Hardness of molecules and the band gap of solids within the Kohn-Sham formalism: A perturbation-scaling approach

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The finite difference expression for the hardness of atoms and molecules, i.e. half the difference between the ionization potential and the electron affinity according to Parr and Pearson [J. Am. Chem. Soc. **105**, 7512 (1983)], is expressed here as an explicit functional of the Kohn-Sham orbitals, of the Kohn-Sham eigenvalue differences, of the Coulomb potential, and of certain parts of the exchange-correlation potential. The functional is derived by exploiting the relationship between uniform coordinate scaling of the electron density and a perturbation theory with respect to the electron-electron interaction. The hardness is obtained as a perturbation expansion consisting of terms which each are connected to a specific order of e^2 with e being the electronic charge. This allows one, in principle, to determine the hardness exactly within the Kohn-Sham method or, in actual applications, up to some chosen order in e^2. The actual expansion is displayed through second order. To some extent the results are also valid in the case of band gaps of solids.

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I. INTRODUCTION

The band gap of solids is the difference between the ionization potential and the electron affinity. The finite difference expression for the hardness of atoms and molecules is identified by Parr and Pearson as half of this difference [1,2]. However, in this work, for notational simplicity, the hardness shall be defined, like the band gap, as the full difference between ionization potential and electron affinity. The hardness is essential for characterizing the chemical behavior and reactivity of a species. The band gap determines the electronic conductivity of solids, a point, which especially for semiconductors, is of great technical importance. Therefore, calculations of hardness and of band gaps are of great interest.

For the theoretical investigation of the electronic structure of atoms or molecules, the Kohn-Sham (KS) procedure [2,3] of the density-functional theory (DFT) [2,3] is quite prevalent. As far as solids are concerned, the KS scheme is the dominant theoretical method to describe electronic structure. However, the KS approach suffers from the so-called band-gap problem, i.e., the fact that even the exact KS band gap, as determined by orbital energy differences, differs from the physical band gap [4−6]. Similarly, the hardness of an atom or molecule is not just given by the difference between the eigenvalues of the lowest unoccupied and the highest occupied KS orbitals.

In this work, we express the physical hardness as a functional of the KS orbitals, the KS eigenvalues, and the exchange-correlation potential. These quantities are obtained in any KS procedure. The perturbation-theory expression derived in this work for the hardness allows its calculation in a straightforward manner after a KS calculation for the neutral compound has been performed. Additional KS calculations for the positively or the negatively charged species are not necessary. We only require that the employed approximate correlation functional and potential obey certain scaling conditions that are known to hold for the exact correlation functional. The energy difference between the eigenvalues of the lowest unoccupied and the highest occupied KS orbitals represents the zeroth-order contribution to the perturbation-theory expansion of the hardness derived here.

The results of this work are valid for all finite electronic systems, including those with periodic boundary conditions. Solids are usually described as systems with periodic boundary conditions in the limit of the system size approaching infinity, i.e., the thermodynamic limit. To some extent the results obtained here are also valid in this limit. The work we report on here exploits relations between uniform coordinate scaling of the electron-density and perturbation-theory expressions of the exchange-correlation energy [7−9].

II. BASIC FORMALISM AND FORMULAS

We consider electronic systems characterized by the Schrödinger equation

$$[\hat{T} + \hat{V}_{ee} + \hat{v}]\Psi(M) = E(M)\Psi(M), \tag{1}$$

with electron numbers $M = N$, $M = N-1$, and $M = N+1$. In Eq. (1), $\hat{T}$ stands for the operator of the kinetic energy $\hat{V}_{ee}$ for the operator of the electron-electron repulsion. The external potential, v(r) leading to the operator $\hat{v}$, is usually generated by the nuclei of the system under consideration. The ground-state wave function $\Psi[N]$ with energy eigenvalue $E[N]$, shall yield the density $n(\mathbf{r})$. The ionization energy $IP(N)$, the electron affinity $EA(N)$, and the hardness or band-gap $\Delta_\mu[n]$ are given by

$$IP(N) = E(N-1) - E(N), \qquad (2a)$$

$$EA(N) = E(N) - E(N+1), \qquad (2b)$$

$$\Delta_\mu[n] = IP(N) - EA(N) = E(N+1) + E(N-1) - 2E(N). \qquad (3)$$

The hardness or band-gap $\Delta_\mu[n]$ is developed in a series expansion

$$\Delta_\mu[n] = \sum_{i=0}^{\infty} c_i[n], \qquad (4)$$

consisting of terms $c_i[n]$ which, like $\Delta_\mu[n]$, are functionals of the ground-state density $n(\mathbf{r})$ of the N-electron system and which are connected to the ith order in e^2 with e being the electronic charge. The terms $c_i[n]$ are given by

