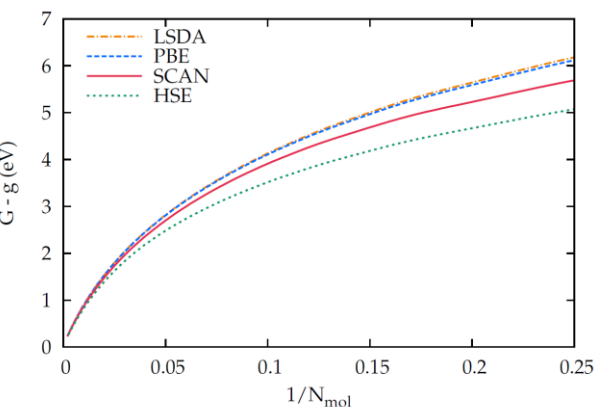


# Understanding Band Gaps of Solids in Generalized Kohn-Sham Theory



Showing that  $G-g$  tends to zero as the number of hydrogen molecules in a linear chain tends to infinity, in LSDA, the PBE GGA, and in the GKS implementations of the SCAN meta-GGA and the HSE hybrid.

J.P. Perdew, W. Yang, K. Burke, Z. Yang, E.K.U. Gross, M. Scheffler, G.E. Scuseria, T.M. Henderson, I.Y. Zhang, A. Ruzsinszky, H. Peng, J. Sun, E. Trushin, and A. Goerling, Proc. Nat. Acad. Sci. (USA) 114, 2801 (2017)

DOI: 10.1073/pnas.1621352114

CCDM Institutions: Temple, Duke, Rice

## Scientific Achievement

Accurate band gaps of solids are often found from hybrid density functionals that include about 25% of exact exchange. We have moved the justification for this from empiricism to first principles.

## Significance and Impact

The fundamental energy gap  $G$  of a solid distinguishes insulators from metals. It is a ground-state energy difference  $I-A$  as well as an excitation energy. The band gap  $g$  in the Kohn-Sham one-electron spectrum is only about 50% of  $G$  in the local spin density approximation (LSDA), the generalized gradient approximation (GGA), and even in the exact Kohn-Sham theory. But in generalized Kohn-Sham (GKS) theory, where the effective one-electron potential minimizes the energy without being constrained to be a multiplication operator,  $g=G$  for a solid. The accuracy of the hybrid functionals (standardly implemented in GKS) for ground-state energy differences makes them accurate for gaps in solids, while the lower accuracy of LSDA and GGA makes them less accurate.

## Research Details

- We give an analytic proof based on a generalized Janak's theorem.
- We give a numerical demonstration for a one-dimensional linear chain of hydrogen molecules, in the limit of infinite chain length.
- We give numerical demonstrations for two three-dimensional periodic solids, one a semiconductor and the other a large-gap insulator.



U.S. DEPARTMENT OF  
**ENERGY**

Office of  
Science



Center for the Computational Design  
of Functional Layered Materials



**TEMPLE**  
UNIVERSITY

---

**g = G for both the PBE GGA and the PBE0 hybrid in GKS, but not for the exact KS potential.**

**Ex. 3D semiconductor AlAs energy gaps (eV)**

<b>PBE g</b>	<b>PBE0 g</b>		<b>Exper. G</b>
<b>GKS=KS</b>	<b>KS</b>	<b>GKS</b>	

---

<b>1.35</b>	<b>1.54</b>	<b>2.58</b>	<b>2.23</b>
-------------	-------------	-------------	-------------

**The GKS xc potential for PBE0 includes 25% of the Hartree-Fock integral operator. The KS xc potential for PBE0 is the optimized effective multiplicative potential.**

---

**Theorem: The ground-state energy difference**

$$G = E(N-1) - 2E(N) + E(N+1)$$

**equals the gap  $g$  in the GKS one-electron energies, for a given approximate functional, if**

- (a) The system is infinitely extended in 1, 2, or 3 dimensions. (Connection to 2D materials).**
- (b) The density changes due to removing or adding an electron are delocalized and thus infinitesimal.**
- (c) The GKS or optimized non-multiplicative xc potential does not change discontinuously when an electron is added or removed.**

---

**These conditions are satisfied for extended periodic systems by LSDA, GGA, meta-GGA, and typical hybrid xc functionals, for which the GKS  $g = G$  improves as the ground-state energy differences improve in that order.**

**These conditions are not satisfied by the exact xc functional. The exact functional cannot be written as an explicit functional of only the occupied orbitals, so it has no GKS XC potential. Its KS xc potential is discontinuous, jumping up by an additive positive constant when the electron number crosses an integer from below.**

**(Perdew, Parr, Levy, and Balduz 1982)**

---

## Summary:

Hybrid density functionals like PBE0 or HSE, as standardly implemented in a generalized Kohn-Sham (GKS) scheme, yield realistic band gaps  $g$  for semiconductors and insulators in 1, 2, or 3 dimensions.

We have shown that this is “the right answer for the right reason”, even though the exact KS band gaps  $g$  seriously underestimate the fundamental gap  $G$ .