \hat{T} | \phi_N \rangle - \int_{\Omega} d\mathbf{r} v(\mathbf{r}) \rho^{\phi_N}(\mathbf{r}) \end{aligned} \quad (22)$$

in the limit of a large number M of unit cells. In this limit the removal of one electron from the system will not change the orbitals $\phi_{i\mathbf{k}}$. Therefore no additional self-consistent KS calculation for the $N - 1$ electron system is required in this case. Merely the energy expression has to be reevaluated for $N - 1$ electrons, which leads to Eq. (22). The removed electron, labeled electron N , is the one of the energetically highest occupied KS orbital ϕ_N . In a semiconductor this is the energetically highest occupied orbital of the \mathbf{k} point representing the top of the valence band. The electron density ρ^{ϕ_N} of this KS orbital is given by $\rho^{\phi_N}(\mathbf{r}) = \phi_N^*(\mathbf{r}) \phi_N(\mathbf{r})$.

The energy difference between the N - and the $(N - 1)$ -electron system is given by

$$\begin{aligned} &{}^{GGA}E_0^N[v] - {}^{GGA}E_0^{N-1}[v] \\ &= \langle \phi_N | \hat{T} | \phi_N \rangle + \int_{\Omega} d\mathbf{r} v(\mathbf{r}) \rho^{\phi_N}(\mathbf{r}) + E_{Hxc}^{GGA}[\rho_0] \\ &- E_{Hxc}^{GGA}[\rho_0^N - \rho^{\phi_N}] \\ &= \varepsilon_N[v + \tilde{v}_{Hxc}] - \int_{\Omega} d\mathbf{r} \tilde{v}_{Hxc}(\mathbf{r}) \rho^{\phi_N}(\mathbf{r}) \\ &+ E_{Hxc}^{GGA}[\rho_0] - E_{Hxc}^{GGA}[\rho_0^N - \rho^{\phi_N}]. \end{aligned} \quad (23)$$

Equation (23) can be easily evaluated. The expectation value $\langle \phi_N | \hat{T} | \phi_N \rangle$ is just one contribution of the sum $\sum_{i\mathbf{k}} \langle \phi_{n\mathbf{k}} | \hat{T} | \phi_{n\mathbf{k}} \rangle$ which is routinely evaluated for the noninteracting kinetic energy. The energies $\int_{\Omega} d\mathbf{r} v(\mathbf{r}) \rho^{\phi_N}(\mathbf{r})$ and $E_{Hxc}^{GGA}[\rho_0^N - \rho^{\phi_N}]$ can be obtained by replacing the density ρ_0 by ρ^{ϕ_N} and by $\rho_0^N - \rho^{\phi_N}$, respectively, in the energy contributions $\int_{\Omega} d\mathbf{r} v(\mathbf{r}) \rho_0^N(\mathbf{r})$

and $E_{Hxc}^{GGA}[\rho_0^N]$ of ${}^{GGA}E_0^N[v]$. Of course, factors of $1/M$ introduced in the evaluation of ${}^{GGA}E_0^N[v]$ for obtaining energies per unit cell have to be removed.

While it is easily possible to evaluate the right-hand side of Eq. (23) it is instructive to add and subtract the contribution $\int_{\Omega} d\mathbf{r} \tilde{v}_{Hxc}^{GGA}(\mathbf{r}) \rho^{\phi_N}(\mathbf{r})$ and to use that $\hat{T} + v(\mathbf{r}) + \tilde{v}_{Hxc}^{GGA}(\mathbf{r})$ represents the KS Hamilton operator. The KS orbital ϕ_N

$$\begin{aligned} E_{Hxc}^{GGA}[\rho_0^N] - E_{Hxc}^{GGA}[\rho_0^N - \rho^{\phi_N}] &= \int_{\Omega} d\mathbf{r} \left. \frac{\delta E_{Hxc}^{GGA}}{\delta(\mathbf{r})} \right|_{\rho=\rho_0^N} \rho^{\phi_N}(\mathbf{r}) - (1/2) \int_{\Omega} d\mathbf{r} d\mathbf{r}' \left. \frac{\delta^2 E_{Hxc}^{GGA}}{\delta(\mathbf{r})\delta(\mathbf{r}')} \right|_{\rho=\rho_0^N} \rho^{\phi_N}(\mathbf{r}) \rho^{\phi_N}(\mathbf{r}') + \dots \\ &= \int_{\Omega} d\mathbf{r} \tilde{v}_{Hxc}(\mathbf{r}) \rho^{\phi_N}(\mathbf{r}) - (1/2) \int_{\Omega} d\mathbf{r} {}^{(2)}f_{Hxc}^{GGA}(\mathbf{r}) [\rho^{\phi_N}(\mathbf{r})]^2 + \dots \end{aligned} \quad (25)$$

using that

$$\left. \frac{\delta^2 E_{Hxc}^{GGA}}{\delta(\mathbf{r})\delta(\mathbf{r}')} \right|_{\rho=\rho_0^N} = {}^{(2)}f_{Hxc}^{GGA}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}'). \quad (26)$$

