DFT for Solids: the HSE functional

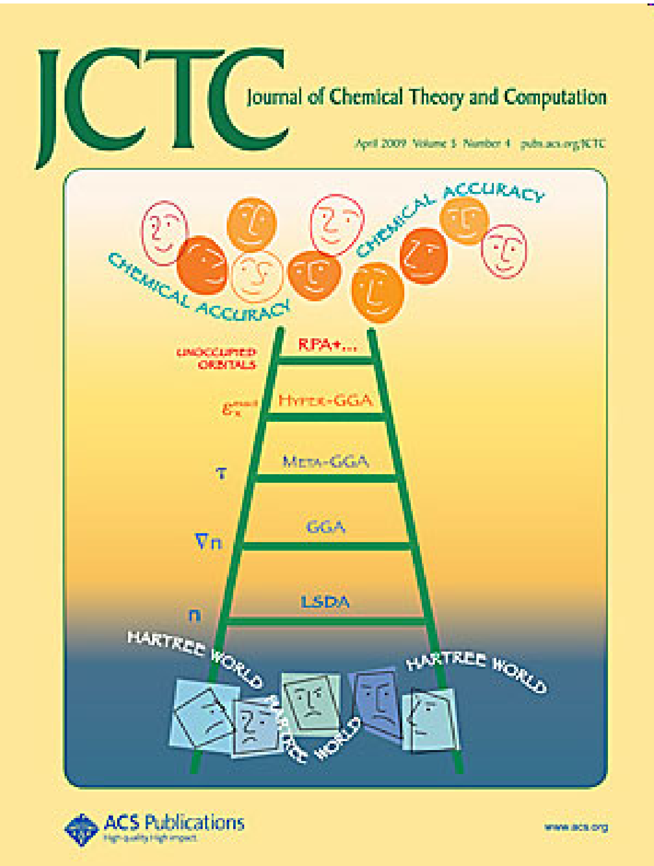
Gustavo E. Scuseria

Los Alamos Computational Condensed Matter Summer School
LANL, 16 June 2025

DFT: a hierarchy of approximations

Unlike wavefunction theory, **DFT** calculations in solids are relatively inexpensive and straightforward

- **LSDA:** functional of electron density
- **GGA** adds gradient of electron density
- **Meta-GGA** adds kinetic energy density
- **Hybrids** add **nonlocal HF-type** exchange
- **Screened exchange hybrids**
  - **LC-ωPBE** works well for **molecules** (keeps **LR HFx**)
  - **HSE** works well for **solids** (keeps **SR HFx**)



Hybrid Functionals

Molecules vs solids

- **Molecules:**
  - Long-range **HFx (1/r) is important**

- **Solids:**
  - **HFx** is problematic (cannot describe metals)
  - **LR-HFx** becomes pathological as the band gap closes
  - Tail of **HFx** is cancelled by correlation effects
  - **1/r** should be screened in exchange for solids

Range-separation for HF exchange

$$\frac{1}{r_{12}} = \frac{1 - erf(\omega\, r_{12})}{r_{12}} + \frac{erf(\omega\, r_{12})}{r_{12}} \qquad \omega \geq 0$$

short-range long-range

- **HF** with <u>only</u> short-range exchange *can* describe *metallic* behavior in periodic solids

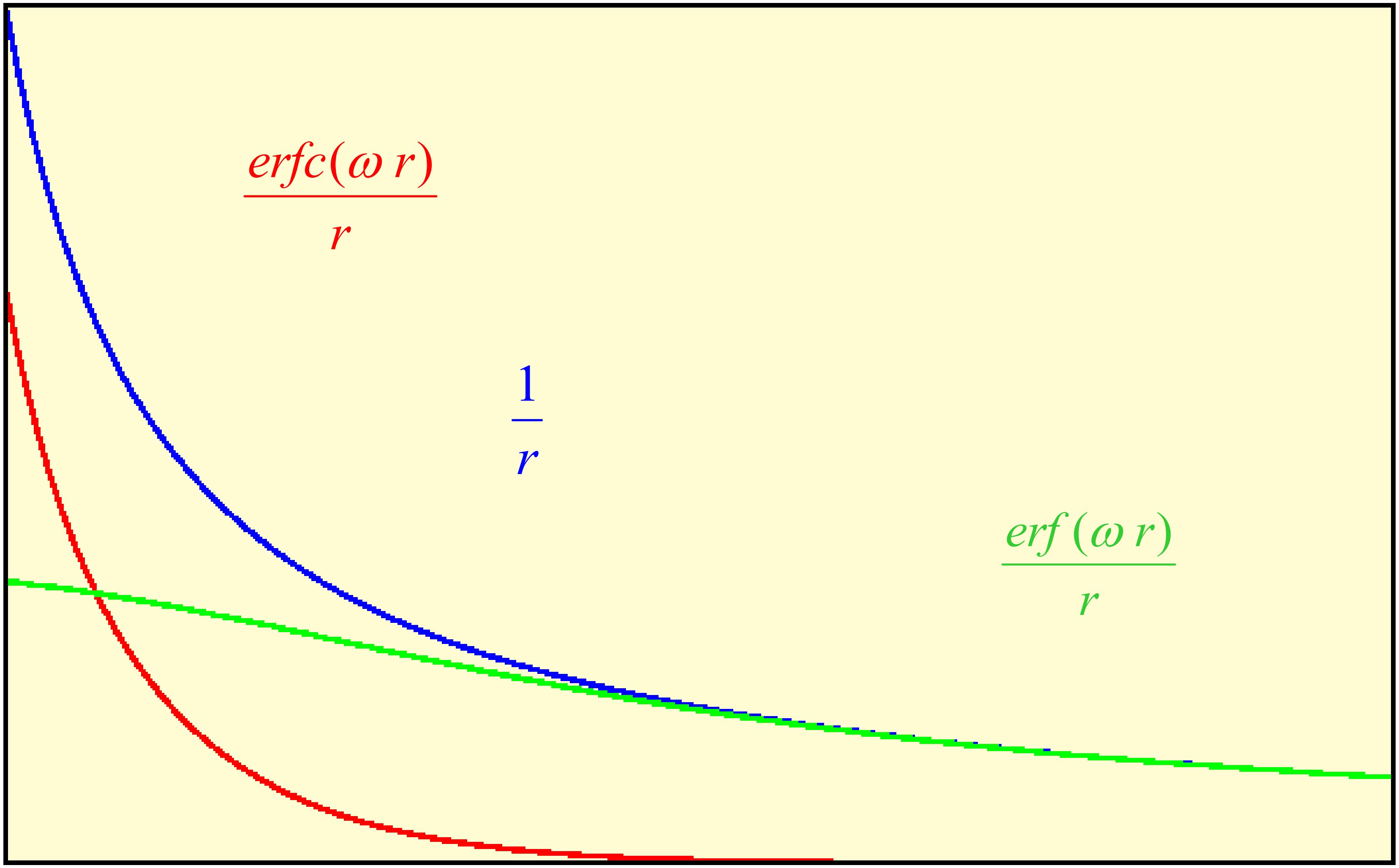
- **Our idea:** neglect LR-**HFx** to avoid the problematic 1/r tail <u>assuming that correlation effects cancel it</u>

- **Erf(wr)/r** is a rapidly decaying function

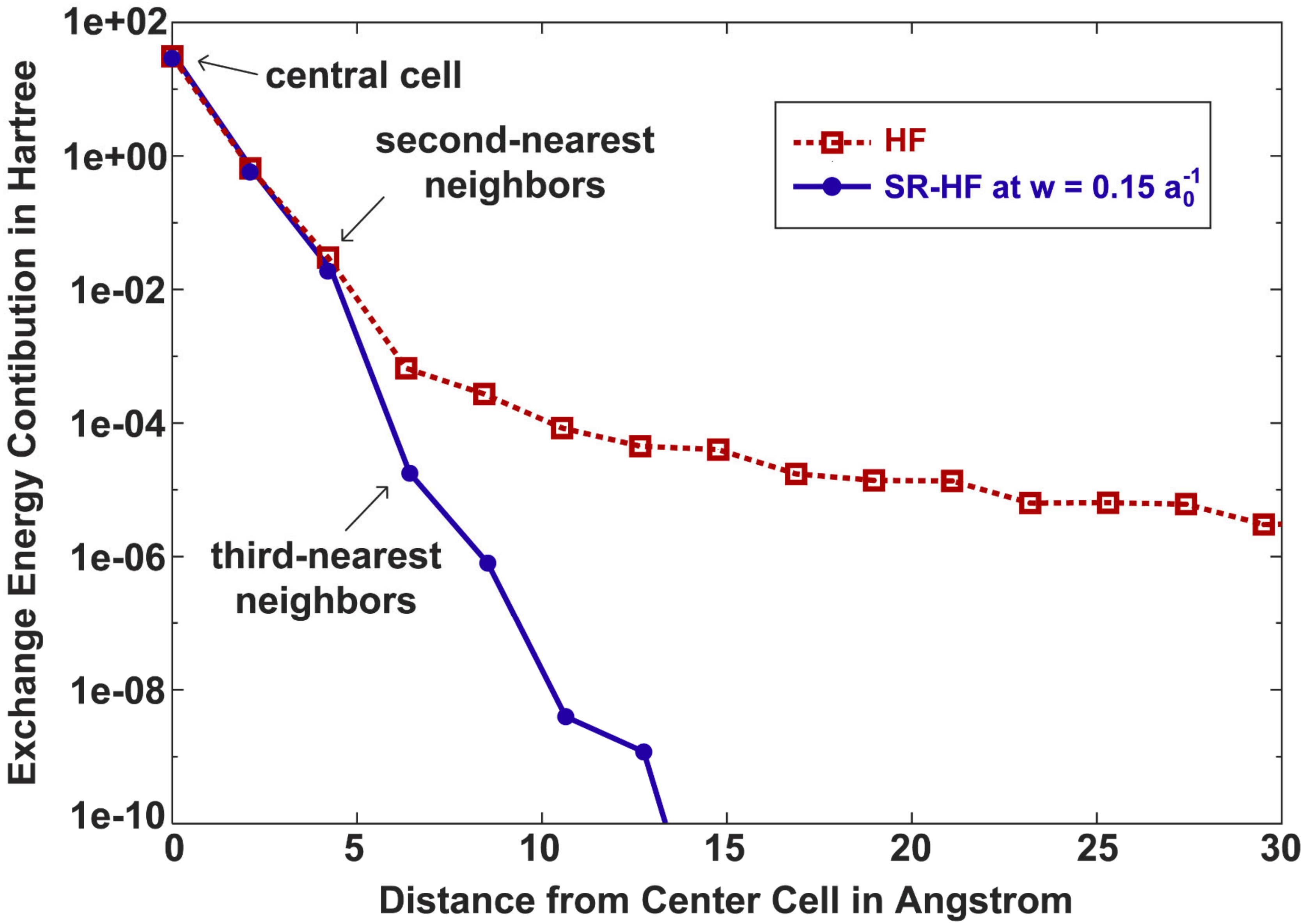
- This is the opposite of what is good for molecules!