$$c_i[n] = H_i^{N+1}[\{\varphi_j[n]\},\{\varepsilon_j[n] - \varepsilon_{j'}[n]\},\{v_1[n], \ldots v_{i-1}[n]\}] + H_i^{N-1}[\{\varphi_j[n]\},\{\varepsilon_j[n] - \varepsilon_{j'}[n]\},\{v_1[n], \ldots v_{i-1}[n]\}]$$

$$- 2H_i^N[\{\varphi_j[n]\},\{\varepsilon_j[n] - \varepsilon_{j'}[n]\},\{v_1[n], \ldots v_{i-1}[n]\}] - [\langle \varphi_{N+1}|\hat{v}_i[n]|\varphi_{N+1}\rangle - \langle \varphi_N|\hat{v}_i[n]|\varphi_N\rangle]. \qquad (5)$$

The expressions H_i^{N+1}, H_i^{N-1}, and H_i^N are explicit functionals of the KS orbitals $\{\varphi_j[n]\}$, differences $\{\varepsilon_j[n] - \varepsilon_{j'}[n]\}$ between KS eigenvalues, and of potentials $v_k([n];\mathbf{r})$ with $1 \leq k \leq (i-1)$. The KS orbitals $\{\varphi_j[n]\}$, the differences $\{\varepsilon_j[n] - \varepsilon_{j'}[n]\}$, and the potentials $v_k([n];\mathbf{r})$ all belong to the N-electron system with density $n(\mathbf{r})$. The potential $v_k([n];\mathbf{r})$ with $k \geq 1$ is the contribution of order k in e^2 to the exchange-correlation potential. This contribution can be obtained from the exchange-correlation potential by a simple projection technique [8] described later on. Because the KS orbitals, the KS eigenvalue differences, and the potentials $v_k([n];\mathbf{r})$, are functionals of $n(\mathbf{r})$, the expressions H_i^{N+1}, H_i^{N-1}, and H_i^N also are functionals of the ground-state density $n(\mathbf{r})$. A crucial property of the expressions H_i^{N+1}, H_i^{N-1}, and H_i^N and subsequently of the terms $c_i[n]$ is that they are not affected by an addition of an arbitrary constant to the potentials $v_k([n];\mathbf{r})$. We emphasize that only quantities belonging to the N-electron system and its density $n(\mathbf{r})$ appear on the right-hand side of Eq. (5). Quantities of the $(N-1)$- and $(N+1)$-electron systems are not involved.

Before Eqs. (4) and (5) are derived, and the expressions H_i^{N+1}, H_i^{N-1}, and H_i^N as well as the potentials $v_k([n];\mathbf{r})$ are defined exactly, we exhibit Eq. (5) for zeroth, first, and second order. The zeroth-order potential $v_0([n];\mathbf{r})$ is the negative of the KS potential $v_s([n];\mathbf{r})$, and H_0^{N+1}, H_0^{N-1}, and H_0^N are given by the kinetic energies of Slater determinants $\Phi(N+1)$, $\Phi(N-1)$, and $\Phi(N)$. The determinant $\Phi(N)$ is the ground-state KS determinant corresponding to the ground-state N-electron system described by the Schrödinger equation (1), i.e., the KS determinant of $n(\mathbf{r})$. The Slater determinants $\Phi(N+1)$ and $\Phi(N-1)$ are obtained from $\Phi(N)$ by occupying the energetically lowest unoccupied KS orbital associated with $\Phi(N)$ and by leaving the energetically highest occupied KS orbital of $\Phi(N)$ unoccupied, respectively. Note, that whereas $\Phi(N)$ is the KS determinant corresponding to $\Psi(N)$, and where $\Psi(N) \to n(\mathbf{r})$, the determinants $\Phi(N+1)$ and $\Phi(N-1)$ are not the KS determinants related to $\Psi(N+1)$ and $\Psi(N-1)$.

