Screened-Exchange Range-Separated Hybrid Functionals for heterogeneous systems

Jiawei Zhan[1], Marco Govoni[1,2,3], and Giulia Galli[1,2,4]

[1]*Pritzker School of Molecular Engineering, University of Chicago*

[2]*Materials Science Division, Argonne National Laboratory*

[3]*Department of Physics, Computer Science, and Mathematics, University of Modena and Reggio Emilia*

[4]*Department of Chemistry, University of Chicago*

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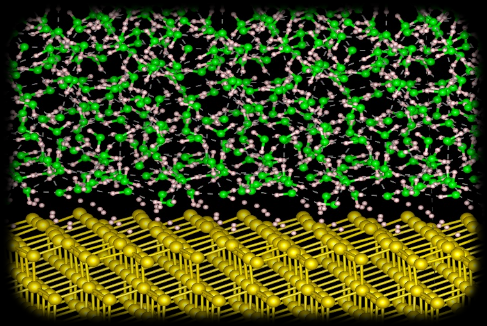
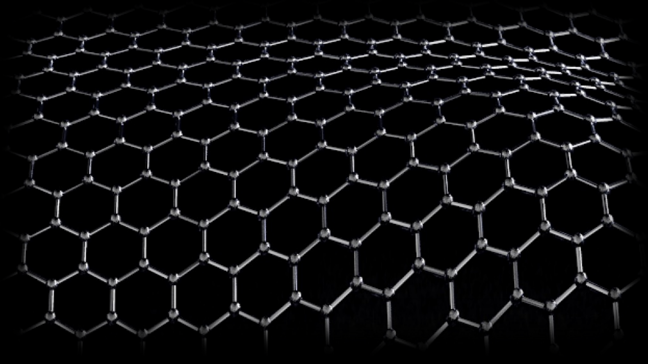
Introduction and Motivation

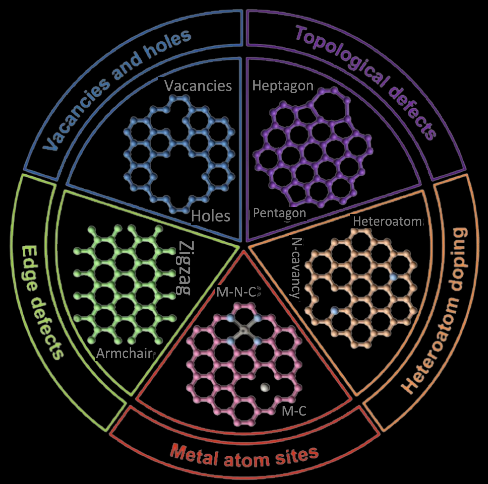
- **Materials** used in devices for the development of any technology exhibit inherent **heterogeneity**



interfaces



2D systems

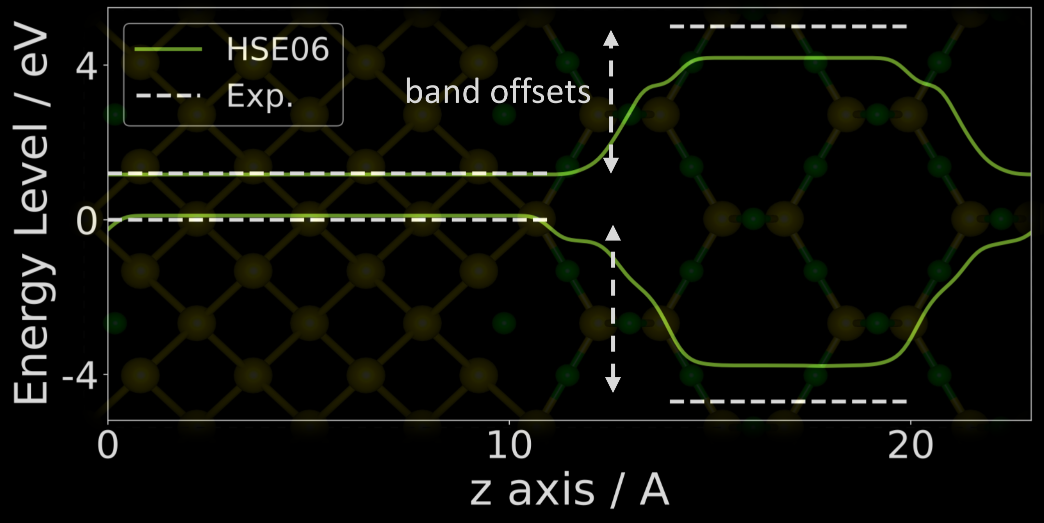


defective systems

- **Density Functional Theory (DFT)** has been widely and successfully used for decades to provide insight into the mechanisms that govern the behavior of materials

- However, it is still **challenging** for available exchange and correlation (xc) functionals to **describe with the same accuracy** the electronic properties of **different components of heterogeneous systems**

Si/SiO_2



Outline

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- Introduction to Screened-Exchange Range-Separated Hybrid (SE-RSH)

- Applications of SE-RSH to
  - analyze the electronic structures of heterogeneous systems:
    - Interfaces
    - Two-dimensional (2D) systems
    - Defective 2D systems
  - metal oxides

- Conclusions and future work

F. Gygi, Ibm J Res Dev **52**, 137 (2008)

Qbox

Dielectric-Dependent Hybrid functional

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Generalized Kohn-Sham theory:

$$\Sigma_x^{\mathrm{GKS}} = \alpha \Sigma_{\mathrm{x}} + (1 - \alpha) V_x^{\mathrm{GGA}}$$

$\alpha \rightarrow$ **ratio** of Fock exchange to semi-local

Global Hybrid Functional[1-2]:

α: constant number

Range-Separated Hybrid Functional[3-11]:

$$\Sigma_x^{\mathrm{GKS}}(\mathbf{r},\mathbf{r}') = \boldsymbol{\alpha}(\mathbf{r},\mathbf{r}'; m, n, \mu) \odot \Sigma_{\mathrm{x}}(\mathbf{r},\mathbf{r}') + (1 - m) V_x^{\mathrm{GGA,lr}}(\mathbf{r}; \mu) + (1 - n)\, V_x^{\mathrm{GGA,sr}}(\mathbf{r}; \mu)$$

[1] P. Mori-Sánchez, A. J. Cohen, and W. Yang, J Chem Phys 125, 201102 (2006)
[2] J. H. Skone, M. Govoni, and G. Galli, Phys Rev B 89, 195112 (2014)
[3] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J Chem Phys 124, 219906 (2006)
[4] I. C. Gerber et al., J Chem Phys 127, 054101 (2007)
[5] T. Yanai, D. P. Tew, and N. C. Handy, Chem Phys Lett 393, 51 (2004)
[6] E. Weintraub, T. M. Henderson, and G. E. Scuseria, J Chem Theory Comput 5, 754 (2009)
[7] W. Chen et al., Phys Rev Mater 2, 073803 (2018)
[8] J. H. Skone, M. Govoni, and G. Galli, Phys Rev B 93, 235106 (2016)
[9] D. K. Lewis, A. Ramasubramaniam, and S. Sharifzadeh, Phys Rev Mater 4, 063803 (2020)
[10] G. Prokopiou et al., J Chem Theory Comput 18, 2331 (2022)
[11] P. Borlido et al., Npj Comput Mater 6, 96 (2020)

Dielectric-Dependent Hybrid functional

Family of Dielectric-Dependent Hybrid:

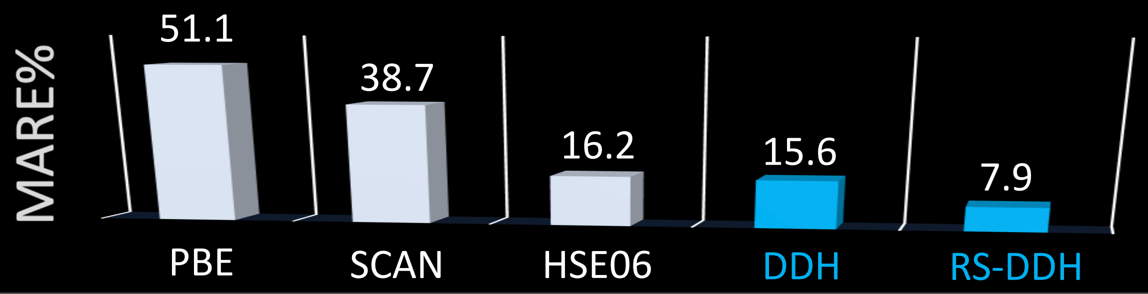
Global Dielectric-Dependent Hybrid (DDH)[1]

$$\alpha = \frac{1}{\epsilon_\infty^{\mathrm{bulk}}}$$

Range-Separated Dielectric-Dependent Hybrid (RS-DDH)[2][3]

$$\alpha\left(\mathbf{r},\mathbf{r}';\frac{1}{\epsilon_\infty^{\mathrm{bulk}}},1,\mu\right) = \frac{1}{\epsilon_\infty^{\mathrm{bulk}}} + \left(1-\frac{1}{\epsilon_\infty^{\mathrm{bulk}}}\right)\mathrm{erfc}(\mu|\mathbf{r}-\mathbf{r}'|)$$

Mean Average Relative Error [MARE%] for computed band gaps of semiconductors & insulators[3]



Introduce spatial dependency into dielectric screening[4-5]

Local dielectric function $\epsilon(\mathbf{r})$ via finite field method:

$$\Delta P(\mathbf{r}) = -e\sum_{i=1}^{N_w}\Delta\mathbf{r}_{wc}^{i}\delta(\mathbf{r}-\mathbf{r}_{wc}^{i})$$

$$\epsilon_{\alpha\beta}(\mathbf{r}) = \delta_{\alpha\beta} + 4\pi\frac{\Delta P_\alpha(\mathbf{r})}{\Delta E_\beta(\mathbf{r})}$$

[1] J. H. Skone, M. Govoni, and G. Galli, Phys Rev B 89, 195112 (2014)
[2] W. Chen et al., Phys Rev Mater 2, 073803 (2018)
[3] J. H. Skone, M. Govoni, and G. Galli, Phys Rev B 93, 235106 (2016)
[4] H. Zheng, M. Govoni, and G. Galli, Phys Rev Mater 3, 073803 (2019)
[5] P. Borlido, M. A. L. Marques, and S. Botti, J Chem Theory Comput 14, 939 (2018)

Screened-Exchange Range-Separated Hybrid(SE-RSH)