Screening the Coulomb Potential

(only for Exchange)



Exchange Interaction Decay in (6,6) Metallic Carbon Nanotube



HSE : two-parameter short-range hybrid

Heyd, Scuseria, Ernzerhof, JCP **118**, 8207 (2003)

$$E(\mathrm{HSE}) = a\, E_x(\omega\mathrm{HF,SR}) + (1-a)\, E_x(\omega\mathrm{PBE,SR}) + E_x(\omega\mathrm{PBE,LR}) + E_c(\mathrm{PBE})$$

choose $a = 0.25$ so that

$\omega \to \infty$ **HSE → PBE**

$\omega \to 0$ **HSE → PBE hybrid (PBE0)**

ω adjusted to reproduce **PBE0** thermochemical data in molecules and best possible band gaps in solids

$\omega = 0.11$ (universal parameter)

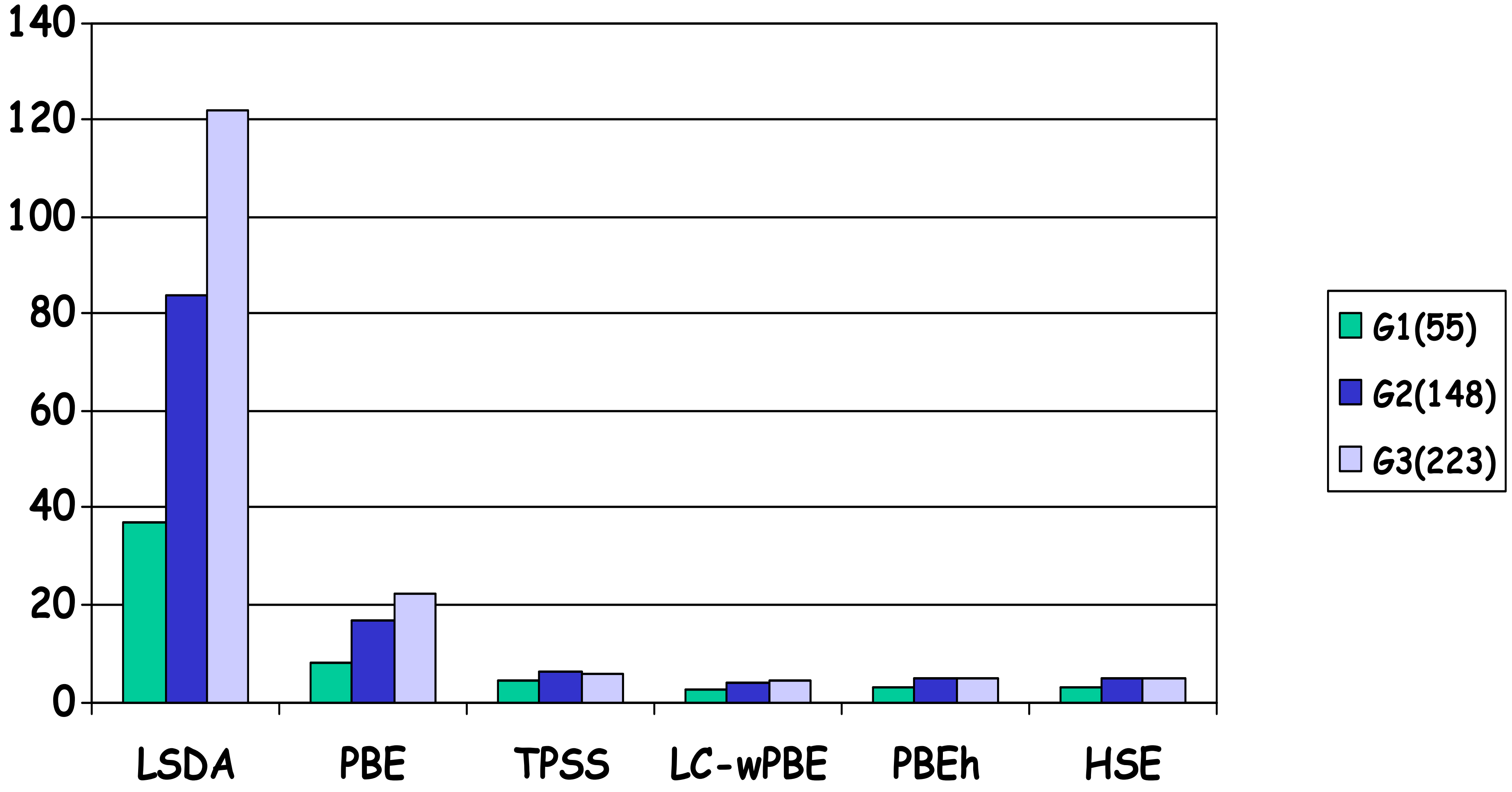
Screening length ~ **9 bohrs** ~ 5 Å
(2nd-3rd nearest neighbors)

Validation Benchmarks
in **Molecules**

Standard Enthalpies of Formation

Mean Absolute Errors (kcal/mol)