Equation (5) for zeroth order, or the $c_0[n]$ in Eq. (4), is

$$c_0[n] = \langle \Phi(N+1)|\hat{T}|\Phi(N+1)\rangle - \langle \Phi(N)|\hat{T}|\Phi(N)\rangle - [\langle \Phi(N)|\hat{T}|\Phi(N)\rangle - \langle \Phi(N-1)|\hat{T}|\Phi(N-1)\rangle]$$

$$- [\langle \varphi_{N+1}|\hat{v}_0[n]|\varphi_{N+1}\rangle - \langle \varphi_N|\hat{v}_0[n]|\varphi_N\rangle],$$

$$= \langle \varphi_{N+1}|\hat{T}|\varphi_{N+1}\rangle - \langle \varphi_N|\hat{T}|\varphi_N\rangle - \langle \varphi_{N+1}|\hat{v}_0[n]|\varphi_{N+1}\rangle + \langle \varphi_N|\hat{v}_0[n]|\varphi_N\rangle$$

$$= \langle \varphi_{N+1}|\hat{T} + \hat{v}_s[n]|\varphi_{N+1}\rangle - \langle \varphi_N|\hat{T} + \hat{v}_s[n]|\varphi_N\rangle, = \varepsilon_{N+1}[n] - \varepsilon_N[n]. \qquad (6)$$

Equation (6) shows that the difference in the energy eigenvalues of the lowest unoccupied and the highest occupied KS orbitals, i.e., the KS hardness, is just the zeroth-order contribution to the physical hardness with respect to e^2.

The potential $v_1([n];\mathbf{r})$ is the sum of the classical Coulomb potential $u([n];\mathbf{r})$ and the exchange potential $v_x([n];\mathbf{r})$, which are the functional derivatives with respect to the density $n(\mathbf{r})$ of the Coulomb energy $U[n]$ and the exchange energy $E_x[n]$, respectively. Equation (5), for first order, gives

$$c_1[n] = \langle \Phi(N+1)|\hat{V}_{ee}|\Phi(N+1)\rangle - \langle \Phi(N)|\hat{V}_{ee}|\Phi(N)\rangle - [\langle \Phi(N)|\hat{V}_{ee}|\Phi(N)\rangle - \langle \Phi(N-1)|\hat{V}_{ee}|\Phi(N-1)\rangle]$$

$$- [\langle \varphi_{N+1}|\hat{v}_1[n]|\varphi_{N+1}\rangle - \langle \varphi_N|\hat{v}_1[n]|\varphi_N\rangle],$$

$$= \langle \varphi_{N+1}|\hat{v}_x^{NL}[n]|\varphi_{N+1}\rangle - \langle \varphi_N|\hat{v}_x^{NL}[n]|\varphi_N\rangle - \langle \varphi_{N+1}|\hat{v}_x[n]|\varphi_{N+1}\rangle + \langle \varphi_N|\hat{v}_x[n]|\varphi_N\rangle, \qquad (7)$$

where $\hat{v}_x[n]$ is equal to $v_x([n];\mathbf{r})$ and where $\hat{v}_x^{NL}[n]$ is equal to

$$v_x^{NL}([n];\mathbf{r},\mathbf{r}') = \sum_{i=1}^{N} \frac{\varphi_i([n];\mathbf{r})\varphi_i([n];\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \qquad (8)$$

when coordinate space is employed. The operator $\hat{v}_x^{NL}[n]$ belonging to the nonlocal potential $\int d\mathbf{r}' v_x^{NL}(\mathbf{r},\mathbf{r}')$ is a "Hartree-Fock-like" exchange operator built from KS orbitals. Note that $\hat{v}_x^{NL}[n]$ is different from $\hat{v}_x[n]$.

Equation (7) shows that $c_1[n]$ can be considered as the exchange contribution to the hardness $\Delta_\mu[n]$. In the limit of systems of infinite size, Eq. (7) for the contribution $c_1[n]$ to $\Delta_\mu[n]$ was previously derived by Perdew [6]. Li, Krieger, and Iafrate [10] derived Eq. (7) for finite systems with boundary conditions that require the electron density to asymptotically decay exponentially. Moreover, for the latter systems, the above authors showed [6,10] that

$$\langle \varphi_N | \hat{v}_x^{NL}[n] | \varphi_N \rangle = \langle \varphi_N | \hat{v}_x[n] | \varphi_N \rangle, \qquad (9)$$

for which a very quick derivation has recently been provided by us [11], for the case of finite systems, through coordinate scaling. Further, the above equality simplifies expression (7) to

$$c_1[n] = \langle \varphi_{N+1} | \hat{v}_x^{NL}[n] | \varphi_{N+1} \rangle - \langle \varphi_{N+1} | \hat{v}_x[n] | \varphi_{N+1} \rangle. \qquad (10)$$