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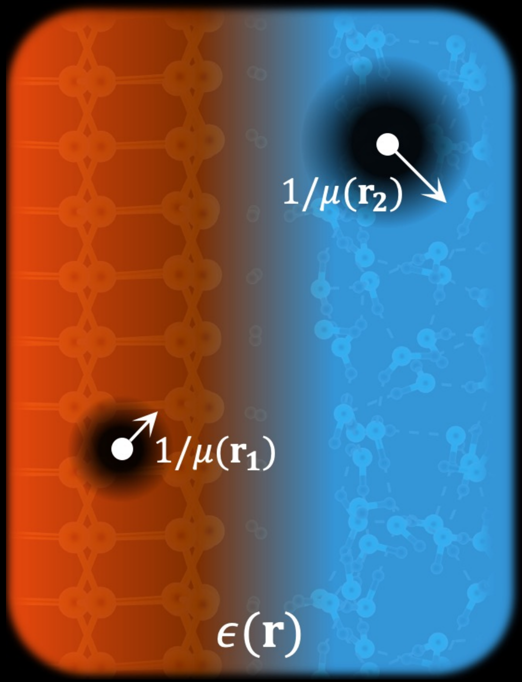
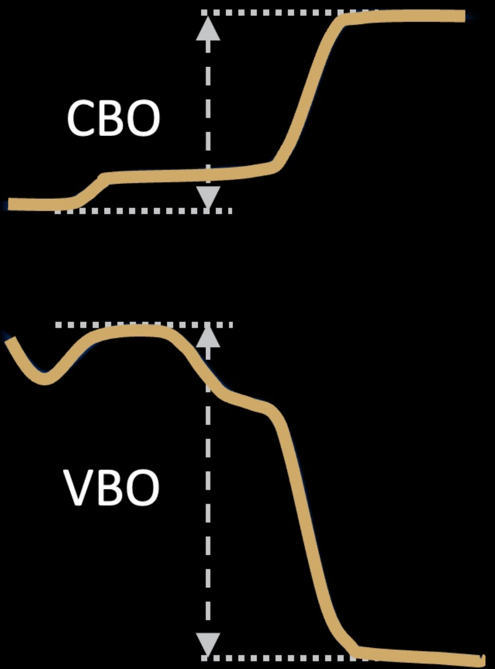
The **ratio** of Fock exchange to semi-local depends on position:

$$\alpha^{\mathrm{SE-RSH}}(\mathbf{r},\mathbf{r}';\epsilon(\mathbf{r}),\mu(\mathbf{r})) = \underbrace{\frac{1}{\sqrt{\epsilon(\mathbf{r})\epsilon(\mathbf{r}')}}}_{\text{long-range screening}} + \underbrace{\left(1-\frac{1}{\sqrt{\epsilon(\mathbf{r})\epsilon(\mathbf{r}')}}\right)\mathrm{erfc}(\mu(\mathbf{r})\mathbf{r}_{12})}_{\text{short-range screening}}$$

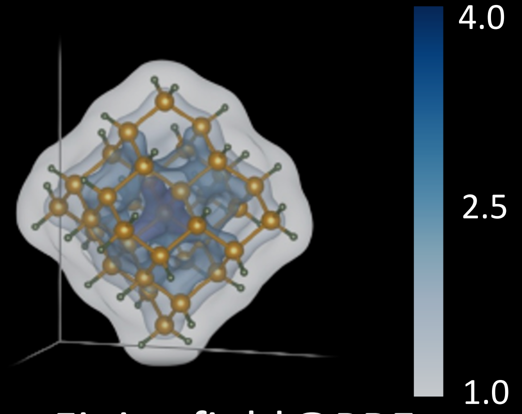
non-empirical



SE-RSH



Local dielectric function $\epsilon(\mathbf{r})$



Finite-field@PBE

Local screening parameter $\mu(\mathbf{r})$

$$\mu(\mathbf{r}) = \frac{1}{2}k_{\mathrm{TF}} = \left(\frac{3\rho(\mathbf{r})}{\pi}\right)^{1/6}$$

SE-RSH **generalizes** the definition of RS-DDH by introducing a **spatially dependent dielectric screening.**

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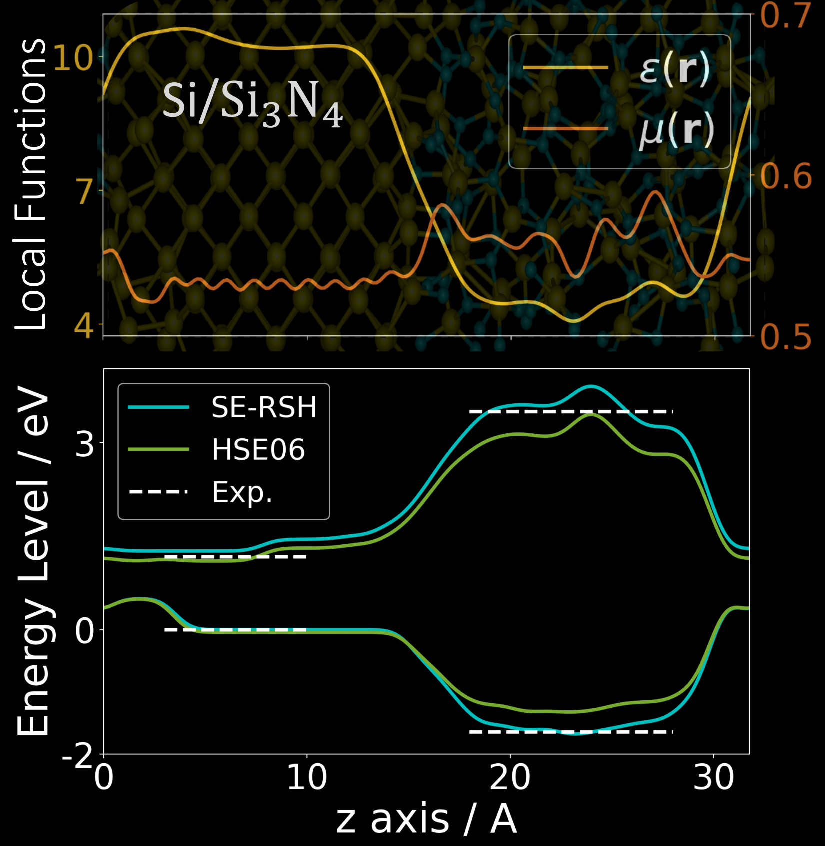
Application of SE-RSH to heterogeneous systems