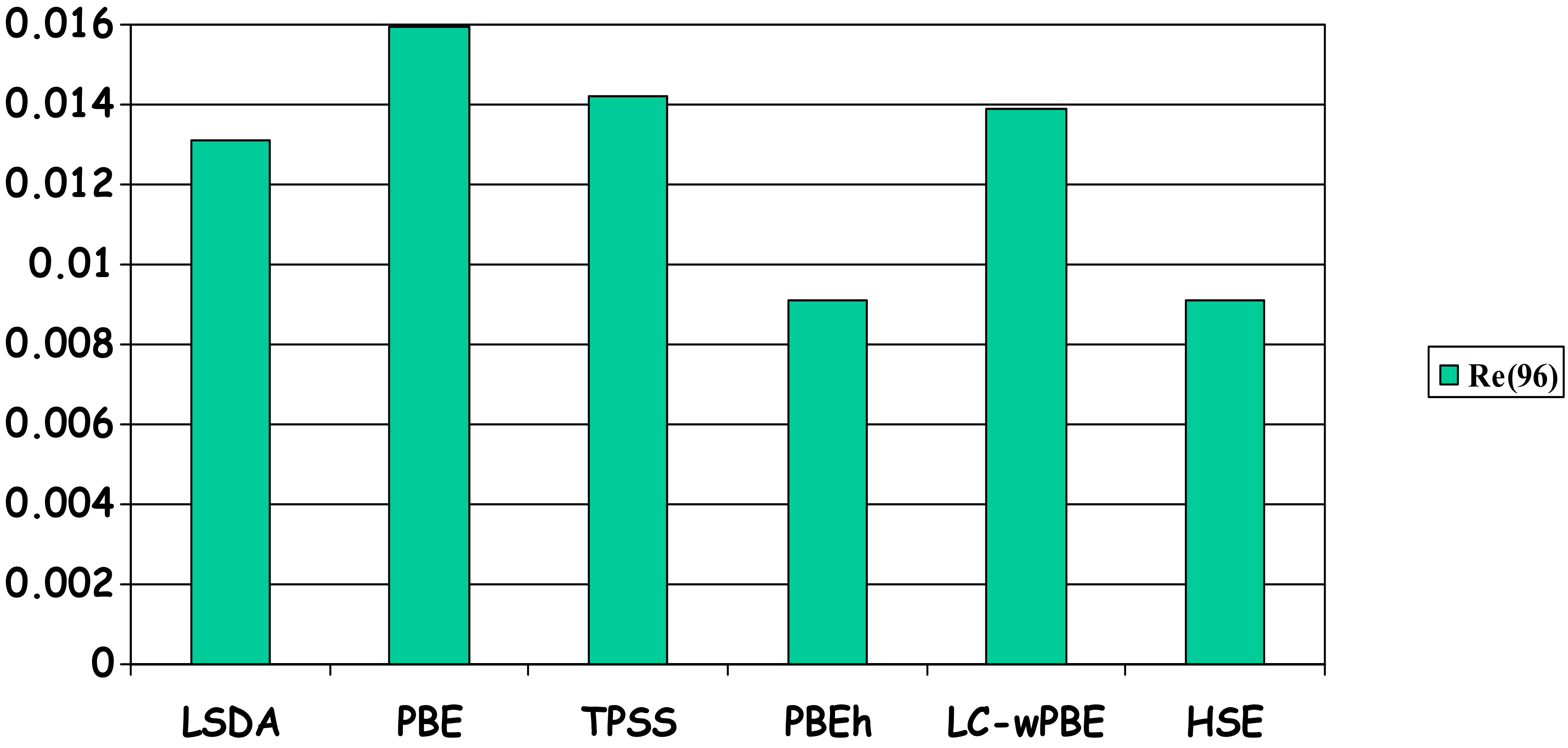
Theory-Experiment

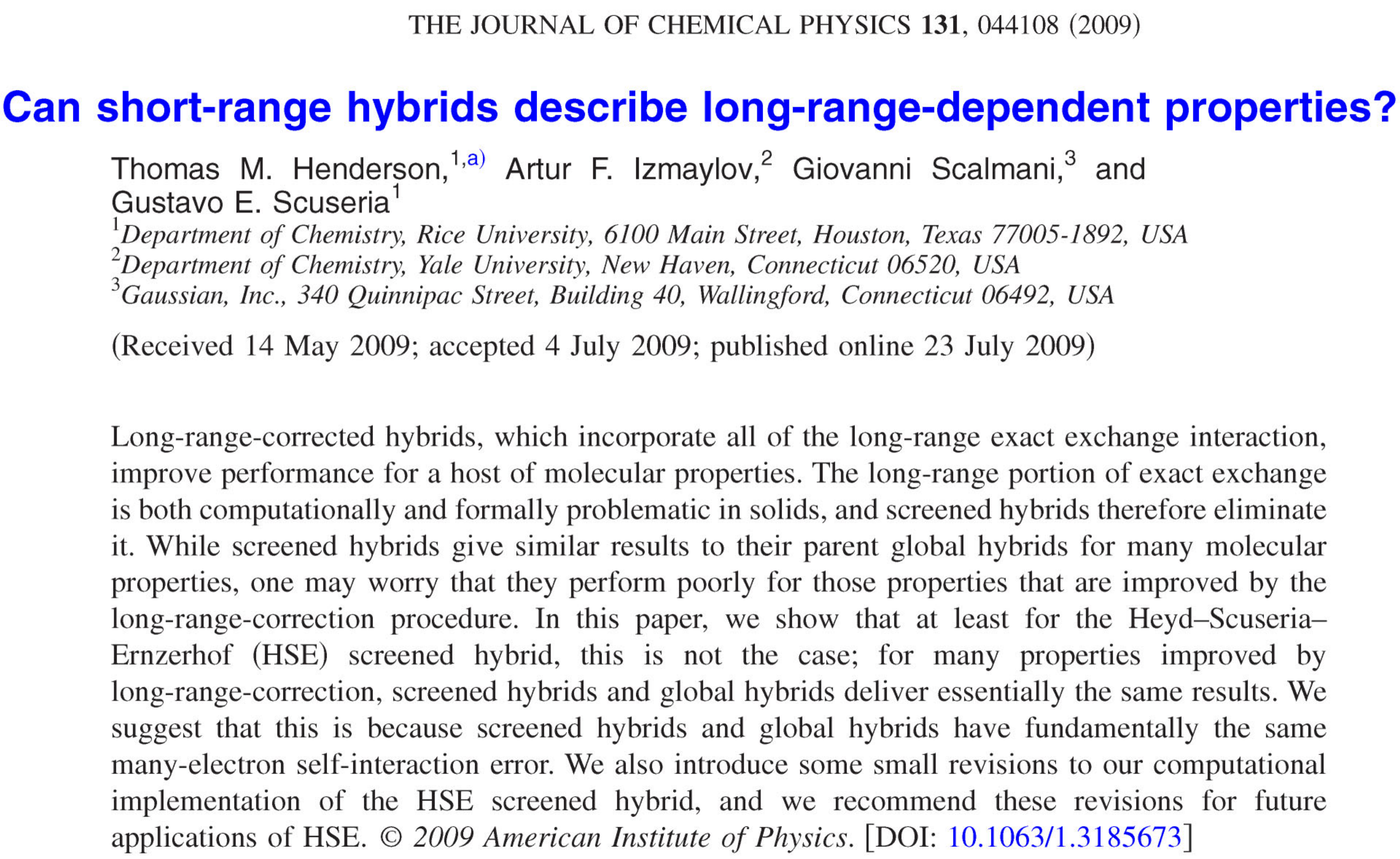


Molecular Equilibrium Geometries

MAE (Å) Theory-Experiment

6-311++G(3df,3pd)





THE JOURNAL OF CHEMICAL PHYSICS **131**, 044108 (2009)

Can short-range hybrids describe long-range-dependent properties?

Thomas M. Henderson,[1,a)] Artur F. Izmaylov,[2] Giovanni Scalmani,[3] and Gustavo E. Scuseria[1]
[1]*Department of Chemistry, Rice University, 6100 Main Street, Houston, Texas 77005-1892, USA*
[2]*Department of Chemistry, Yale University, New Haven, Connecticut 06520, USA*
[3]*Gaussian, Inc., 340 Quinnipiac Street, Building 40, Wallingford, Connecticut 06492, USA*

(Received 14 May 2009; accepted 4 July 2009; published online 23 July 2009)

Long-range-corrected hybrids, which incorporate all of the long-range exact exchange interaction, improve performance for a host of molecular properties. The long-range portion of exact exchange is both computationally and formally problematic in solids, and screened hybrids therefore eliminate it. While screened hybrids give similar results to their parent global hybrids for many molecular properties, one may worry that they perform poorly for those properties that are improved by the long-range-correction procedure. In this paper, we show that at least for the Heyd–Scuseria–Ernzerhof (HSE) screened hybrid, this is not the case; for many properties improved by long-range-correction, screened hybrids and global hybrids deliver essentially the same results. We suggest that this is because screened hybrids and global hybrids have fundamentally the same many-electron self-interaction error. We also introduce some small revisions to our computational implementation of the HSE screened hybrid, and we recommend these revisions for future applications of HSE. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3185673]

The answer is YES.

In **molecules**, **HSE** seems to have enough **LR** exchange to yield ***qualitatively correct*** **LR** properties.

Validation Benchmarks in **Solids**

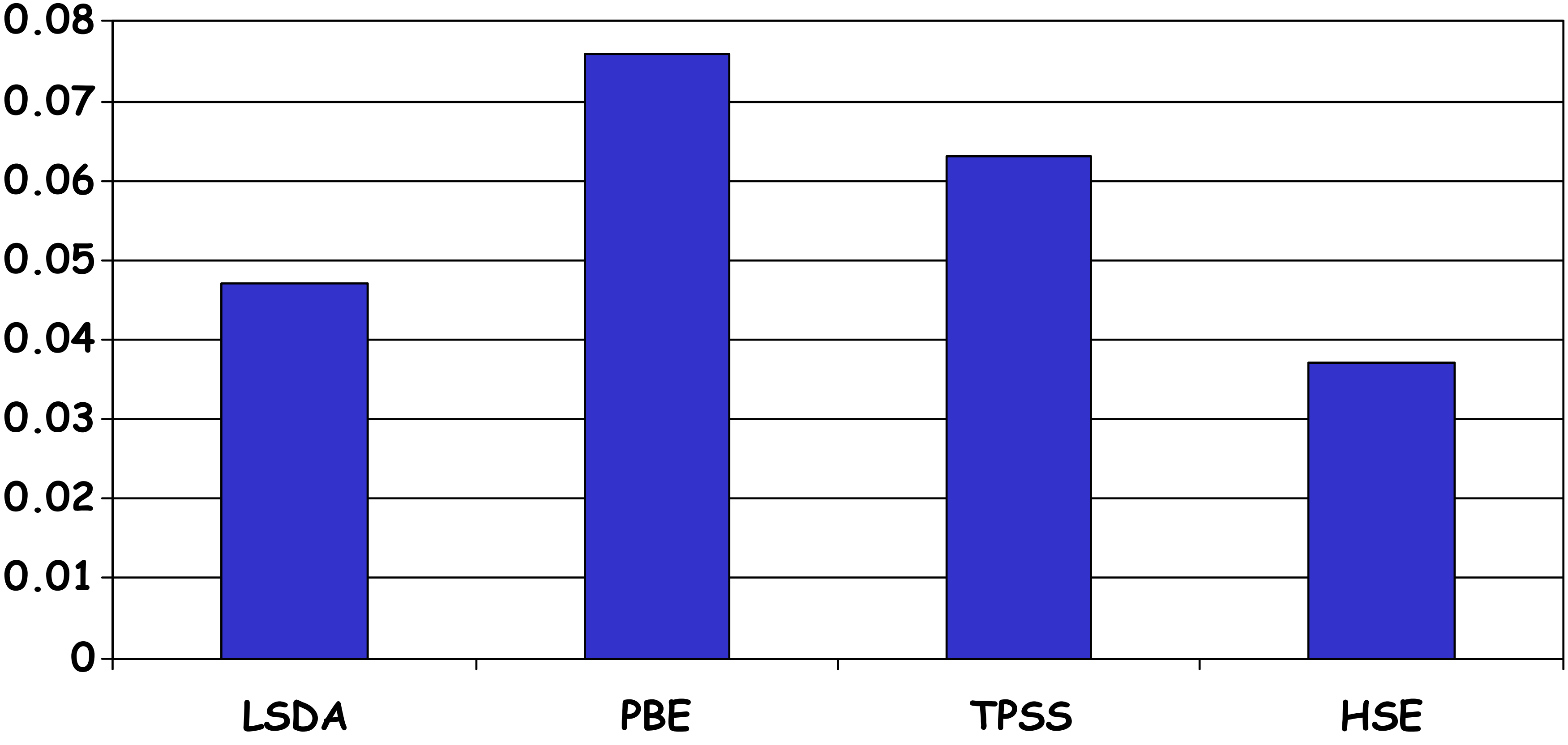
- Using our **periodic** code [Kudin & Scuseria, **PRB** (2000)]
  - –**Gaussian** orbitals
  - –All real-space
  - – **FMM** for Coulomb problem

    [Strain, Scuseria & Frisch, **Science** (1996)]

Equilibrium Lattice Constants

MAE (Å) Theory-Experiment

40 benchmarked systems (semiconductors)