Equations (9) and (10), in contrast to all other equalities appearing in this work, are *not* invariant with respect to the addition of a constant to the involved local potential, namely, to $v_x([n];\mathbf{r})$. In this paragraph $v_x([n];\mathbf{r})$ is instead completely defined within the more general ensemble DFT allowing noninteger electron densities. This definition leaves no freedom of additive constants and gives the potential $v_x([n];\mathbf{r})$ as the functional derivative with respect to the density of the exchange energy taken from the electron deficiency side of the density $n(\mathbf{r})$ integrating to N. Finite systems that require the electron density to asymptotically decay exponentially constitute a special case. For those systems, the definition of $v_x([n];\mathbf{r})$ given above is equivalent with the condition that $v_x([n];\mathbf{r})$ goes to zero asymptotically. The latter can be achieved by the addition of an appropriate constant to $v_x([n];\mathbf{r})$ if necessary.

While the zeroth- and first-order potentials $v_1([n];\mathbf{r})$ are connected to the KS potential and the sum of the Coulomb and the exchange potentials, the higher-order potentials sum up to the correlation potential

$$v_c([n];\mathbf{r}) = \sum_{i=2}^{\infty} v_i([n];\mathbf{r}). \qquad (11)$$

The various contributions $v_i([n];\mathbf{r})$, with $i \geqslant 2$, can be generated from $v_c([n];\mathbf{r})$ by a projection technique exploiting the behavior of the $v_i([n];\mathbf{r})$ under uniform coordinate scaling of the density $n(\mathbf{r})$ [8],

$$v_i([n_\lambda];\mathbf{r}) = \lambda^{2-i} v_i([n];\lambda\mathbf{r}), \qquad (12)$$

with the uniformly scaled density $n_\lambda(\mathbf{r})$ being defined by

$$n_\lambda(\mathbf{r}) = \lambda^3 n(\lambda\mathbf{r}). \qquad (13)$$

The second-order potential $v_2([n];\mathbf{r})$ can now be obtained as

$$v_2([n];\mathbf{r}) = \lim_{\lambda\to\infty} v_c([n_\lambda];\mathbf{r}/\lambda). \qquad (14)$$

The third-order potential $v_3([n];\mathbf{r})$ is accessible by subtraction of $v_2([n];\mathbf{r})$ from $v_c([n];\mathbf{r})$, multiplication of the remainder by λ, replacement of $\mathbf{r}$ by $\mathbf{r}/\lambda$, and consideration of the result for densities $n_\lambda(\mathbf{r})$ in the limit $\lambda\to\infty$. The higher-order potentials $v_i([n];\mathbf{r})$ can be constructed in an analogous way. Equations (11)–(14) follow from similar equations for the correlation energy $E_c[n]$, namely, from

$$E_c[n] = \sum_{i=2}^{\infty} F_i[n], \qquad (15)$$

$$F_i[n_\lambda] = \lambda^{2-i} F_i[n], \qquad (16)$$

and

$$F_2[n] = \lim_{\lambda\to\infty} E_c[n_\lambda], \qquad (17)$$

because $v_c([n];\mathbf{r})$ and $v_i([n];\mathbf{r})$ are the functional derivatives, with respect to $n(\mathbf{r})$, of $E_c[n]$ and $F_i[n]$, respectively [8]. The noninteracting kinetic energy, i.e., the kinetic energy of the KS determinant $\Phi(N)$ corresponding to the density $n(\mathbf{r})$, is identified with $F_0[n]$, whereas the sum of the Coulomb energy $U[n]$ and the exchange energy $E_x[n]$ is identified with $F_1[n]$. The sum of the $F_i[n]$ to all orders then is equal to the Hohenberg-Kohn functional [2,3] for the density $n(\mathbf{r})$.

Equation (15) is a special case of the equation

$$E_c^\alpha[n] = \sum_{i=2}^{\infty} \alpha^i F_i[n], \qquad (18)$$

where $E_c[n]$ is identical to $E_c^1[n]$. The energy $E_c^\alpha[n]$ is the correlation energy corresponding to the density $n(\mathbf{r})$ if the electron-electron interaction is scaled by a coupling-constant α ($\alpha=0$ corresponds to a noninteracting system, $\alpha=1$ to a fully interacting one) [8]. Combination of Eq. (18) with the following relation [7]:

$$E_c^\alpha[n] = \lambda^{-2} E_c^1[n_\lambda] = \lambda^{-2} E_c[n_\lambda] = \alpha^2 E_c[n_{1/\alpha}],$$