Band offset at interfaces

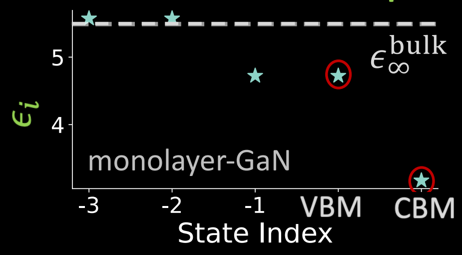


band gap (eV) of 2D systems

systems*	HSE06	SE-RSH	G_0W_0 [Ref.]
phosphorene	1.50	2.07	2.00 [2]
MoS_2	2.17	2.63	2.58 [3]
GaN	3.53	4.41	4.44 [1]
...	......		...
BN	5.7	7.59	7.49 [4]
MAE(eV)	1.28	0.21	
MARE(%)	29.4	6.4	

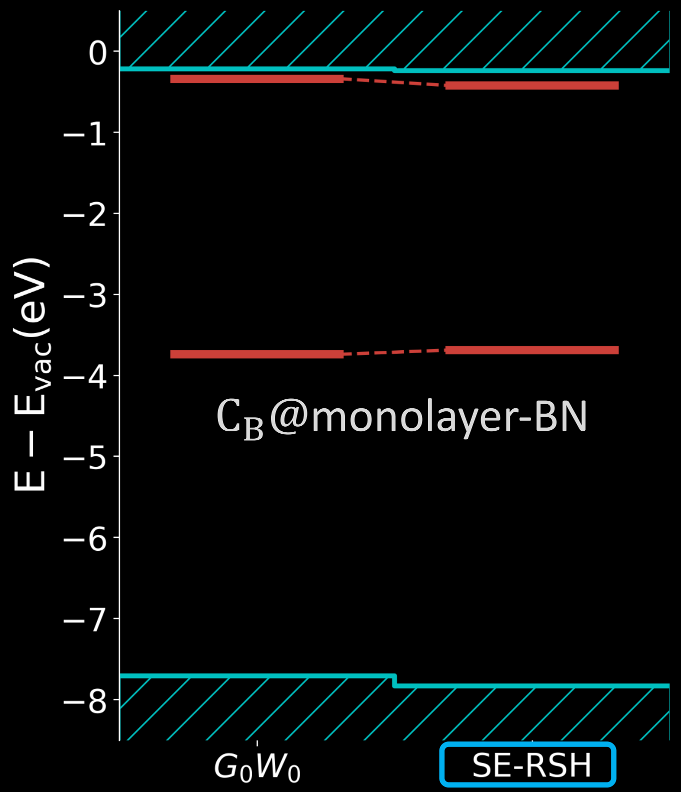
* A total of 9 2D systems were tested

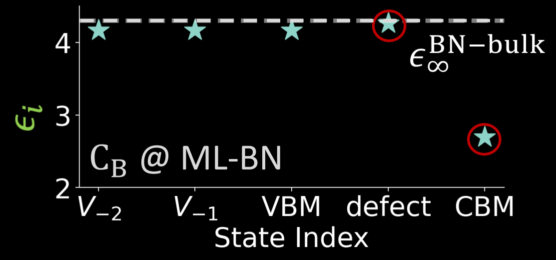
State-dependent screening



$$\epsilon_i = \int \epsilon(\mathbf{r})|\psi_i(\mathbf{r})|^2 \, d\mathbf{r}$$

Defects in 2D systems





Application of SE-RSH to heterogeneous systems

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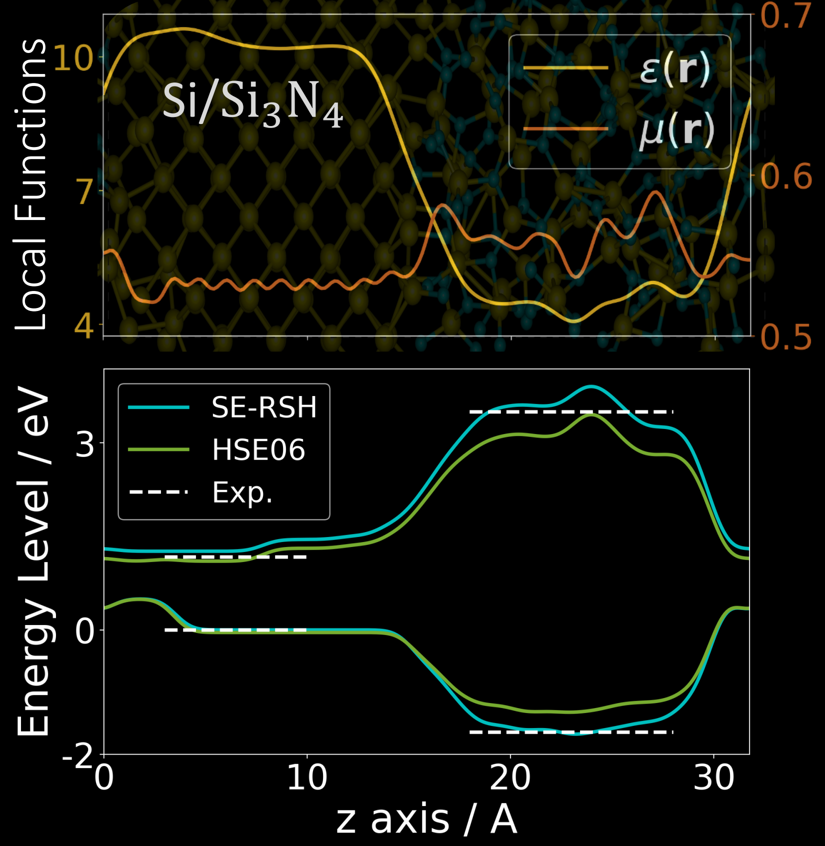
Band offset at interfaces