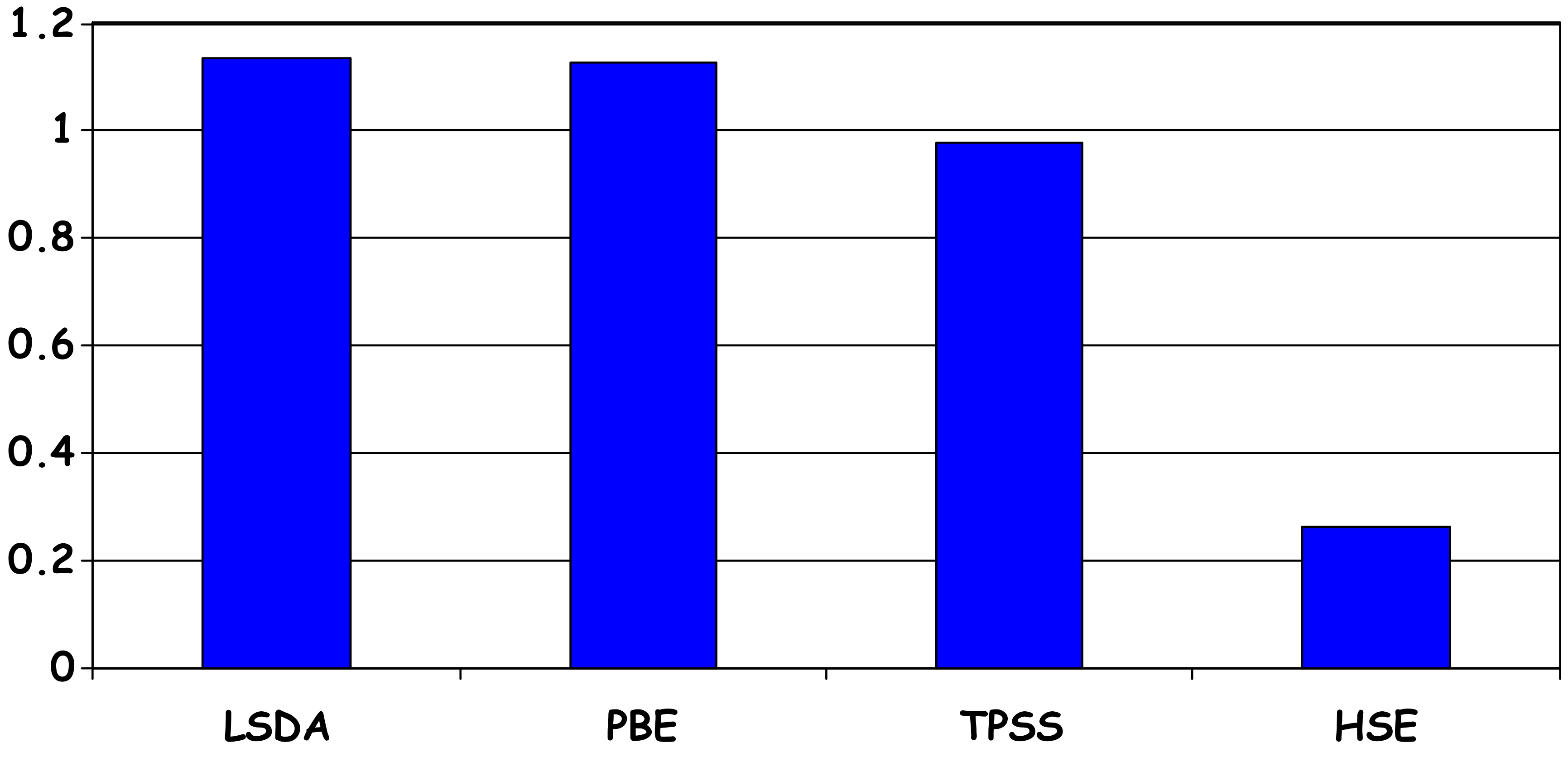


Heyd, Peralta, Scuseria, and Martin, JCP 122, 084108 (2005)

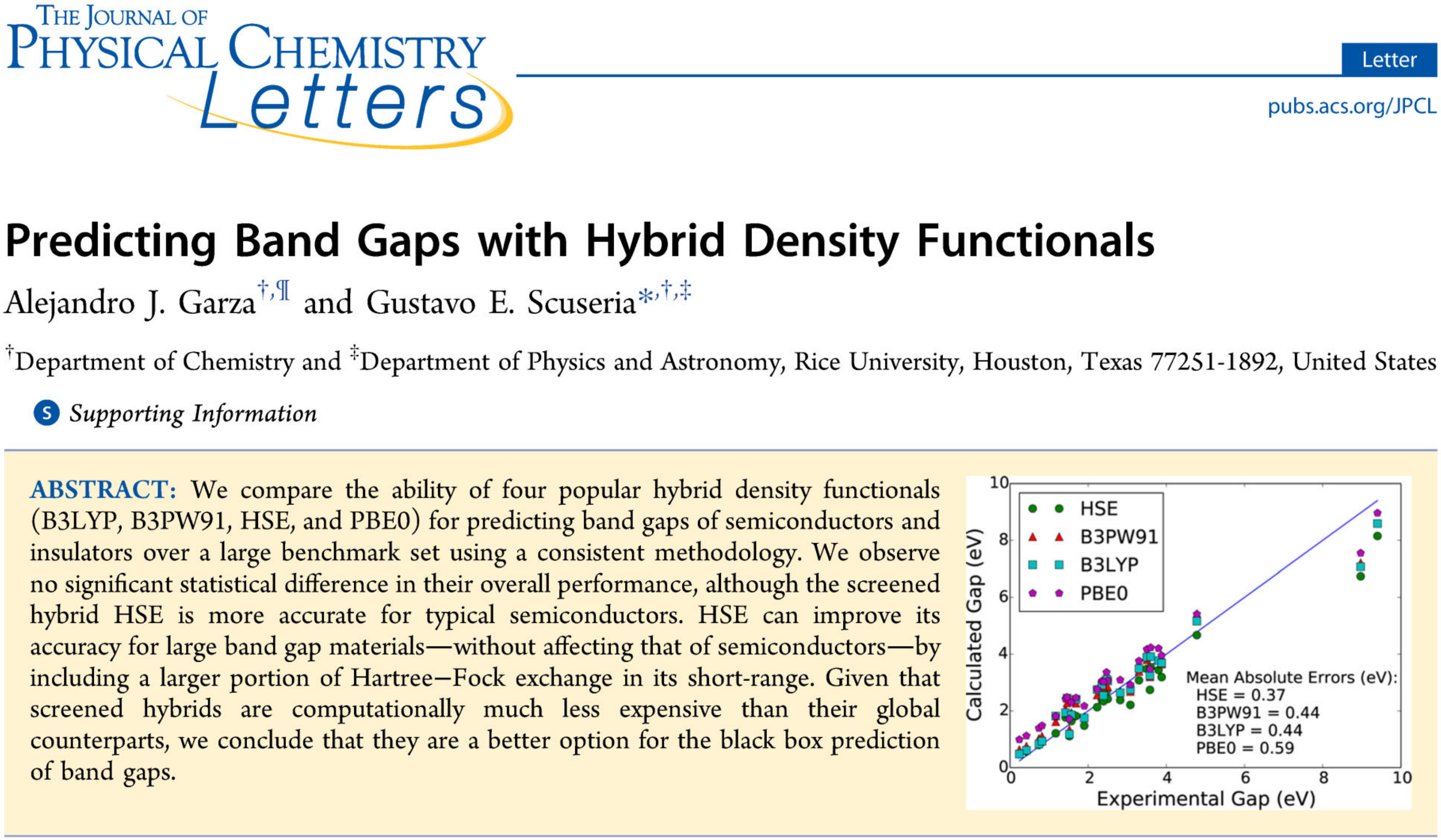
The Band Gap Problem

MAE (eV) Theory-Experiment

40 benchmarked systems (semiconductors)



Heyd, Peralta, Scuseria, and Martin, JCP 122, 084108 (2005)



THE JOURNAL OF PHYSICAL CHEMISTRY Letters

Letter

pubs.acs.org/JPCL

Predicting Band Gaps with Hybrid Density Functionals

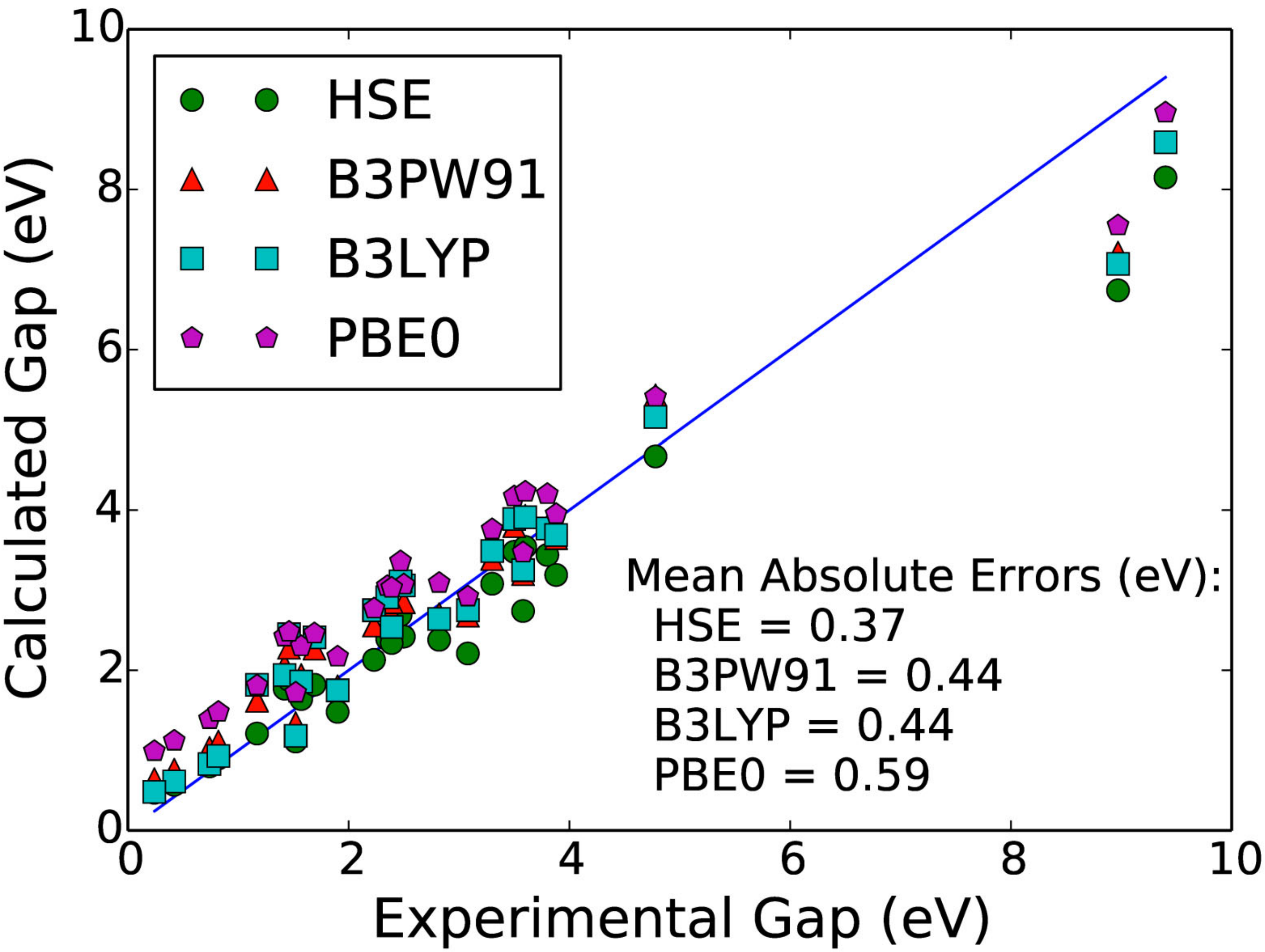
Alejandro J. Garza[†,¶] and Gustavo E. Scuseria[*,†,‡]

