

Understanding Band Gaps of Solids in Generalized Kohn-Sham Theory

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Introduction. The fundamental energy gap of a periodic solid distinguishes insulators from metals and characterizes low-energy single-electron excitations. But the gap in the band-structure of the exact multiplicative Kohn-Sham (KS) [1,2] potential substantially underestimates the fundamental gap, a major limitation of KS density functional theory. Here we give a simple proof of a new theorem: In generalized KS theory (GKS), the band gap *equals* the fundamental gap for the approximate functional if the GKS *potential operator* is continuous and the density change is delocalized when an electron or hole is added. Our theorem explains how GKS band gaps from meta-generalized gradient approximations (meta-GGAs) and hybrid functionals can be more realistic than those from GGAs or even from the exact KS potential. It also follows from earlier work [3-6]. The band edges in the GKS one-electron spectrum are also related to measurable energies. A linear chain of hydrogen molecules provides a numerical illustration.

Band-gap problem in Kohn-Sham density functional theory. The most basic property of a periodic solid is its fundamental energy gap G , which vanishes for a metal but is positive for semiconductors and other insulators. G is the lowest single-electron excitation energy of a solid, controlling not only the conductivity but also the optical and thermal properties. It is also the unbound limit of an exciton series. So G is an excitation energy, but it is also a difference of ground-state energies: If $E(M)$ is the ground-state energy for a solid with a fixed number of nuclei and M electrons, and if $M = N$ for electrical neutrality, then

$$G = I(N) - A(N) = [E(N-1) - E(N)] - [E(N) - E(N+1)] \quad (1)$$

is the difference between the first ionization energy $I(N)$ and the first electron affinity $A(N)$ of the neutral solid. While I and A can be measured for a macroscopic solid, they can be computed directly (as ground-state energy differences) by starting from finite clusters and extrapolating to infinite cluster size, a computational challenge for three-dimensional solids.

Kohn-Sham density functional theory [1,2] is a formally-exact way to compute the ground-state energy and electron density of M interacting electrons in a multiplicative external potential. This theory sets up a fictitious system of non-interacting electrons with the same ground-state density as the

real interacting system, found by solving self-consistent one-electron Schrödinger equations. These electrons move in a *multiplicative* effective Kohn-Sham potential, the sum of the external and Hartree potentials and the derivative of the density functional for the exchange-correlation energy, $E_{xc}[n_{\uparrow}, n_{\downarrow}]$, which must be approximated. The simplest local spin density approximation (LSDA) [1] is already usefully accurate for many solids. Better still are generalized gradient approximations (GGAs) (e.g., [7]), meta-GGAs (e.g., [8,9]), and hybrids of GGA with exact exchange (e.g., [10,11]). The additional ingredients in higher-level functionals can in principle satisfy more exact constraints, or fit data better, achieving higher accuracy. KS theory has become the most widely-used method to calculate the ground-state energies, energy differences, electron densities, and equilibrium structures of molecules and solids, and, with less justification, the electronic band structures of solids. For a solid, KS theory produces a band structure, one-electron energies as functions of Bloch wavevector and band index, in which there can be a non-zero band gap,

$$g = \varepsilon^{LU} - \varepsilon^{HO} , \quad (2)$$

the difference between the lowest-unoccupied (LU) and highest-occupied (HO) one-electron energies.

In principle, should the band gap g equal the fundamental energy gap G ? In the early 1980's, band structure calculations were accurate enough to show that LSDA band gaps for semiconductors were often about half the measured fundamental energy gaps. Was this a failure of the LSDA effective potential to mimic the exact KS potential, or an inability of the exact KS potential (for the neutral solid) to predict the fundamental gaps, or both?