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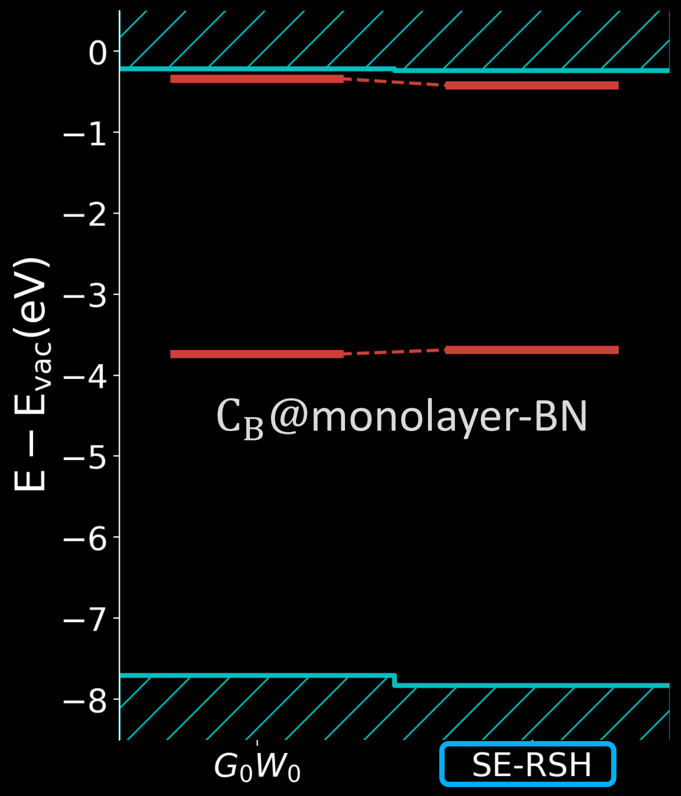
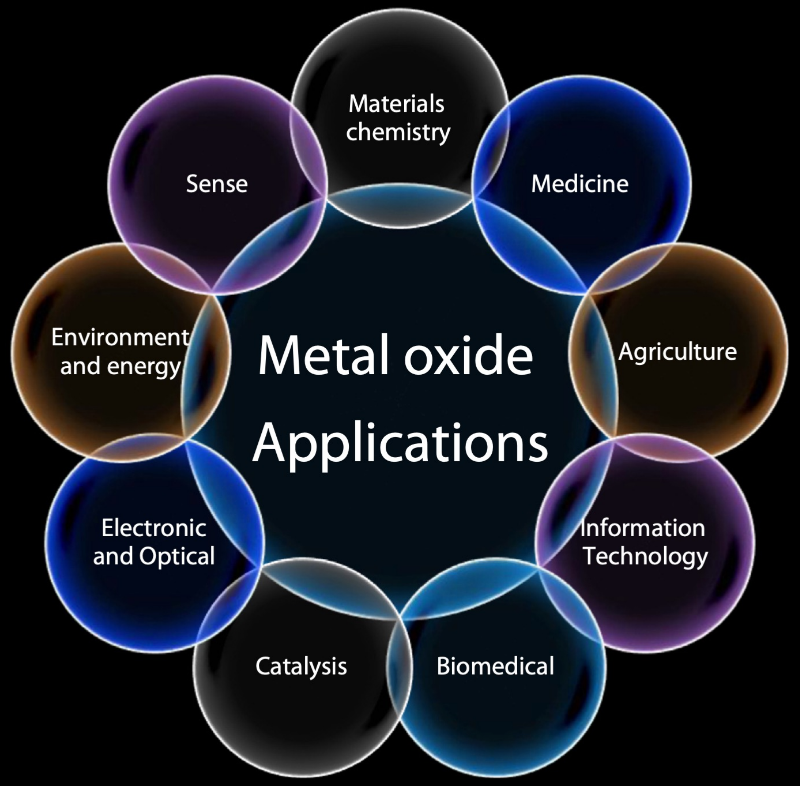


SE-RSH is a **nonempirical hybrid functional** that enable accurate calculations of the electronic properties of heterogeneous systems.

J. Zhan, M. Govoni, and G. Galli, *J. Chem. Theory Comput.*, 2023, doi: 10.1021/acs.jctc.3c00580.

Controversial results for metal oxides

- **Applications of metal oxides are found in a wide range of fields.**



Dielectric-Dependent Hybrid functionals tends to **overestimate** the bandgap of metal oxide.

systems	DD-RSH-CAM* [1]	Exp. + ZPR
In_2O_3	3.51	2.7 ~ 2.9 [2]
TiO_2	4.18	3.65 ~ 3.95 [3]
MnO	4.93	3.9~4.1 [4]
CoO	5.61	2.6 [4]
NiO	6.34	4.0 ~ 4.3 [4]

*DD-RSH-CAM is a dielectric-dependent hybrid that achieve high accuracy in various semiconductors and insulators.