[†]Department of Chemistry and [‡]Department of Physics and Astronomy, Rice University, Houston, Texas 77251-1892, United States

Supporting Information

ABSTRACT: We compare the ability of four popular hybrid density functionals (B3LYP, B3PW91, HSE, and PBE0) for predicting band gaps of semiconductors and insulators over a large benchmark set using a consistent methodology. We observe no significant statistical difference in their overall performance, although the screened hybrid HSE is more accurate for typical semiconductors. HSE can improve its accuracy for large band gap materials—without affecting that of semiconductors—by including a larger portion of Hartree–Fock exchange in its short-range. Given that screened hybrids are computationally much less expensive than their global counterparts, we conclude that they are a better option for the black box prediction of band gaps.

J. Phys. Chem. Lett. **7**, 4165 (2016)



41 systems including semiconductors (from **SC40** set), metal oxides (**FeO, CoO, NiO, MnO, VO_2**) and large gap salts (**NaCl, LiCl, LiF**)

Proc. Nat. Acad. Sci. **114**, 2801 (2017)

Understanding band gaps of solids in generalized Kohn–Sham theory

John P. Perdew[a,b,1], Weitao Yang[c], Kieron Burke[d,e], Zenghui Yang[a,2], Eberhard K. U. Gross[f], Matthias Scheffler[g,h,i], Gustavo E. Scuseria[j,k], Thomas M. Henderson[j,k], Igor Ying Zhang[g], Adrienn Ruzsinszky[a], Haowei Peng[a], Jianwei Sun[l], Egor Trushin[m], and Andreas Görling[m]

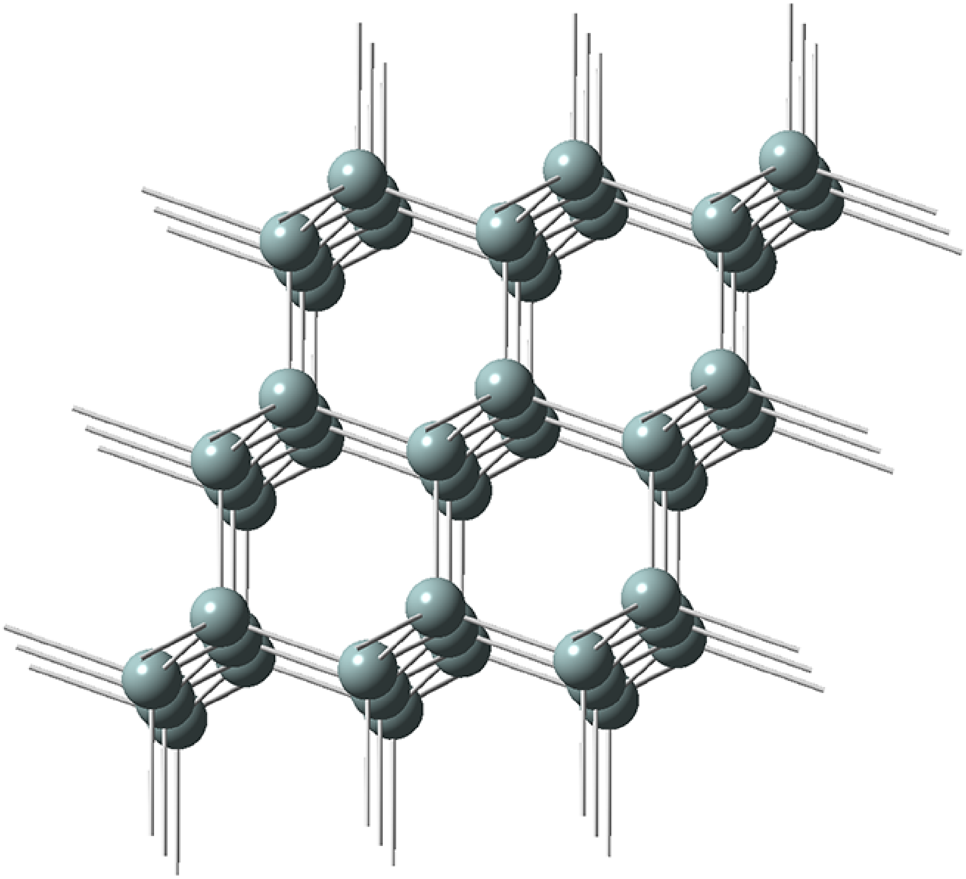
[a]Department of Physics, Temple University, Philadelphia, PA 19122; [b]Department of Chemistry, Temple University, Philadelphia, PA 19122; [c]Department of Chemistry, Duke University, Durham, NC 27708; [d]Department of Chemistry, University of California, Irvine, CA 92697; [e]Department of Physics, University of California, Irvine, CA 92697; [f]Max-Planck Institut für Mikrostrukturphysik, D-06120 Halle, Germany; [g]Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-14195 Berlin, Germany; [h]Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106; [i]Materials Department, University of California, Santa Barbara, CA 93106; [j]Department of Chemistry, Rice University, Houston, TX 77005; [k]Department of Physics and Astronomy, Rice University, Houston, TX 77005; [l]Department of Physics, The University of Texas at El Paso, El Paso, TX 79968; and [m]Department of Chemistry and Pharmacy, Friedrich-Alexander Universität Erlangen-Nürnberg, 91058 Erlangen, Germany

Contributed by John P. Perdew, February 2, 2017 (sent for review December 30, 2016; reviewed by Roi Baer and Stephan Kuemmel)

Significance

Semiconductors and insulators have a fundamental energy gap and absorb light at a continuum of photon energies above this gap. They also have a band structure of one-electron energies, and a band gap separating unoccupied from occupied one-electron states. When should these gaps be equal? It is known that they are not equal in the exact Kohn–Sham density-functional theory but are equal in commonly used density-functional approximations, such as the generalized gradient approximation (GGA). We show here that they are also equal (and improved) in higher level approximations, such as the meta-GGA or the hybrid of GGA with exact exchange, when the effective one-electron potential is not constrained to be a multiplication operator.

Silicon: Diamond Structure

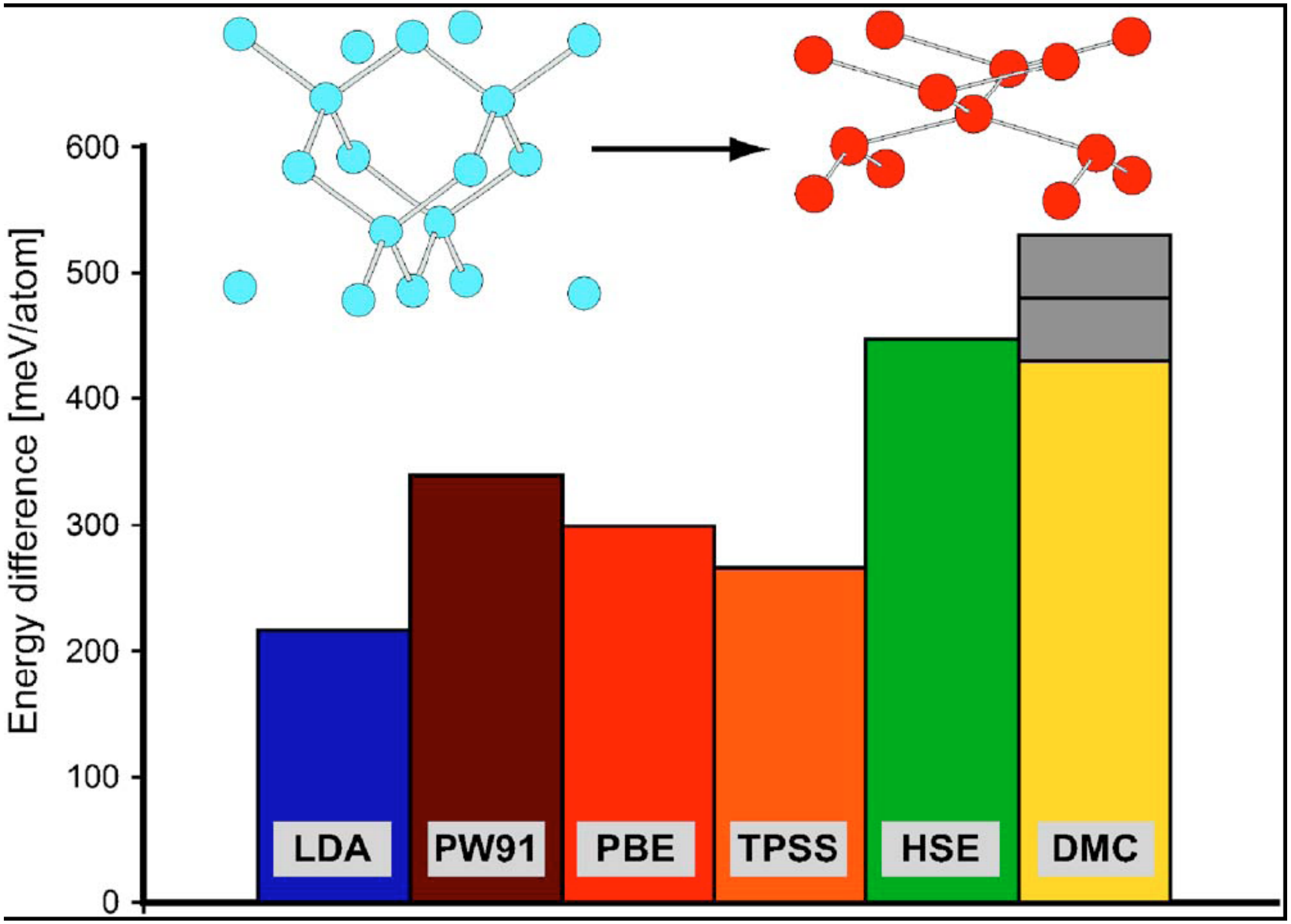


Functional	Band gap (eV)
LSDA	0.58
PBE	0.75
TPSS	0.84
B3LYP	1.89
PBEh	1.86
HSE	1.29
Exp.	1.17