$$\text{with } \lambda = 1/\alpha \qquad (19)$$

leads to the fundamental Eq. (16) which connects perturbation theory with respect to the electron-electron interaction and uniform scaling of the electron density. Equation (18), and subsequently also Eqs. (15) and (16), as well as Eqs. (11) and (12), are based upon the assumption that the correlation energy, and therewith also the total energy of an electronic system, can be developed in a Taylor series with respect to a coupling constant $\alpha=e^2$ of the electrons for $0 \leqslant \alpha \leqslant 1$. This

assumption is reasonable and generally made in many-electron theory. Equation (17) is derived in Ref. [7] without making this assumption. Equation (17) explains why the first term in the series expansion of $E_c^\alpha[n]$ is of second order in α.

Approximations to the correlation functional and potential should allow a decomposition into components $E_i[n]$ and $v_i([n];\mathbf{r})$, respectively. In fact the question to what extent this decomposition is possible can be used as a criterion for the quality of approximate correlation functionals and potentials. The limits (14) and (17) exist for some approximate functionals [12] and do not exist for others including the common local-density approximation (LDA) [2,3]. The violation of Eq. (17) by the LDA is not surprising because the LDA originates from the homogeneous electron gas. For the latter model system a norm conserving uniform coordinate

scaling of the density is not possible. However, real systems are always finite.

The theoretical treatment of solids formally can be split into two steps. First, a finite system with periodic boundary conditions is considered and later, the thermodynamic limit is taken. As long as the theoretical treatment is based on normalizable wave functions, including those with periodic boundary conditions, the described projection technique should be applicable. Therefore, approximate exchange-correlation functionals should be designed in such a way that they allow the use of the projection technique. This requirement is especially important because the same approximate exchange-correlation functionals are used to treat solids as well as atoms and molecules.

Using the operator $\hat{v}_2[n]$ corresponding to the potential $v_2([n];\mathbf{r})$ of Eq. (14), the second-order contribution $c_2[n]$ to the hardness $\Delta_\mu[n]$ is given by

$$c_2[n] = \sum_k \frac{|\langle \Phi(N+1)|\hat{V}_{ee} - \hat{u}[n] - \hat{v}_x[n]|\Phi^k(N+1)\rangle|^2}{E_0(N+1) - E_0^k(N+1)} + \sum_k \frac{|\langle \Phi(N-1)|\hat{V}_{ee} - \hat{u}[n] - \hat{v}_x[n]|\Phi^k(N-1)\rangle|^2}{E_0(N-1) - E_0^k(N-1)}$$

$$- 2\sum_k \frac{|\langle \Phi(N)|\hat{V}_{ee} - \hat{u}[n] - \hat{v}_x[n]|\Phi^k(N)\rangle|^2}{E_0(N) - E_0^k(N)} - [\langle \varphi_{N+1}|\hat{v}_2[n]|\varphi_{N+1}\rangle - \langle \varphi_N|\hat{v}_2[n]|\varphi_N\rangle]. \tag{20}$$

In Eq. (20), $\Phi^k(M)$, with M being $N-1$, N, or $N+1$ denotes excited Slater determinants which are obtained by substituting occupied orbitals building the Slater determinants $\Phi(M)$ by unoccupied ones. The index k runs over all single and doubly excited determinants, i.e., all determinants in which one or two occupied orbitals are substituted. For higher excited determinants the expectation values in Eq. (20) vanish. The energies $E_0^k(M)$ are given by the sum of the KS eigenvalues of the KS orbitals building the corresponding determinant $\Phi^k(M)$. Similarly, $E_0(M)$ is the energy associated with the basic Slater determinants $\Phi(M)$. The subscript 0 attached to the energies $E_0^k(M)$ and $E_0(M)$ symbolizes that the energies belong to Slater determinants which can be associated with model systems of hypothetical noninteracting electrons. Because the determinants $\Phi^k(M)$ are built by the KS orbitals $\{\varphi_i[n]\}$ and the energies $E_0^k(M)$ as well as $E_0(M)$ are sums of the KS orbital eigen-

values ε_i, Eq. (20) has, as required, the form of Eq. (5). If the single parts on the right-hand side of Eq. (2) are expressed by KS orbitals $\{\varphi_i[n]\}$ and by eigenvalue differences $\{\varepsilon_j[n] - \varepsilon_{j'}[n]\}$ then a large number of the emerging terms cancel. This simplifies the employment of Eq. (20) in actual calculations.