[1] Chen, Wei, et al. *Phys. Rev. Mater. 2.7* (2018)
[2] Scherer, V., et al., Appl. Phys. Lett. 100.21 (2012)
[3] Rangan, Sylvie, et al. J. Phys. Chem. C. 114.2 (2010)
[4] P. Liu et al., J. Phys.: Condens. Matter. 32, 015502 (2019)

Spatial dependence of screening in metal oxides

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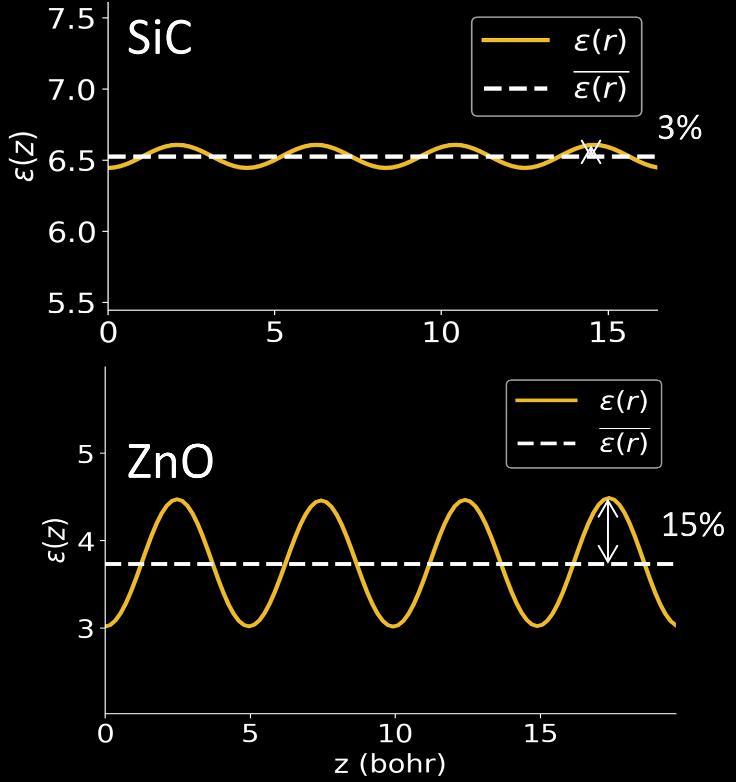
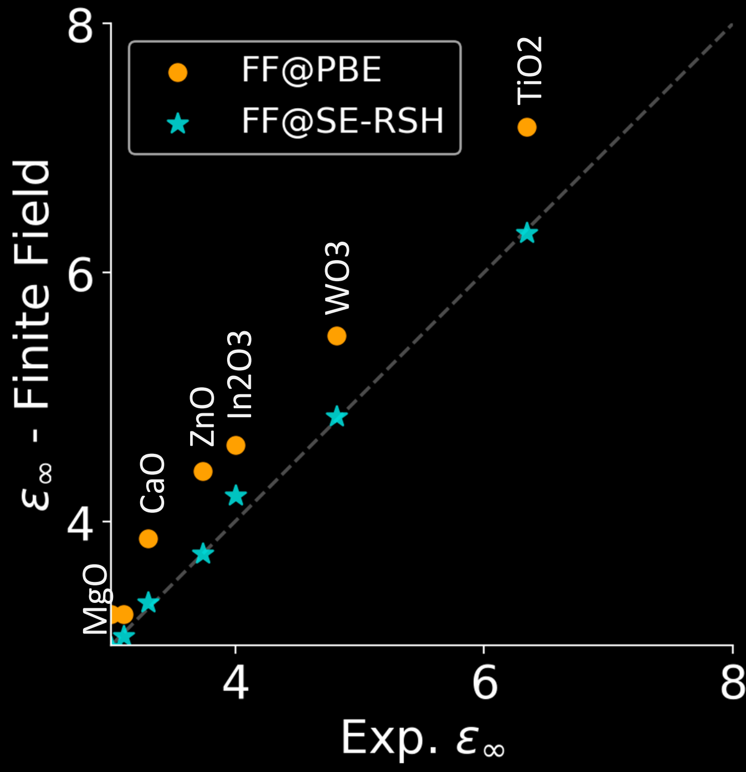
Challenges in applying DDH to metal oxides:

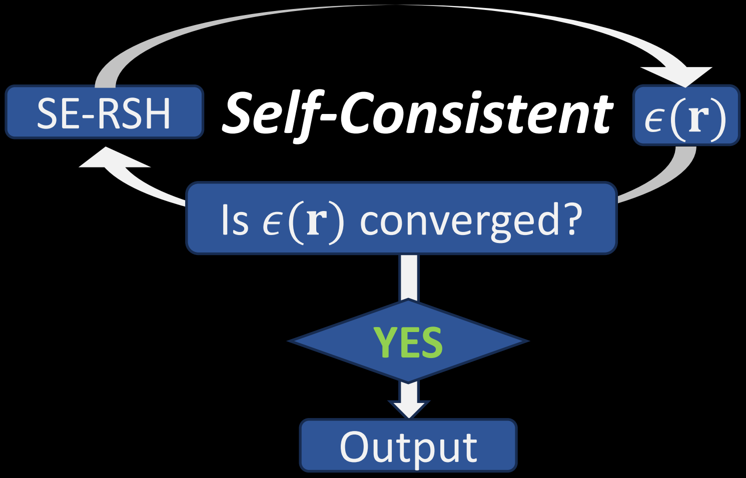


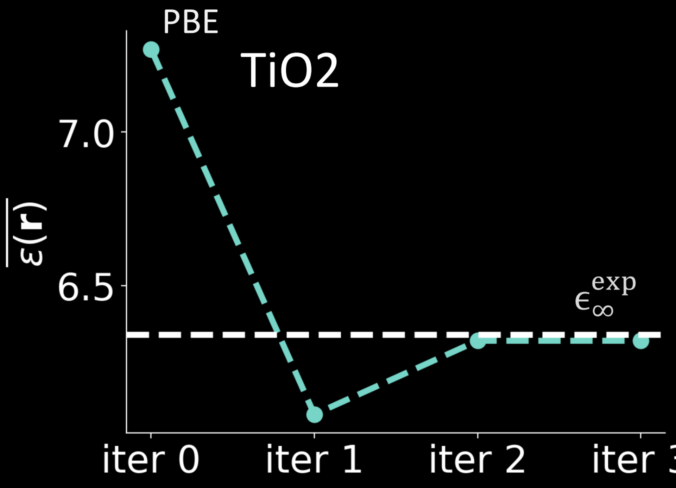
Marked spatial dependence of screening in ionic-bonded systems.