Regarding the fundamental gap G as an excitation energy, we do not expect it to equal the band gap g of the exact KS potential. But thinking of it as a ground-state energy difference, we might hope that it is. Williams and von Barth [12] gave a clear argument to support this hope, based on three assumptions: (I) Janak's theorem [13,14]: The one-electron energies of KS theory are derivatives of the total energy with respect to occupation number, in both finite and extended systems. This is unquestionably true. (II) When an electron is added or removed from a solid, the density change is infinitesimal and periodic. This assumption, only possible for an extended system, is often true, although there may be exceptions in which added electrons or holes get

stuck in localized states; see Refs. [15,16] for possible examples in one dimension. (III) When an electron is added or removed, the KS potential changes only infinitesimally. This assumption seemed to follow so naturally from (II) that it was only implicit in the argument, yet assumption III is incorrect.

Other work [17-20] of the early 1980's showed that the exact Kohn-Sham potential jumps up by an additive-constant *discontinuity* when an electron is added to a neutral solid, making

$$G^{exact} = g^{exact} + xc_discontinuity \quad (3)$$

The discontinuity spoils the interpretation of g , shifting the one-electron energies without changing the density. The KS potential is a mathematical fiction, acting on non-interacting electrons to yield the true ground-state density of the neutral solid and making the one-electron energy for the highest partly-occupied one-electron state equal to the true chemical potential $\mu = \partial E / \partial M$, which is itself discontinuous for an insulator when M crosses N . The xc discontinuity is absent in the LSDA and GGA approximations to the multiplicative exchange-correlation potential, for which [20]

$$G^{approx} = g^{approx}. \quad (4)$$

In Eq. (4), G of Eq. (1) and g of Eq. (2) are evaluated with the same approximate functional. While GGA improves ground-state energies and electron densities over LSDA, both approximations yield nearly the same band gaps g and hence fundamental gaps G . It has long been suspected (e.g., [20] that LSDA and GGA band gaps are close to exact KS band gaps (but not to true fundamental gaps).

Band-gap problem in generalized Kohn-Sham (GKS) theory. A simple, self-contained proof of our theorem will be given here. Refs. [3-6] by themselves also imply this result, as discussed in a later section.

Based mostly upon empiricism, realistic fundamental gaps for semiconductors (e.g., [21,22]) have been estimated from band gaps of hybrid functionals in GKS, which is also an excellent starting point for simple quasi-particle corrections [23]. A global hybrid replaces a fraction (e.g., 25%) of GGA exchange with that of Hartree-Fock, and replaces the same fraction of the GGA exchange potential with that of Hartree-Fock (an integral operator,

not a multiplication operator). Screened hybrids (e.g., [11]) additionally screen the interelectronic Coulomb potential in the exchange term, and typically improve results for semiconductors [21].

We argue that Eq. (4) is also valid for typical approximations in GKS theory, as typically implemented, extending the argument of Williams and von Barth [12] from KS to GKS theory. Thus the improvement in the hybrid band gap reflects an improvement in the hybrid value for G of Eq. (1). Our detailed argument, presented in the Methods section, generalizes assumption (I) of the Williams-von Barth argument [12] from KS to GKS theory, and notes that the GKS potentials, like the LSDA and GGA ones, have no discontinuity, consistent with Refs. [3-6].

While there is a formally-exact GKS theory [24], here we view GKS as a small step out of KS theory, in which one can use nonempirical approximations to E_{xc} that are constructed to satisfy the known exact constraints of KS theory. In rigorous KS density functional theory, the occupied Kohn-Sham one-electron states are demonstrably *implicit* functionals of the electron density that can be used to construct a density functional approximation, such as an *explicit* functional of the KS one-electron density matrix. For example, use the non-interacting kinetic energy density to construct a meta-GGA (e.g., [8]), or use the full KS density matrix to construct the Hartree-Fock exchange energy for a global hybrid [10]. Because the one-electron states are only implicit functionals of the density, the KS potential can be constructed only by the cumbersome optimized effective potential (OEP) method [25]. It is computationally faster to find the variationally optimized potential that minimizes the energy with respect to the non-interacting density matrix. The resulting GKS potential is not a multiplication operator, but is in practice continuous and self-adjoint. It is an integral (Fock) operator for hybrids [14], but a differential operator for meta-GGA's [26,27].