III. DERIVATION

In order to derive the basic Eq. (5), we consider the Schrödinger equations

$$[\hat{T} + \alpha\hat{V}_{ee} + \hat{v}^\alpha[n]]\Psi^\alpha(M) = E^\alpha(M)\Psi^\alpha(M), \tag{21}$$

with $M=N$, $M=N-1$, and $M=N+1$ and with the coupling constant α taking on values between zero and one. The potential $v^\alpha([n];\mathbf{r})$ is given by [8]

$$v^\alpha([n];\mathbf{r}) = -\frac{\delta T_s[n]}{\delta n(\mathbf{r})} - \alpha\frac{\delta([U[n] + E_x[n]])}{\delta n(\mathbf{r})} - \alpha^2\frac{\delta E_c[n_{1/\alpha}]}{n(\mathbf{r})},$$

$$= -\frac{\delta T_s[n]}{\delta n(\mathbf{r})} - \alpha\frac{\delta(U[n] + E_x[n])}{\delta n(\mathbf{r})} - \frac{E_c^\alpha[n]}{\delta n(\mathbf{r})},$$

$$= v_s([n];\mathbf{r}) - \alpha u([n];\mathbf{r}) - \alpha v_x([n];\mathbf{r}) - \alpha^2 v_c([n_{1/\alpha}];\alpha\mathbf{r}),$$

$$= -\sum_{i=0}^\infty \alpha^i v_i([n];\mathbf{r}), \tag{22}$$

with

$$v_c([n_{1/\alpha}];\alpha\mathbf{r}) = \frac{\delta E_c[n_{1/\alpha}]}{\delta n(\mathbf{r})}, \quad v_i([n];\mathbf{r}) = \frac{\delta F_i[n]}{\delta n(\mathbf{r})},$$

(23)

and with $v_0([n];\mathbf{r}) = -v_s([n];\mathbf{r})$, $v_1([n];\mathbf{r}) = u([n];\mathbf{r}) + v_x([n];\mathbf{r})$, and $v_i([n];\mathbf{r})$ for $i \geq 2$ being defined by Eqs. (11)–(17).

If, as in this work, densities are constrained to yield integer electron numbers, then the functional derivatives appearing in Eqs. (22) and (23), and subsequently also $v^\alpha([n];\mathbf{r})$, are defined only up to an additive constant. Therefore, the energy $E^\alpha[M]$ of Eq. (21) is undefined at this point. To remove this ambiguity we chose, for each order of α, one arbitrary member out of the one-dimensional manifold given by the functional derivatives $\delta F_i[n]/\delta n(\mathbf{r})$ to define the potentials $v_i([n];\mathbf{r})$ completely. The only condition in this otherwise arbitrary choice is that the equation

$$v^1([n];\mathbf{r}) = v(\mathbf{r})$$

(24)

is obeyed. Because of condition (24) the equation $E^1(M) = E(M)$ holds with $E(M)$ coming from the original Schrödinger Eq. (1). Of course, $\Psi^0(M) = \Phi(M)$ and $\Psi^1(M) = \Psi(M)$ are also valid.

In a DFT for ensembles, which allows densities to integrate to arbitrary electron number, no ambiguities due to additive constants in functional derivatives occur. At integer electron numbers, where derivative discontinuities appear, functional derivatives can be defined completely as the limit coming from the electron deficiency or surplus side. One then has to add a constant μ to the right-hand side of Eq. (22) in order to define the potential $v^\alpha([n];\mathbf{r})$ in such a way that Eq. (24) is obeyed. If the functional derivatives are taken from the electron deficiency side the constant μ turns out to be the ionization potential IP(N) [of the system described by Eq. (21)] which can be shown not to change along the coupling-constant path, i.e., not to change for different values of the coupling constant α in Eq. (21). The electron affinity $EA(N)$ on the other hand does change with the coupling-constant α if the potential $v^\alpha([n];\mathbf{r})$ is defined in this way. (These aspects are taken into account if the results of this paper are derived within the ensemble DFT framework [13].)