Equation (26) is a consequence of the form of GGA functionals. A GGA functional for the xc energy can be written as an integral $\int_{\Omega} d\mathbf{r} {}^{(0)}f_{xc}^{GGA}(\mathbf{r})$ with an integrand which is a function ${}^{(0)}f_{xc}^{GGA}(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}))$ of the electron density $\rho(\mathbf{r})$ and its gradient $\nabla\rho(\mathbf{r})$, i.e., the first-order derivatives of ρ with respect to the spatial coordinates x, y, z . The first functional derivative of the GGA xc energy with respect to ρ , the xc potential $\tilde{v}_{xc}^{GGA}(\mathbf{r})$, is a function ${}^{(1)}f_{xc}^{GGA}(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), d^2\rho(\mathbf{r})/dx^2, \dots)$ of $\rho(\mathbf{r})$, $\nabla\rho(\mathbf{r})$ and second-order spatial derivatives of ρ , like $d^2\rho(\mathbf{r})/dx^2$. The second functional derivative of the GGA xc energy with respect to ρ then is a function ${}^{(2)}f_{Hxc}^{GGA}(\mathbf{r})$ of $\rho(\mathbf{r})$ and its spatial functional derivatives up to third order times a δ function $\delta(\mathbf{r}' - \mathbf{r})$. Higher-order functional derivatives in a similar way are functions ${}^{(n)}f_{Hxc}^{GGA}(\mathbf{r})$ times products of δ functions.

The crucial point now is the scaling behavior of the density $\rho^{\phi_N}(\mathbf{r})$ with the system size, i.e., with the number M of unit cells. The density $\rho^{\phi_N}(\mathbf{r})$ scales with $1/M$ because the KS orbitals scale with $1/\sqrt{M}$. This is a consequence of the normalization condition $\int_{\Omega} d\mathbf{r} \rho^{\phi_N}(\mathbf{r}) = 1$ of the KS orbitals with respect to the crystal volume Ω which equals MV and thus scales with M . As a result of these scalings the first term $\int_{\Omega} d\mathbf{r} \tilde{v}_{Hxc}(\mathbf{r}) \rho^{\phi_N}(\mathbf{r})$ of the Taylor series (25) of the energy difference $E_{Hxc}^{GGA}[\rho_0] - E_{Hxc}^{GGA}[\rho_0 - \rho^{\phi_N}]$ has a nonzero value because the $1/M$ scaling of $\rho^{\phi_N}(\mathbf{r})$ and the scaling of the integration volume Ω with M compensate each other. The quadratic term $\int_{\Omega} d\mathbf{r} {}^{(2)}f_{Hxc}^{GGA}(\mathbf{r}) (\rho^{\phi_N}(\mathbf{r}))^2$ of this Taylor series, however, scales with $1/M$ because it contains the square of the electron density which scales according to $1/M^2$ and again an integration over the crystal volume scaling with M . Therefore this contribution vanishes for $M \rightarrow \infty$. The same holds true for terms of the Taylor series of higher orders n which scale as $1/M^{n-1}$ with M . This means in the limit $M \rightarrow \infty$ all terms of the Taylor series of $E_{Hxc}^{GGA}[\rho_0] - E_{Hxc}^{GGA}[\rho_0 - \rho^{\phi_N}]$ vanish except the leading linear term $\int_{\Omega} d\mathbf{r} \tilde{v}_{Hxc}(\mathbf{r}) \rho^{\phi_N}(\mathbf{r})$. This term, however, is canceled by the second term on the right-hand side of Eq. (24) which leads to

$${}^{GGA}E_0^N[v] - {}^{GGA}E_0^{N-1}[v] = \varepsilon_N^{GGA}[v + \tilde{v}_{Hxc}] \text{ for } M \rightarrow \infty. \quad (27)$$

is an eigenstate to this Hamilton operator with eigenvalue $\varepsilon_N[v + \tilde{v}_{Hxc}]$. This leads to Eq. (24). The tilde above \tilde{v}_{Hxc}^{GGA} indicates that the Hxc potential is the one obtained as straightforward functional derivative of the GGA Hxc energy.