The step outside KS to GKS barely affects the occupied one-electron states, the electron density, and the total energy, but not so the one-electron energies. This was first shown by comparing exchange-only OEP (KS) and Hartree-Fock (GKS) results for atoms [25,28], and more recently [27] by comparing the corresponding KS and GKS implementations of meta-GGAs (exchange and correlation together) for solids. They produce closely similar

results for total energies, but the KS meta-GGA band gap is close to that of LSDA and GGA, while the GKS meta-GGA band gap is significantly larger and more realistic.

Within exchange-correlation approximations using the non-interacting density matrix, relaxing the KS demand for a multiplicative effective potential is a “practical” approximation with an unexpected benefit: It yields the interpretation of Eq. (4) for the GKS band gap of a solid, explaining how meta-GGAs and especially hybrids can improve the estimation of the fundamental energy gap of a solid: For a given approximate functional, the GKS band gap g is the ground-state energy difference G . Improvements in G correlate at least roughly with other improvements in ground-state energy differences.

Numerical demonstration. Because computational effort scales roughly like the cube of the number of atoms, three- and even two-dimensional periodic clusters are much harder to converge to the mesoscopic length scale, so we consider as a model a finite *one-dimensional* linear chain of realistic H_2 molecules. The separation between the nuclei of neighboring molecules is taken to be 1.25 times the separation between nuclei within a molecule (0.74 Å). With an even number (two) of electrons per unit cell, this is a band insulator. We consider chains with one to 500 molecules, and extrapolate carefully to an infinite number of molecules. The quadratic extrapolation is simplified by the observation that, at large numbers N_{mol} of molecules, the correction to the limit $N_{mol} \rightarrow \infty$ is of order $1/N_{mol}$ [16]. Figure 1 shows that, for all tested approximate functionals, $G - g$ tends to zero as $N_{mol} \rightarrow \infty$. Table 1 shows limiting values. Within numerical accuracy, as $N_{mol} \rightarrow \infty$, $I \rightarrow -\varepsilon^{HO}$, $A \rightarrow -\varepsilon^{LU}$, and $G \rightarrow g$.

The negative ions computed here are resonances, with negative electron affinity, captured by the finite basis set. But the resonance can evolve smoothly [29] to that of a bound state with positive electron affinity as the chain length grows. In contrast, even the resonant one-electron states can be converged with respect to basis set.

Relation to other previous work. The relation between GKS frontier orbitals and electron addition/removal energies was first shown in Refs. [3-6] for both extended and finite systems, and was demonstrated numerically for molecules in Ref. [3]. Refs. [3-6] by themselves imply our main result. Ref. [3] derives

the generalized Janak’s theorem for a differentiable functional of the one-particle density matrix (in its Eq. 10), namely, the GKS LU/HO orbital energies are the chemical potentials for electron addition/removal for both finite and extended systems, in a way that differs from the derivation in our Methods section. Refs. [3, 4] show that the GKS one-electron energy gap matches the GKS derivative gap -- the discontinuity in chemical potentials for electron addition and removal (Eq. 5 of [4]), which is equal to G for the exact functional and for functionals with linear behavior in M on either side of N , but generally differs from G for finite systems with approximate functionals (Eq. 6 of [4]). Ref. [4] further shows that the $E(M)$ curves are linear over M on either side of N for approximate functionals in periodic solids, and also for non-periodic systems as $N \rightarrow \infty$ when the approximate functionals have delocalization error. But the GKS derivative gap, is not equal to G for non-periodic systems as $N \rightarrow \infty$ for functionals with localization error, such as hybrid functionals with high fractions of exact exchange that localize an added electron or hole [4]. Combined, these statements yield our main conclusion.

Conclusions. The fundamental energy gap is the most basic property of a periodic solid. It cannot be found from a single Kohn-Sham band-structure calculation, even with the unattainable exact density functional. But high-level approximations, implemented in an efficient generalized KS scheme, yield band gaps equal to the fundamental gap for a given approximate functional. Future all-purpose non-empirical approximate functionals could predict usefully-correct gaps for most solids. The band edges in the GKS one-electron spectrum [30], relevant to interface formation and redox catalysis, can also be interpreted as measurable energy differences, as shown by Eq. (6) and illustrated in Table 1. They can be found in principle by extrapolating the GKS one-electron energies of a slab or cluster.