Calculation of ϵ@ PBE overestimates screening

Finite field method @ SE-RSH





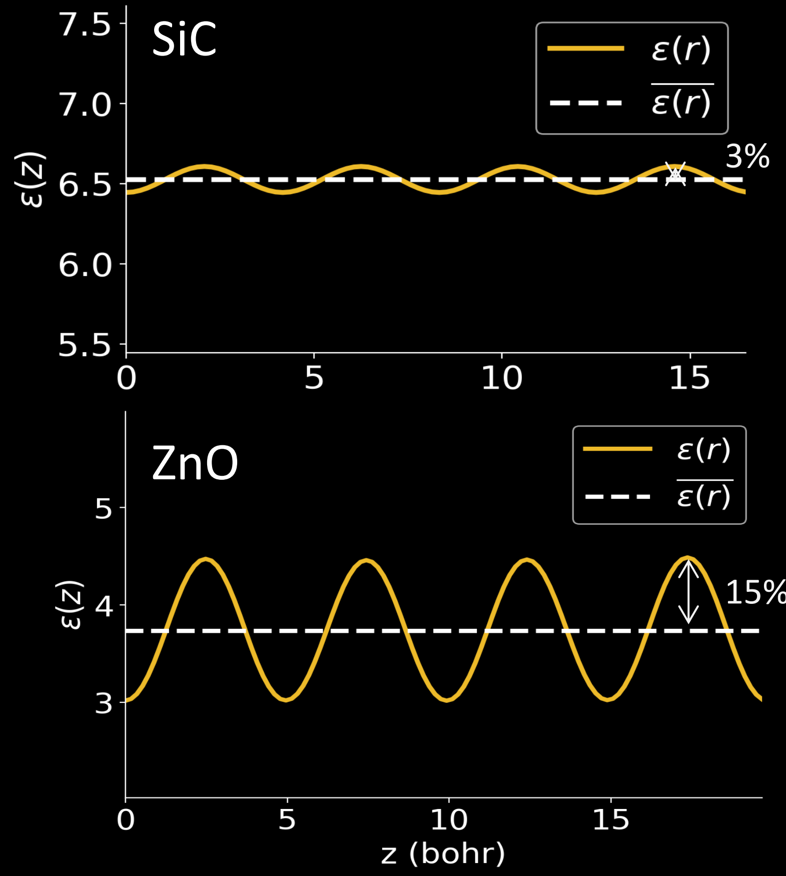
variation of $\epsilon(\mathbf{r})$ along sc cycle

Application of SE-RSH to metal oxides

Electronic band gap (eV) of metal oxides

systems*	DD-RSH-CAM[1]	SE-RSH	Exp. + ZPR
In_2O_3	3.51	2.99	2.7 ~ 2.9 [2]
TiO_2	4.18	4.02	3.65 ~ 3.95 [3]
ZnO	3.74	3.56	3.61 [4]
Al_2O_3	9.51	9.45	9.1 ~ 9.5 [5]
CaO	7.17	7.05	7.43 [6]
MgO	8.19	8.17	8.3 [7]
WO_3	3.92	3.70	3.7 ~ 3.8 [8]
MAE(eV)	0.286	0.213	
MARE(%)	6.87	3.70	

[1] Chen, Wei, et al. *Phys. Rev. Mater. 2.7* (2018)
[2] Scherer, V., et al., *Appl. Phys. Lett. 100.21* (2012)
[3] Rangan, Sylvie, et al. *J. Phys. Chem. C.* 114.2 (2010)
[4] Reynolds, D. C., et al. *Phys. Rev. B* 60.4 (1999)
[5] French, Roger H., *J. Am. Ceram. Soc. 73.3* (1990)
[6] Whited, R. C. et al. *Solid State Commun.* 13.11 (1973)
[7] Onuma, Takeyoshi, et al. *Appl. Phys. Lett.* 119.13 (2021)
[8] Meyer, Jens, et al. *Appl. Phys. Lett.* 96.19 (2010)



SE-RSH results appear to be more accurate than RSH results, due to the inclusion of the spatial variation of the screening.