The Hamiltonian operator $\hat{T} + \alpha\hat{V}_{ee} + \hat{v}^\alpha[n]$, the wave functions $\Psi^\alpha(M)$, and the energies $E^\alpha(M)$, can be developed with respect to $\alpha = e^2$ into

$$\hat{T} + \alpha\hat{V}_{ee} + \hat{v}^\alpha[n]$$

$$= \hat{T} - \hat{v}_0[n] + \alpha[\hat{V}_{ee} - \hat{v}_1[n]] - \sum_{i=2}^{\infty} \alpha^i v_i[n],$$

(25)

$$\Psi^\alpha(M) = \sum_{i=0}^{\infty} \alpha^i \Psi_i(M),$$

(26a)

$$E^\alpha(M) = \sum_{i=0}^{\infty} \alpha^i E_i(M).$$

(26b)

The contributions $\Psi_i(M)$ and $E_i(M)$ are accessible by the perturbation theory [8]. The only difference from the standard perturbation theory is that the perturbation is not linear in α but contains terms to all orders in α. The unperturbed Hamiltonian operator $\hat{T} - \hat{v}_0[n]$ is equal to $\hat{T} + \hat{v}_s[n]$ because $v_0([n];\mathbf{r}) = -v_s([n];\mathbf{r})$. Therefore, the corresponding N-electron eigenstates, for $\alpha = 0$, are Slater determinants built of KS orbitals (for the ground-state $\Psi^0(M) = \Psi_0(M) = \Phi[M]$). Remember, that the determinant $\Phi[M]$ is the KS determinant of the interacting system described by the Schrödinger equation (1) only for $M = N$. The KS orbitals, of course, are the eigenstates of the one-electron equation corresponding to the Hamiltonian operator $\hat{T} + \hat{v}_s[n]$. The terms H_i^M appearing in Eq. (5) are defined as

$$H_i^M[\{\varphi_j[n]\},\{\varepsilon_j[n] - \varepsilon_{j'}[n]\},\{v_1[n], \ldots v_{i-1}[n]\}]$$

$$= E_i(M) - \langle\Psi_0(M)|\hat{v}_i[n]|\Psi_0(M)\rangle.$$

(27)

The functionals H_i^M and the energies $E_i(M)$ for second-order ($i = 2$) can be found in Ref. [8]. Equation (27) demonstrates the close relation of the functionals H_i^M to the perturbation-theory expressions $E_i(M)$. The calculation of higher-order functionals H_i^M is somewhat tedious but straightforward. All functionals H_i^M for orders $i \geq 2$ contain integrals of the type

$$\int d\mathbf{r}\, d\mathbf{r}' \frac{\varphi_i^*(\mathbf{r})\varphi_j^*(\mathbf{r}')\varphi_k(\mathbf{r})\varphi_l(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|},$$

which are not encountered in standard KS procedures. However, the evaluation of such integrals is well known from Hartree-Fock methods. Once the integrals are determined, the calculation of the functionals H_i^M requires basically only summations that can be carried out highly efficiently on modern computers. Therefore, the calculation of the contributions $c_i[n]$ to the hardness seems feasible, at least to second order.

Next, we have to show that the value of the functionals H_i^M is independent of our arbitrary choice of an additive constant in the potentials $v_i([n];\mathbf{r})$. For this, assume we add a constant β to the potential $v_i([n];\mathbf{r})$. This is tantamount to adding a constant $\alpha^i\beta$ to the potential $v^\alpha([n];\mathbf{r})$ in Eq. (21) and therefore shifts by $M\alpha^i\beta$ the energy $E^\alpha(M)$ of Eqs. (21) and (26b) and by $M\beta$ the energy $E_i[M]$ of Eq. (26b), i.e., the first term on the right-hand side of Eq. (27). The same energetic shift $M\beta$ occurs in the second term on the right-hand side of Eq. (27) and the two energetic shifts cancels each other. Therefore, H_i^M, as well as all terms to orders of α other than i, are not affected by the addition of a constant β to a potential $v_i([n];\mathbf{r})$.

Now the ionization potential and the electron affinity are expressed as

$$IP(N) = E^1(N) - E^1(N+1)$$

and

$$EA(N) = E^1(N-1) - E^1(N);$$

(28)

then energies $E^1(M)$ are developed in the perturbation series of Eq. (26b), and finally $IP(N)$ and $EA(N)$ are substituted into Eq. (3). The expressions (5) for the components of the

band gap result if one uses that, for $\alpha = 0$, the Hamiltonian operator of Eq. (21) turns into $\hat{T} + \hat{v}_s[n]$.