Typical approximate functionals, as typically implemented, obey Eq. (4). For three-dimensional solids [27], there is little or no improvement in G^{approx} from LSDA to GGAs, but substantially more from GGAs to meta-GGAs and especially hybrids, which introduce a fully-nonlocal dependence on the electron density, suggesting that, in solids, the exchange-correlation effects are more long-ranged (e.g., [21]) than in atoms and small molecules.

Methods. The self-consistent results reported here were found using the Gaussian code [S1] with a small cc-pvDZ basis set, to speed up the hybrid calculations for the longer chains. Many results were checked with the ADF [S2] (TZP basis) and FHI-aims [S3] (NAO-VCC-2Z basis) codes. The effect of increasing the basis from cc-pvDZ to TZP is to increase the $N_{mol} \rightarrow \infty$ limits of I and A in PBE by 0.14 and 0.10 eV, respectively, and to stabilize the negative-ion resonances for some of the larger finite chains. All codes show $G - g \rightarrow \sim 0.02$ eV, which we attribute to the slow convergence of G with increasing system size (Supplementary Material). All extrapolations display the increase of I and decrease of A from LSDA to HSE06.

Here, we derive the generalized Janak's theorem, and prove that the band gap and band edges of generalized Kohn-Sham theory are the appropriate ground-state energy differences, for a given approximate functional. In any constrained minimization, the Lagrange multiplier is the derivative of the minimized quantity with respect to the value of the constraint. Consider minimizing the orbital functional $E_v[\{f_j\},\{\psi_j\}]$, where $n(\vec{r}) = \sum_i f_i |\psi_i(\vec{r})|^2$ and the occupation numbers are restricted to the range $0 \leq f_i \leq 1$ with $\sum_i f_i = N$, subject to constraints $f_j \int d^3r |\psi_j(\vec{r})|^2 = f_j$ guaranteeing normalization of the occupied or partly-occupied orbitals. The Euler-Lagrange equation for this problem is $\delta\{E_v[\{f_j\},\{\psi_j\}] - \sum_i \varepsilon_i f_i \int d^3r |\psi_i(\vec{r})|^2\} = 0$, where the ε_i are Lagrange multipliers. The interpretation is

$$\varepsilon_i = \partial E / \partial f_i. \quad (5)$$

This is a *generalized* Janak's theorem. The same statement and derivation apply to the ungeneralized KS theory [13]. The minimizing one-electron wavefunctions are solutions of a one-electron Schrödinger equation with an optimal variational potential operator.

Consider a GKS calculation for an extended solid with an approximate xc functional, in which the ground-state delocalizes the density of the added electron or hole over the infinite solid. The variation of the approximated E is linear in f_i because the relaxation effect on the optimal variational potential

associated with the removal or addition of one electron is negligible. Then, by Eq. (5),

$$\begin{aligned} E(N) - E(N-1) &= \varepsilon^{HO}(N-\delta) \\ E(N+1) - E(N) &= \varepsilon^{LU}(N+\delta) \end{aligned} \quad (6)$$

where $\delta = 0^+$, and

$$I(N) - A(N) = \varepsilon^{LU}(N+\delta) - \varepsilon^{HO}(N-\delta). \quad (7)$$

Here HO and LU label the one-electron states of the $(N-\delta)$ -electron system, which change only infinitesimally when M increases through integer N . If the approximate xc potential in GKS theory has no discontinuity as the electron number crosses integer N , then

$$I(N) - A(N) = \varepsilon^{LU}(N) - \varepsilon^{HO}(N). \quad (8)$$

For a meta-GGA or hybrid functional, the optimum variational potential operator has been found explicitly (e.g., Eq. (7) of Ref. [27], Eq. (1.7) of Ref. [14]) and is continuous. Thus within LSDA, GGA, meta-GGA, or hybrid approximations, when implemented in GKS, the band gap equals the ground-state total energy difference.