Conclusions and future work

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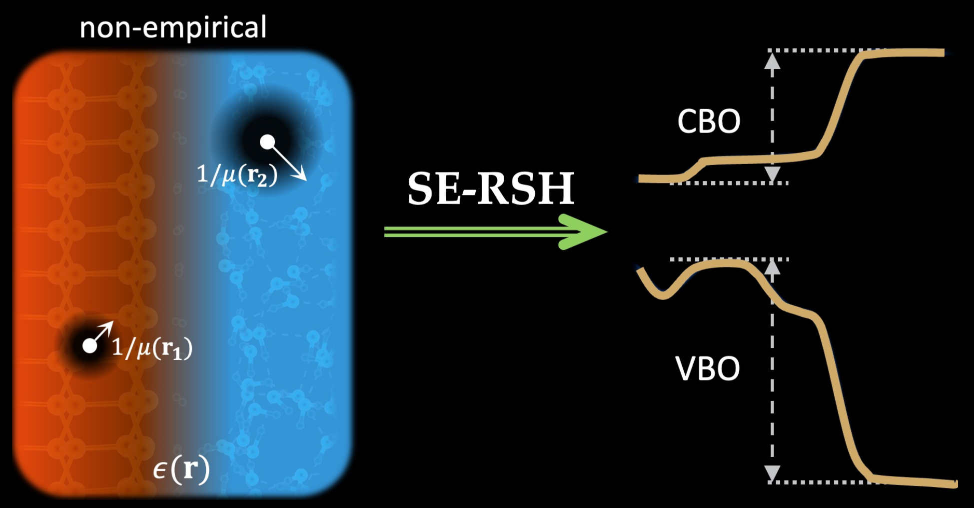
We proposed a nonempirical range-separated hybrid functional with spatially dependent screened exchange, SE-RSH, enabling accurate calculations of the electronic properties of heterogeneous systems and metal oxides.

The validation of our results for diverse materials shows that:

1. **Utilization of local dielectric function $\epsilon(\mathbf{r})$** help SE-RSH achieve high accuracy.
2. **Metal oxides** exhibit a strong spatial variation of the screening, which is captured by **SE-RSH.**



Future Work

1. Study metal-oxide interfaces w/wo defects.
2. Integrate Time-Dependent Density Functional Theory (TDDFT) with SE-RSH.
3. Accelerate exact exchange calculations in SE-RSH for modeling large-scale complex systems.

J. Zhan, M. Govoni, and G. Galli, *J. Chem. Theory Comput.*, 2023, doi: 10.1021/acs.jctc.3c00580.

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GW Static Screening is well approximated by α^{SE-RSH}

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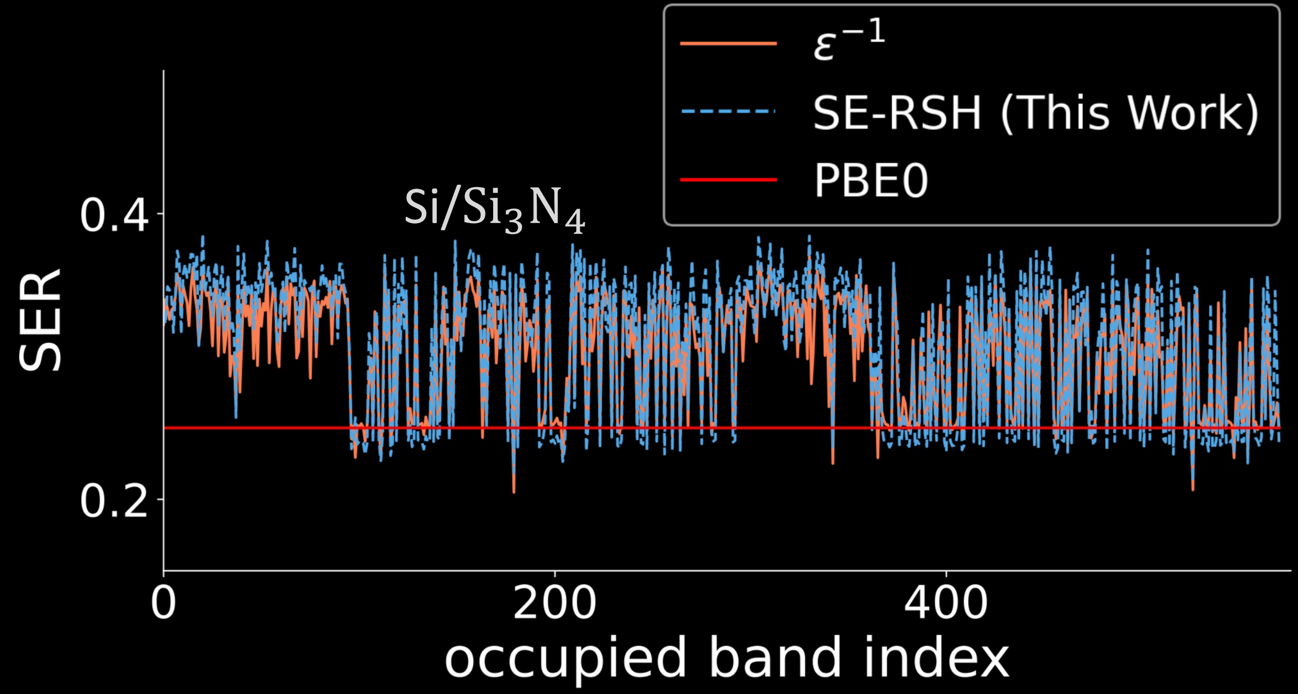
$$\sum_j \langle ij|\alpha \odot v_c|ji\rangle \quad \text{vs.} \quad \sum_j \langle ij|\epsilon^{-1} v_c|ji\rangle$$

ϵ^{-1} : full dielectric matrix
v_c : bared coulomb interaction
$\{|i\rangle\}$: Maximally Localized Wannier Functions

screened exchange ratio (SER):

$$\mathrm{SER}_i^{\alpha} = \frac{\sum_j \langle ij|\alpha \odot v_c|ji\rangle}{\sum_j \langle ij|v_c|ji\rangle}$$

$$\mathrm{SER}_i^{\epsilon^{-1}} = \frac{\sum_j \langle ij|\epsilon^{-1} v_c|ji\rangle}{\sum_j \langle ij|v_c|ji\rangle}$$



α^{SE-RSH} effectively approximates and accurately describes non-dynamical screening