IV. CONCLUDING REMARKS

Equations (4) and (5) allow one, in principle, to determine the exact hardness within a KS scheme. Of course, the exact exchange and correlation potentials are unknown and one therefore has to resort to approximations that inevitably introduces inaccuracies. However, for given approximations to the exchange and correlation functionals, application of Eqs. (4) and (5) results in the physical hardness or band gap associated with these approximations, i.e., the best possible hardness or band gap to these approximations. In actual calculation, clearly, only a certain number of terms of expansion (4) may be taken into account [as mentioned above, evaluation of Eq. (5) should be possible up to second order]. How rapidly expansion (4) for the hardness converges remains to be seen and may depend on the type of the electronic system being considered.

The treatment of band gaps in solids according to the formalism introduced in this work leads to an additional difficulty because in this case one takes the thermodynamic limit, i.e., the limit of the system size approaching infinity. For a finite system with periodic boundary conditions all of the results of this work are valid. The thermodynamic limit of the zero- and first-order contributions to the band gap pose no problems and they can be calculated according to Eqs. (6) and (7) (compare also Ref. [6]). To evaluate the right-hand side of Eq. (7), techniques known from Hartree-Fock calculations for solids [14] have to be employed. From second order on, the question remains to be investigated whether individual contributions $c_i[n]$ to the band gap $\Delta_\mu[n]$ diverge if the size of the system is increased. At this point similar problems might occur as for the treatment of the electronic energy of the homogeneous electron gas for which perturbation-theory contributions to each single order in e^2 also diverge for orders higher than one. The approach of summing to infinity certain parts of expansion (4) also remains to be investigated. For alternative approaches to tackling the band-gap problem see, for example, Ref. [15].

Besides being used in their present form in actual calculations, the results of this work may be the starting point for further developments. So one could try to take into account higher-order contributions in Eq. (4) in an approximate way. This might lead to computationally more efficient procedures. Also, as already mentioned, techniques to analytically sum up terms or parts of terms of Eq. (4) may be investigated.

Of importance also is that the results presented give insight into formal aspects related to the hardness and band gap. For example, they illustrate that the hardness of a finite electronic system, such as an atom or molecule, is a functional of KS orbitals $\varphi_j[n]$, KS eigenvalue differences $\varepsilon_j[n] - \varepsilon_{j'}[n]$, and potentials $v_k([n];\mathbf{r})$ emerging exclusively from the KS treatment of the N-electron system. The corresponding $(N+1)$- and $(N-1)$-electron systems are not considered explicitly. Because the KS orbitals $\varphi_j[n]$, the KS eigenvalue differences $\varepsilon_j[n] - \epsilon_{j'}[n]$, and the potentials $v_k([n];\mathbf{r})$ are functionals of the ground-state density $n(\mathbf{r})$, this illustrates that the hardness is a functional of the ground-state electron density of the N-electron system alone, despite the fact that in the definition of the hardness the ground-state energy of the $(N-1)$- and $(N+1)$-electron systems appears.

Insight is also gained into the common separation of the hardness and band-gap $\Delta_\mu[n]$ into the difference $\varepsilon_{N+1}[n] - \varepsilon_N[n]$ between the lowest unoccupied and the highest occupied KS eigenvalues and the derivative discontinuity of the exchange-correlation potential at the integer electron number N in an ensemble DFT formalism. This derivative discontinuity is identified as the sum of the terms $c_i[n]$ for $i \geq 1$ as determined in Eqs. (4) and (5).

The correlation energy and potential in the ensemble DFT also can be developed into a series of the form of Eqs. (18) and (22). For densities integrating to integer electron numbers, the functional derivatives $\delta F_i[n]/\delta n(\mathbf{r}) = v_i([n];\mathbf{r})$ with $i \geq 1$ exhibit a discontinuity in ensemble DFT which is given by the constants $c_i[n]$ [13]. Similarly, the potential $v_0([n];\mathbf{r})$ which is related to the KS potential and the exchange potential, within ensemble DFT, are associated with discontinuities $c_0[n]$ and $c_1[n]$, respectively. Thus all contributions $c_i[n]$ to $\Delta_\mu[n]$ correspond to derivative discontinuities.

A comparison of values for the hardness calculated by the scheme given in this work with values obtained by performing separate KS calculations for the corresponding neutral, ionized, and negatively charged species, and subsequent employment of Eqs. (2) and (3), would be interesting. Such a comparison may be used as a test of the quality of approximate exchange-correlation density functionals because both approaches, of course, should lead to the same value for the hardness. [This requires that all nonnegligible terms of expansions (4) be taken into account.]

This work is a continuation of previous investigations of KS perturbation theory expansions of the exchange and correlation energies and their relations to a coordinate scaling of the electron density [7–9].

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