In contrast, within an *ungeneralized* KS scheme, this statement remains true in LSDA and GGA, but *not* in meta-GGA or hybrid approximations. For meta-GGA and hybrid approximations, treated in OEP, as for exact KS theory [18],

$$\begin{aligned} I(N) - A(N) &= \varepsilon_{OEP}^{LU}(N+\delta) - \varepsilon_{OEP}^{HO}(N-\delta) = \\ &= \{\varepsilon_{OEP}^{LU}(N-\delta) - \varepsilon_{OEP}^{HO}(N-\delta)\} + \{\varepsilon_{OEP}^{LU}(N+\delta) - \varepsilon_{OEP}^{LU}(N-\delta)\}, \end{aligned} \quad (9)$$

where the first curly bracket is the OEP or KS band gap and the second is the contribution from the discontinuity of the OEP or KS potential [18,19].

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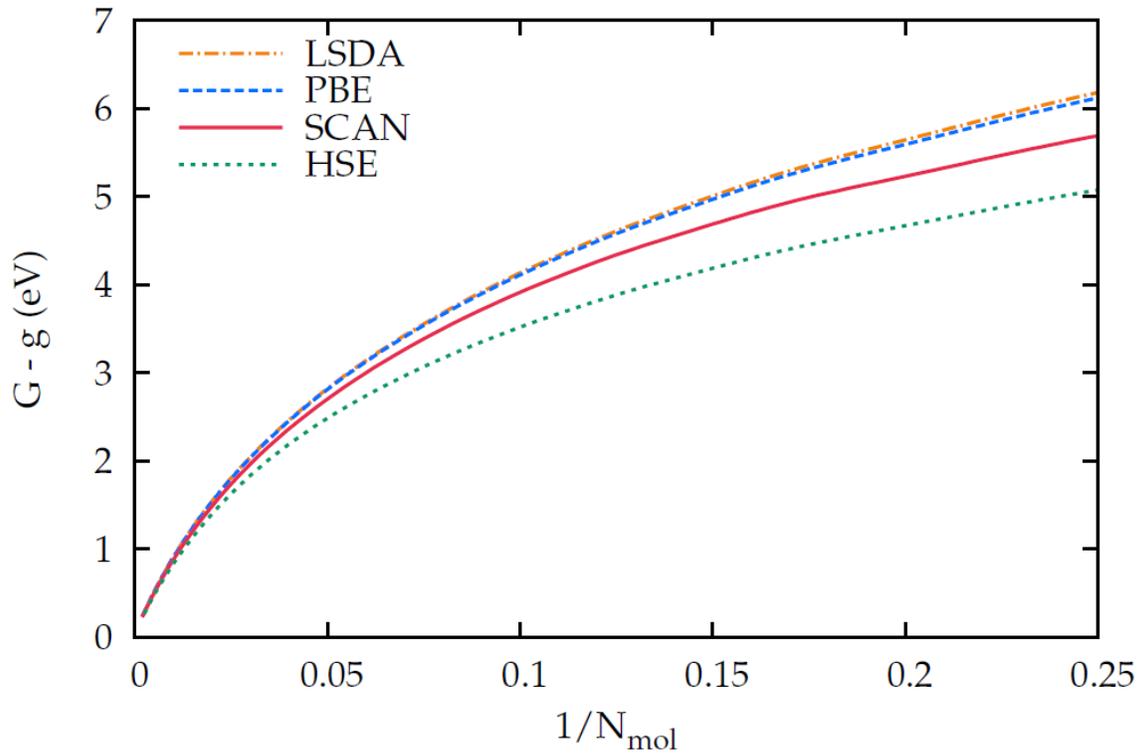


Fig. 1. Difference between the fundamental gap $G = I - A$ and the GKS band gap $g = \varepsilon^{LU} - \varepsilon^{HO}$ for a linear periodic chain of N_{mol} hydrogen molecules,