For GGA functionals the energy contribution $E_{Hxc}^{GGA}[\rho_0^N] - E_{Hxc}^{GGA}[\rho_0^N - \rho^{\phi_N}]$ in Eqs. (23) and (24) can be expanded in a Taylor series around ρ_0^N as

This means, for GGA functionals, Δ SCF calculations simply yield the eigenvalue $\varepsilon_N^{GGA}[v + \tilde{v}_{Hxc}]$ of the highest occupied KS orbital as total-energy difference of the N - and $(N-1)$ -electron system in the case of infinite systems.

As a consequence of Eq. (27) the potential adjustor

$$\begin{aligned} {}^{GGA}\Delta_{Hxc}^{N-}[{}^{GGA}\tilde{v}_{Hxc}] &= {}^{GGA}E_0^N[v] - {}^{GGA}E_0^{N-1}[v] - \varepsilon_N^{GGA}[v + \tilde{v}_{Hxc}] \\ &= \varepsilon_N^{GGA}[v + \tilde{v}_{Hxc}] - \varepsilon_N^{GGA}[v + \tilde{v}_{Hxc}] \\ &= 0 \text{ for } M \rightarrow \infty. \end{aligned} \quad (28)$$

Similarly it can be shown for $M \rightarrow \infty$ that ${}^{GGA}E_0^{N+1}[v] - {}^{GGA}E_0^N[v] = \varepsilon_{N+1}^{GGA}[v + \tilde{v}_{Hxc}]$ and subsequently that also the potential adjustor ${}^{GGA}\Delta_{Hxc}^{N+}[{}^{GGA}\tilde{v}_{Hxc}] = 0$. As a consequence

$${}^{GGA}v_{Hxc}^{N-}(\mathbf{r}) = {}^{GGA}v_{Hxc}^{N+}(\mathbf{r}) = {}^{GGA}\tilde{v}_{Hxc}(\mathbf{r}) \text{ for } M \rightarrow \infty \quad (29)$$

and

$${}^{GGA}\Delta_{Hxc}^N = {}^{GGA}v_{Hxc}^{N+}(\mathbf{r}) - {}^{GGA}v_{Hxc}^{N-}(\mathbf{r}) = 0 \text{ for } M \rightarrow \infty. \quad (30)$$

This means for periodic systems in the limit of an infinite number of \mathbf{k} points the GGA potential adjustors vanish, the GGA Hxc potential ${}^{GGA}\tilde{v}_{Hxc}$ obtained as straightforward functional derivative of the GGA Hxc energy equals the corresponding GGA Hxc potentials ${}^{GGA}v_{Hxc}^{N-}$ and ${}^{GGA}v_{Hxc}^{N+}$, and the GGA derivative discontinuity ${}^{GGA}\Delta_{Hxc}^N$ vanishes. Remember that this holds true only in the limit of infinite system, while for finite systems the GGA potential adjustors are nonzero, ${}^{GGA}\tilde{v}_{Hxc} \neq {}^{GGA}v_{Hxc}^{N-} \neq {}^{GGA}v_{Hxc}^{N+}$, and the GGA Hxc potential exhibits a finite discontinuity. Moreover, note that the vanishing GGA potential adjustors and the vanishing derivative discontinuity are a consequence of a shortcoming of the GGA xc energy, namely that, in the limit of infinite systems, GGA total-energy differences between the N - and $(N-1)$ -electron system and between the $(N+1)$ - and (N) -electron system equal the N th and $(N+1)$ th KS eigenvalue, respectively. This is completely in line with the results presented in this work. If, e.g., the Hxc potential ${}^{GGA}v_{Hxc}^{N-} = {}^{GGA}\tilde{v}_{Hxc}$ is used in the KS equation then the energetically highest occupied KS eigenvalue equals the negative of the ionization energy as it results from a GGA Δ SCF calculation because the latter, as just

shown, is simply $\varepsilon_N^{GGA}[v + \tilde{v}_{Hxc}]$. Furthermore, the GGA KS band gap plus the GGA derivative discontinuity $^{GGA}\Delta_{Hxc}^N = 0$ equals the physical band gap calculated by differences of GGA Δ SCF calculations of the total GGA energies of the N -, the $(N - 1)$ -, and the $(N + 1)$ -electron system, which also equals the GGA KS band gap. Thus the problem to calculate physical band gaps with GGA methods does not originate from the GGA xc potentials but is a consequence of the fact that GGA energy functionals are not suitable for this purpose.

The shortcoming of GGA xc energies to describe ionization potentials and electron affinities of periodic systems in the limit of infinite size has its origin in their functional form. Indeed such shortcomings will plague any xc energy functional with functional derivatives with respect to the electron density that have the form $^{(2)}f_{Hxc}^{GGA}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')$ for the second-order derivative and correspondingly the form $^{(n)}f_{Hxc}^{GGA}(\mathbf{r}_1)$ times products of δ functions in the variables $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n$ for the n th-order functional derivative. Thus, due to basic limitations of the ansatz, there is no chance to develop GGA-type xc functionals that can correctly describe the physical band gap of semiconductors.