m-6-311G(2d)* basis

Silicon

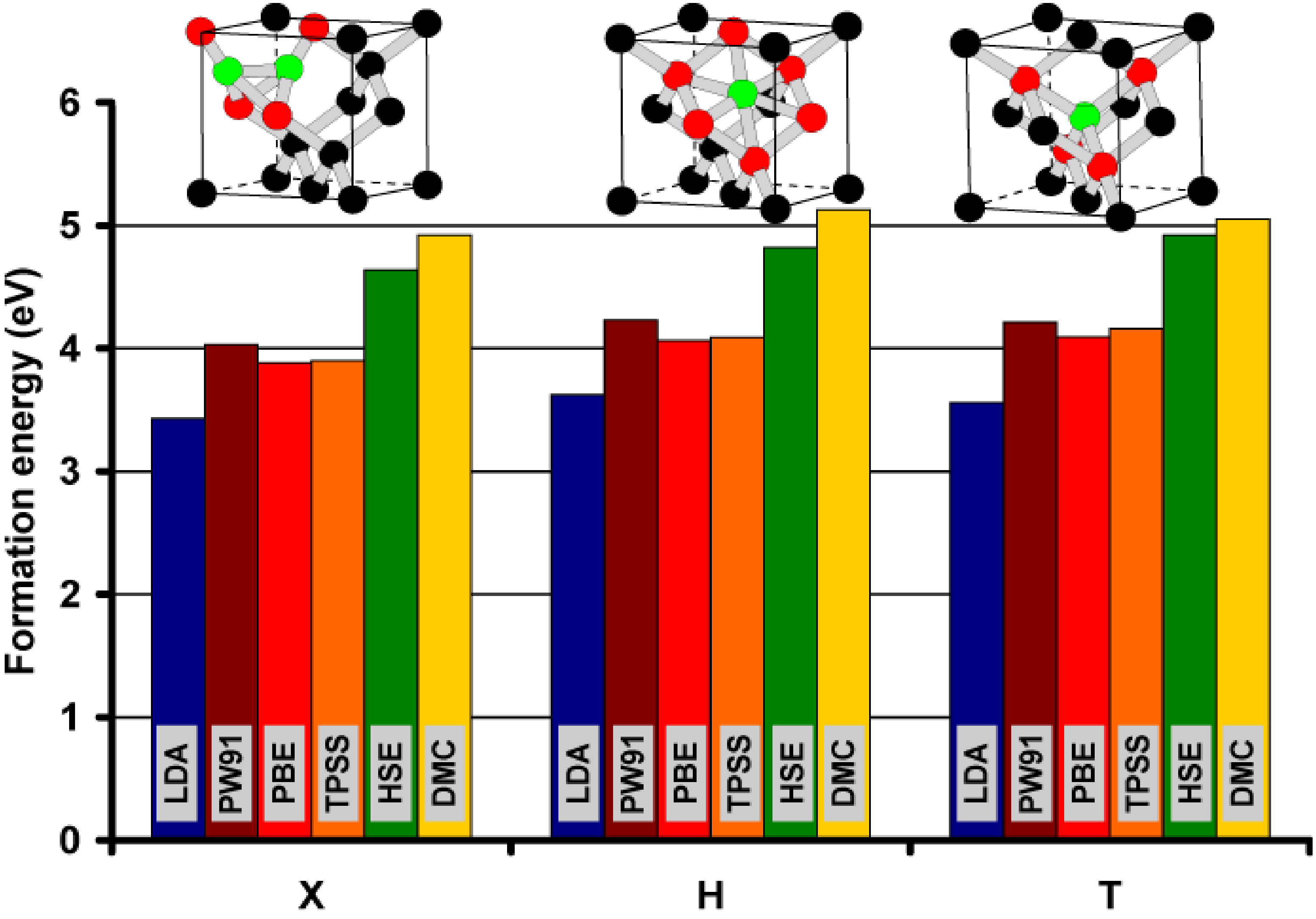
Energy difference between β-Tin (<u>metallic</u>) and diamond (<u>semiconducting</u>) phases



Batista et al, PRB 74, 121102 (2006)

m-6-311G(2d) basis

Silicon Interstitial Energy

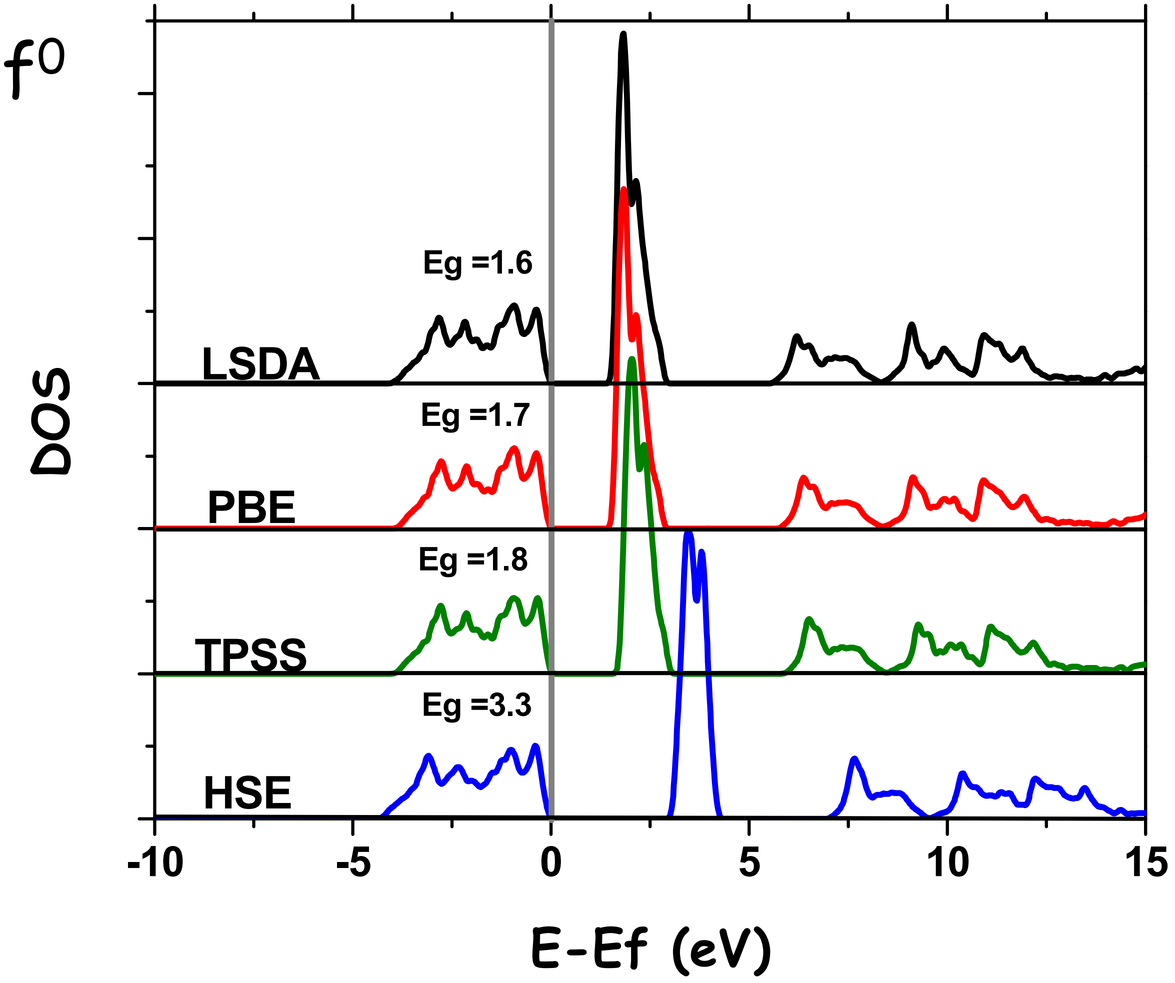


Batista et al, PRB 74, 121102 (2006)