(eV)	$(I+A)/2$	I	$-\varepsilon^{HO}$	A	$-\varepsilon^{LU}$	G	g
LSDA	1.65	3.14	3.13	0.16	0.17	2.98	2.96
PBE	1.67	3.24	3.23	0.09	0.10	3.15	3.13
SCAN	1.68	3.33	3.31	0.01	0.02	3.32	3.29
HSE06	1.82	3.92	3.91	-0.29	-0.28	4.21	4.18

Table 1. Ionization energy I , electron affinity A , and fundamental gap $G=I-A$ of an infinite linear chain of H_2 molecules, evaluated by extrapolation from finite chains, and the band edges ε^{HO} , ε^{LU} and band gap $g = \varepsilon^{LU} - \varepsilon^{HO}$, in the LSDA, PBE GGA [7], SCAN meta-GGA [9], and HSE06 range-separated hybrid [11] functionals. The extrapolated band energies agree closely with those from a periodic-boundary-condition calculation (shown). $(I+A)/2$, the energy difference from the gap center to the vacuum level, depends only weakly on the approximation.

Supplementary Material

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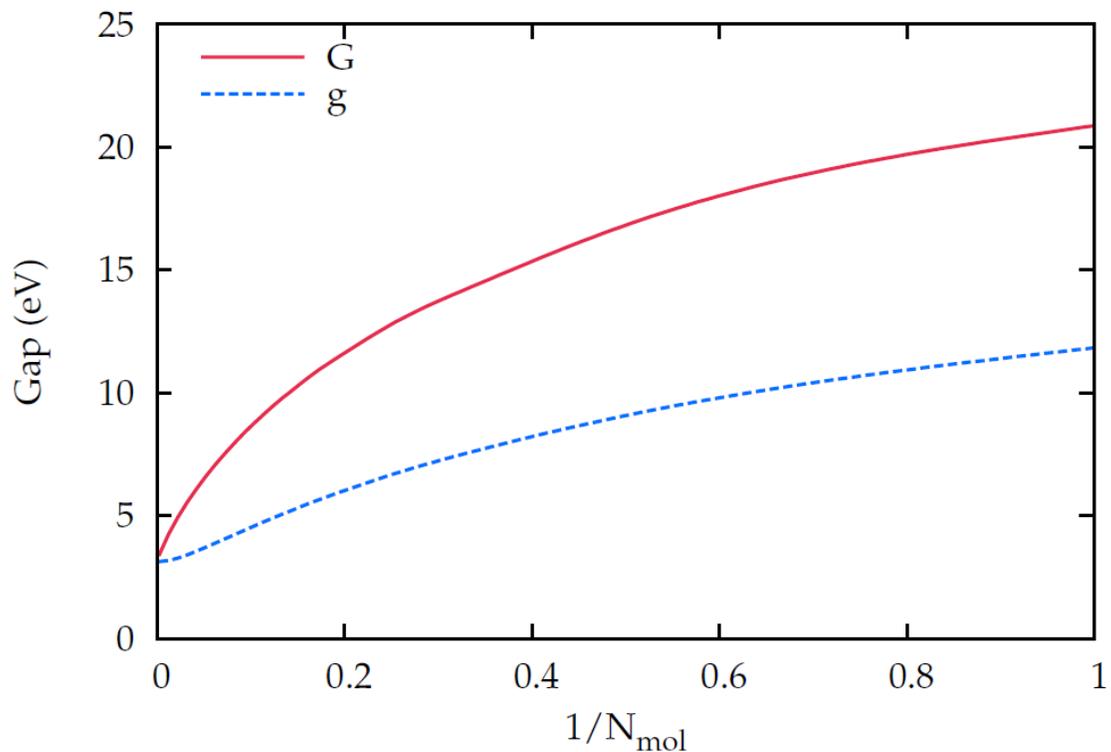


Figure S1. The PBE fundamental gap G and band gap g for a linear chain of N_{mol} H_2 molecules. Note that G converges to the limit $N_{mol} \rightarrow \infty$ much more slowly than g does.

Our electronic structure calculations have been made with three different codes: Gaussian [S1], ADF [S2], and FHI-aims [S3]. Our LSDA calculations used the parametrization of Ref. [S4].

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