It is crucial to note that the incapability of GGA functionals to describe band gaps of infinite systems is a failure of the GGA but not of the KS formalism itself. Approximate functionals for the xc energy with a form different from that of GGA functionals, in particular orbital-dependent functionals [30], exhibit nonzero potential adjustors $\Delta_{Hxc}^{N-}[\tilde{v}_{Hxc}]$ and $\Delta_{Hxc}^{N+}[\tilde{v}_{Hxc}]$ and nonzero derivative discontinuities Δ_{Hxc}^N not only for finite but also for infinite systems. The exact-exchange (EXX) only KS method [36–39], i.e., a method which treats the exchange energy and the corresponding local multiplicative KS exchange potential exactly but neglects correlation completely, e.g., leads to large derivative discontinuities $^{EXX}\Delta_{Hxc}^N$ of the Hartree plus exchange energy and large potential adjustors $^{EXX}\Delta_{Hxc}^{N-}[\tilde{v}_{Hxc}]$ and $^{EXX}\Delta_{Hxc}^{N+}[\tilde{v}_{Hxc}]$ in semiconductors [35]. The derivative discontinuity $^{EXX}\Delta_{Hxc}^N$ equals the linear term in an expansion of the derivative discontinuity along the adiabatic connection introduced in Ref. [40]. If $^{EXX}\Delta_{Hxc}^N$ is added to the EXX KS band gap the resulting physical band gaps are much larger than those found in experiment. This can be attributed to the neglect of correlation. If the exact treatment of exchange is accompanied by some suitable correlation functional, e.g., within the random-phase approximation, then reasonable band gaps should be obtained.

If the GGA xc functional is considered as ensemble density functional in a naive straightforward way then the difference of the GGA Hxc energies for an electron number N and a fractional electron number q with $N - 1 < q < N$ is given by Eq. (25) with ρ_0^N replaced by $(N - q)\rho_0^N$. Because the quadratic and higher-order terms on the right-hand side of Eq. (25) vanish, the GGA Hxc energy changes linearly with the electron number q in the limit of an infinite system. This means even if GGA functionals are used in a naive and straightforward way as ensemble functionals, then GGA xc energies correctly change linearly with the electron number in the limit of infinite systems. Thus, for infinite systems, GGA functionals do not suffer from localization and delocalization errors as they are described in Refs. [10,11] for finite systems. Nevertheless GGA xc potentials do not exhibit a discontinuity

at integer electron numbers and show the various other shortcomings typical for GGA functionals. Thus the concept of localization and delocalization errors for detecting and analyzing shortcomings of xc density functionals seems to be questionable in the case of infinite systems.

VI. CONCLUSIONS

It was shown that approximate xc potentials generally exhibit discontinuities at integer electron numbers for finite systems provided functional derivatives are taken in the correct way. In contrast to hitherto common belief, this is also true for GGA xc potentials. Discontinuities of xc potentials were identified as derived quantities which automatically emerge if the xc potentials are constructed properly with the use of potential adjustors presented here. By the integer electron ensemble approach (IEEA) introduced here it could be moreover demonstrated that all relevant objects of the ensemble KS formalism can be expressed in terms of quantities readily available in the KS formalism of integer electron numbers. This has strong implications for strategies to construct new xc functionals. *Efforts for the development of xc functionals only need to concentrate on energy functionals for integer electron numbers.* Specific attempts to generate discontinuities in xc potentials at integer electron numbers are not necessary.

In the limit of infinite systems GGA xc potentials do not exhibit discontinuities at integer electron numbers even if the derivatives are taken properly via the IEEA. On the other hand, the GGA xc energy correctly behaves linearly with the particle number in the limit of infinite systems even if the GGA xc functional in a naive straightforward way is used as ensemble density functional. This means in the limit of infinite systems GGA functionals despite their shortcomings do not exhibit localization or delocalization errors, which means that the concept to analyze approximate xc functionals in terms of these errors seems not to make sense in this case. It is important to recognize that the lack of discontinuities in infinite systems is a shortcoming of the GGA energy functional but not a general shortcoming of the KS formalism. For orbital-dependent functionals for the xc energy the IEEA leads to xc potentials with discontinuities even in the limit of infinite systems. Indeed with the potential adjustors emerging in the IEEA it is possible to convert KS band structures in approximate quasiparticle band structures which exhibit the exact fundamental quasiparticle band gap. In practice, of course, the band gaps would not be exact but their quality would depend on the quality of the orbital-dependent xc functional. Thus the potentials adjustors of the IEEA open up a new route to fundamental band gaps completely within the KS formalism without the need to resort to many-body perturbation theory approaches like the GW method.

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