m-6-311G(2d) basis

Ceria (CeO_2) Band Gap

Ce $4f^0$

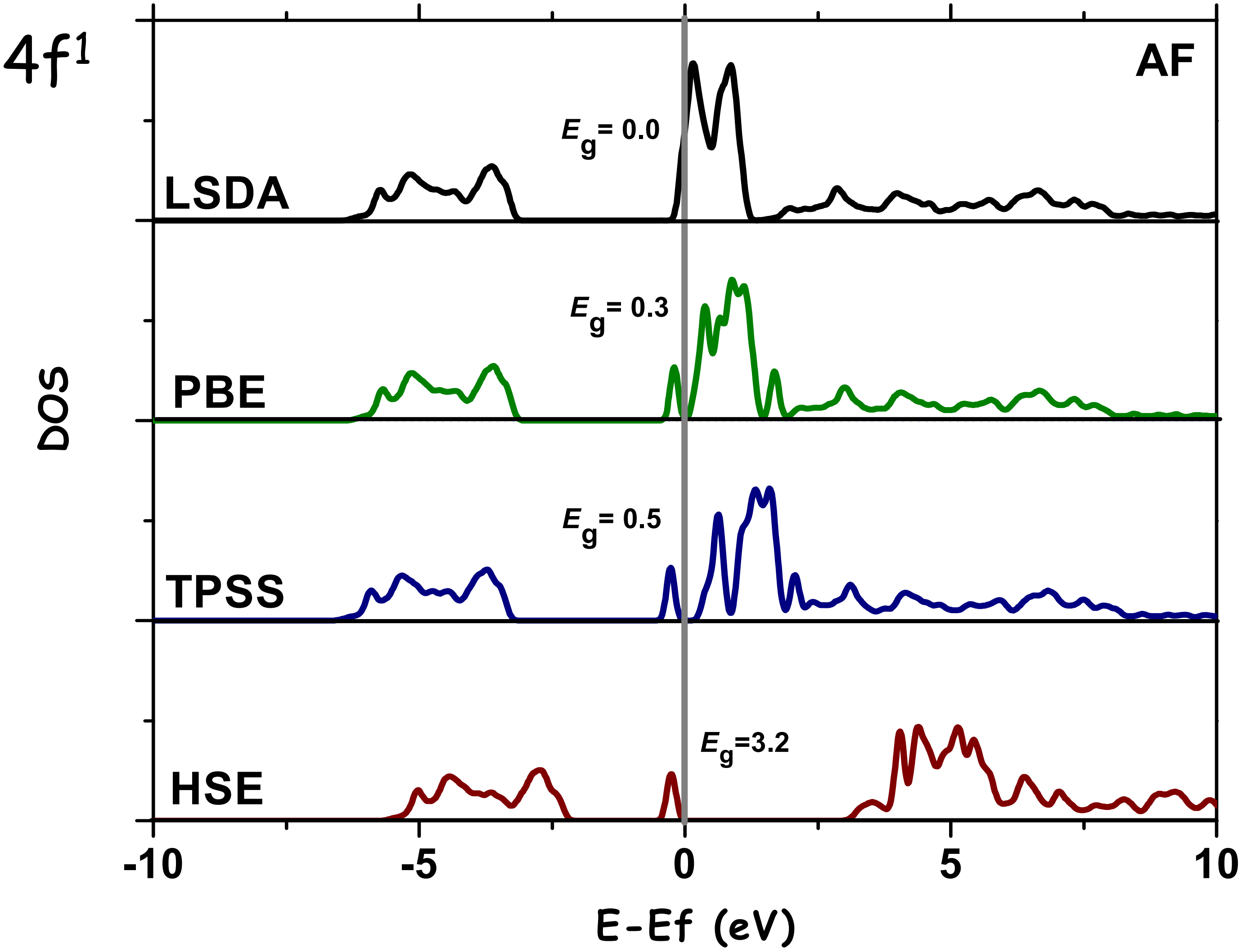


Exp. Eg ~3 eV

Hay, Martin, Uddin, Scuseria, JCP 125, 034712 (2006)

Reduced Ceria (Ce_2O_3)

Ce $4f^1$



Exp. E_g ~2.5 eV

Hay, Martin, Uddin, Scuseria, JCP 125, 034712 (2006)

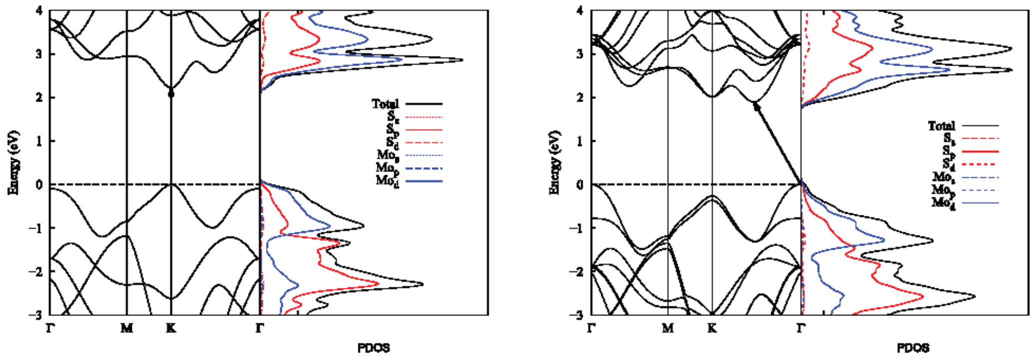
APPLIED PHYSICS LETTERS **99**, 261908 (2011)

The indirect to direct band gap transition in multilayered MoS_2 as predicted by screened hybrid density functional theory

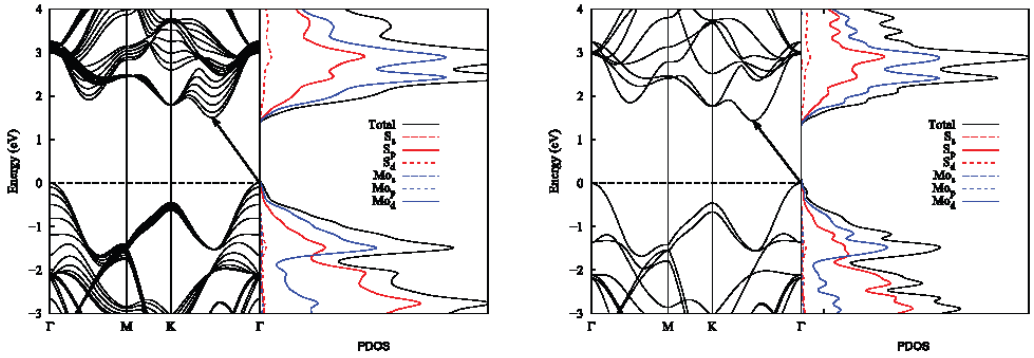
Jason K. Ellis,[1,2,a)] Melissa J. Lucero,[1] and Gustavo E. Scuseria[1,2]
[1]*Department of Chemistry, Rice University, Houston, Texas 77005-1827, USA*
[2]*Department of Physics and Astronomy, Rice University, Houston, Texas 77005-1827, USA*

(Received 7 November 2011; accepted 3 December 2011; published online 29 December 2011)

Molybdenite (MoS_2) undergoes a transition from an indirect to direct gap semiconductor exhibiting strong photoluminescence when confined in a 2D monolayer. We investigate the effect of interlayer interactions on the band structure and density of states using the screened hybrid functional of Heyd, Scuseria, and Ernzerhof. We show that for the bulk and monolayer systems, our short-range screened hybrid functional produces band gaps in good agreement with experiment. Our functional includes only interlayer interactions of non-van der Waals origin, predicts properties consistent with recent experiments, and provides predictions for few-layered systems. © *2011 American Institute of Physics*. [doi:10.1063/1.3672219]



(a)Monolayer (b)2-Layer



(c)6-Layer (d)Bulk

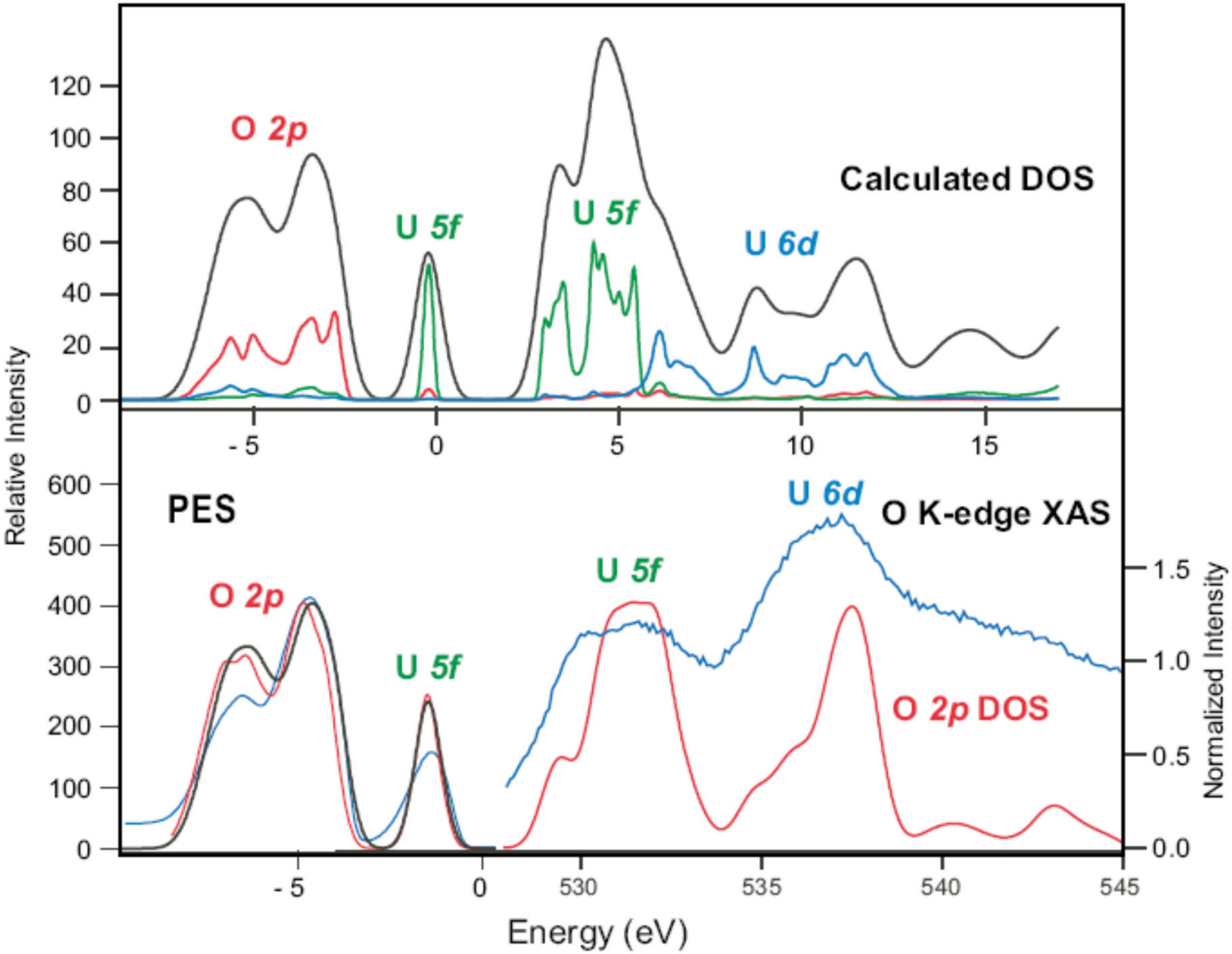
UO_2

Kudin, Scuseria, Martin, PRL (2002)
Prodan, Scuseria, Martin PRB (2006)

U $5f^2$	Band gap (eV)		Lattice constant (Å)		Bulk modulus (GPa)		$E_F - E_{AF}$ (meV)
	F	AF	F	AF	F	AF	
LSDA	m	m	5.317	5.289	239	216	-98
PBE	m	m	5.425	5.449	206	218	-159
TPSS	m	m	5.437	5.445	202	191	-124
HSE	1.6	2.4	5.463	5.463	226	219	+7
Exp	~2.1		5.470		207		>0

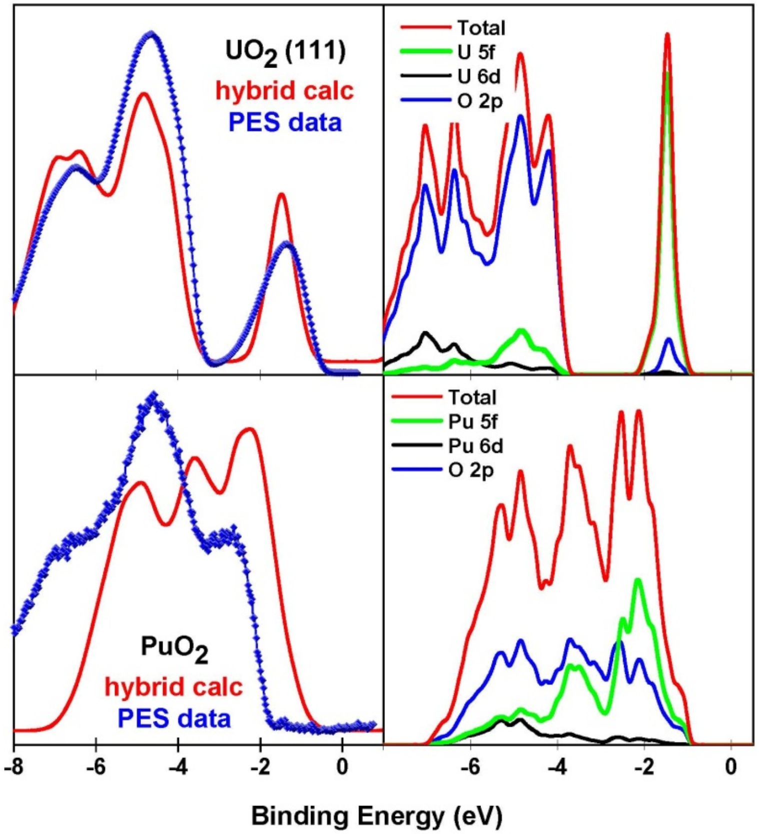
F= Ferromagnet AF= AntiFerromagnet m= metal

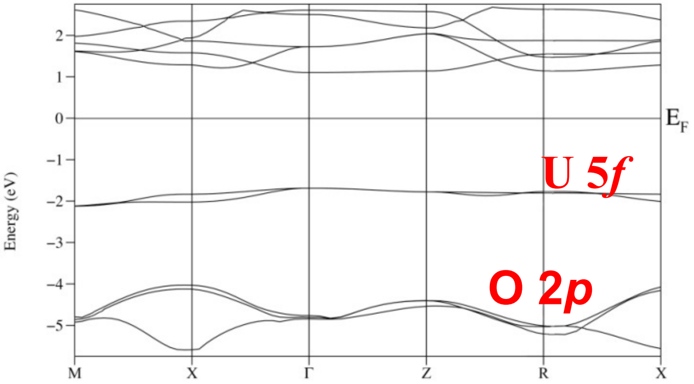
UO_2 : HSE vs Experiment (K-edge)



Bulk UO_2 and PuO_2

HSE gives good agreement w/ experiment not only for band gap but also for density of states and overall band structure

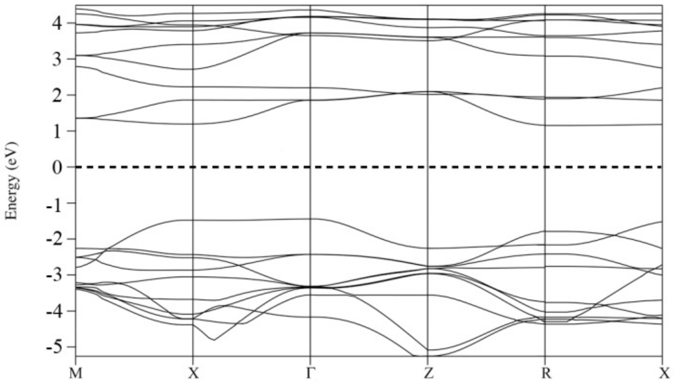




UO_2

U 5*f*

O 2*p*



PuO_2

Pu 5*f* / O 2*p*

In PuO_2 , HSE yields the right answer for the wrong reason !
PuO_2 is diamagnetic
HSE breaks spin symmetry ➔ strong correlation is present

Roy, Durakiewicz, Martin, Peralta, Scuseria, Olson, Joyce, Guziewicz, J. Comp. Chem. 29, 2288 (2008)

DFT dirty laundry list

- Too many functionals!
- Rampant **empiricism** and uncontrolled approximations
- No clear route to get systematically improvable answers
- Difficulties with strong correlation: **DFT** and entanglement do not get along
- Problems with spin multiplets
- **DFT** way forward seems to be **adding a piece of wave function theory** (**HF**, **RPA**, etc.)
- **Computational cost** for functionals beyond screened hybrids is a concern

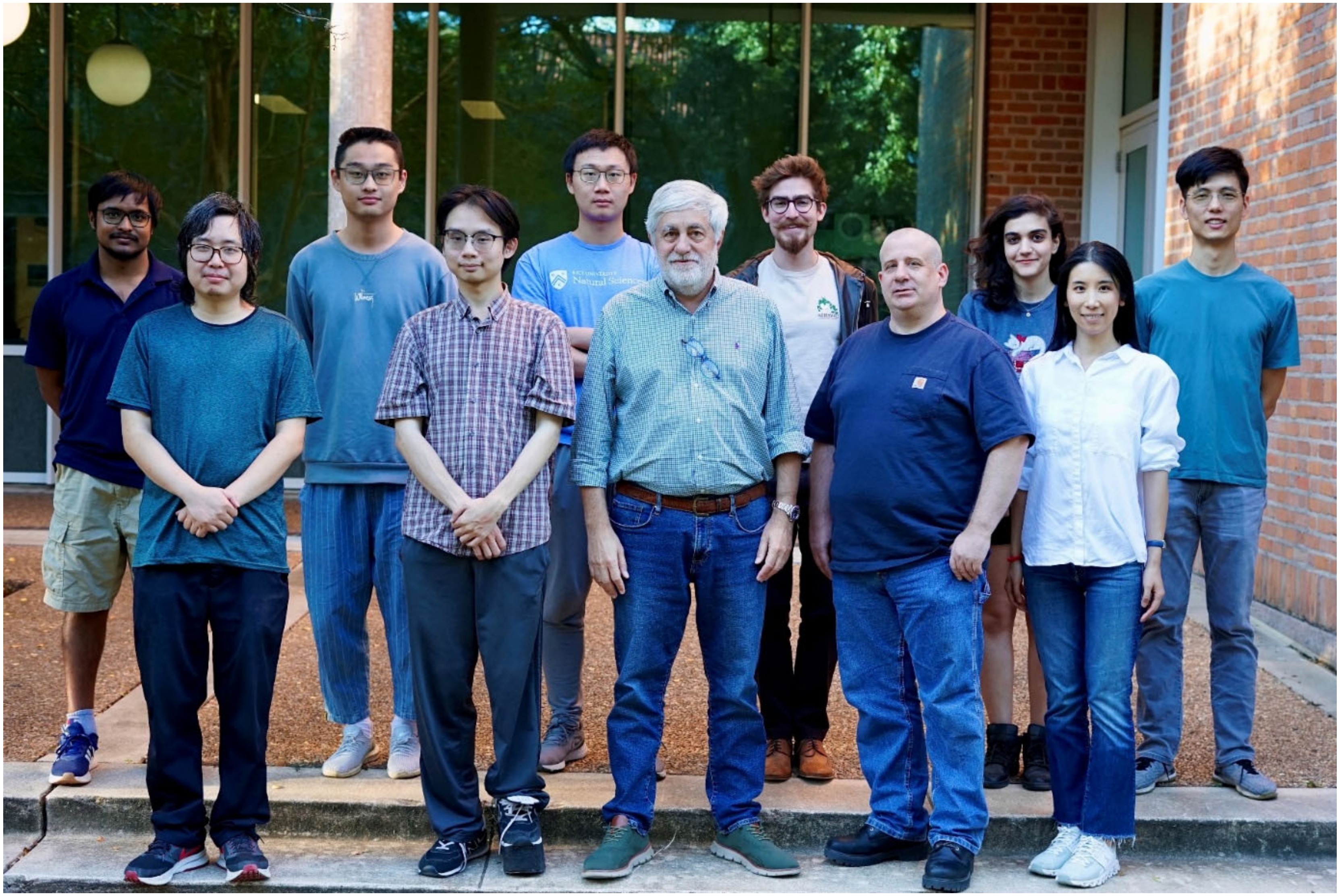
Summary

- The important role of range separation for constructing better **DFT** functionals

- **The HSE functional for modelling materials:** successes, limitations, and prospects

- **GKS** band energy differences are honest fundamental band gaps

Acknowledgments



$ DOE, NSF, The Welch Foundation, Gaussian Inc.