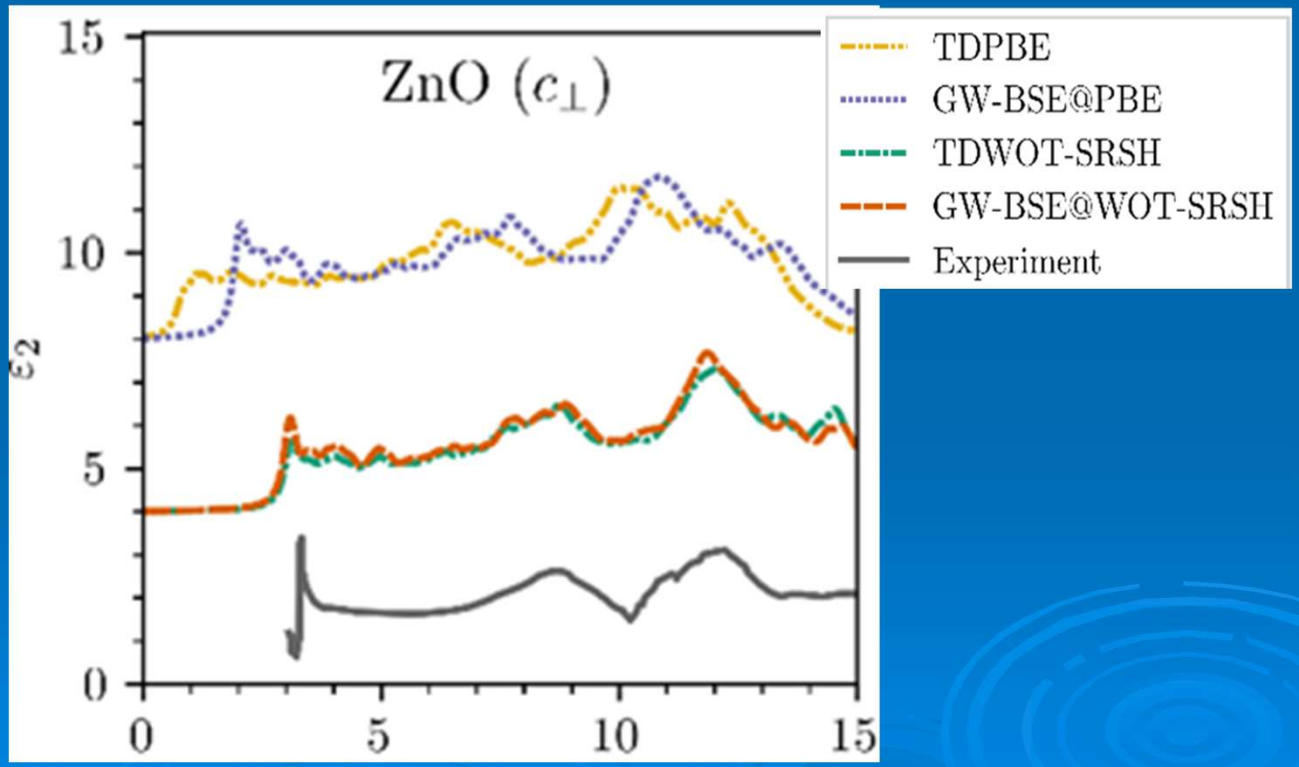
Accurate prediction of electronic and optical excitations in 3d and 2d materials from density functional theory

Solving the solid-state band gap and optical absorption problems of density functional theory

Leeor Kronik

Weizmann Institute of Science, Rehovoth, Israel



10th TDDFT Meeting, Benasque, Spain, April 2025

Mind the gap

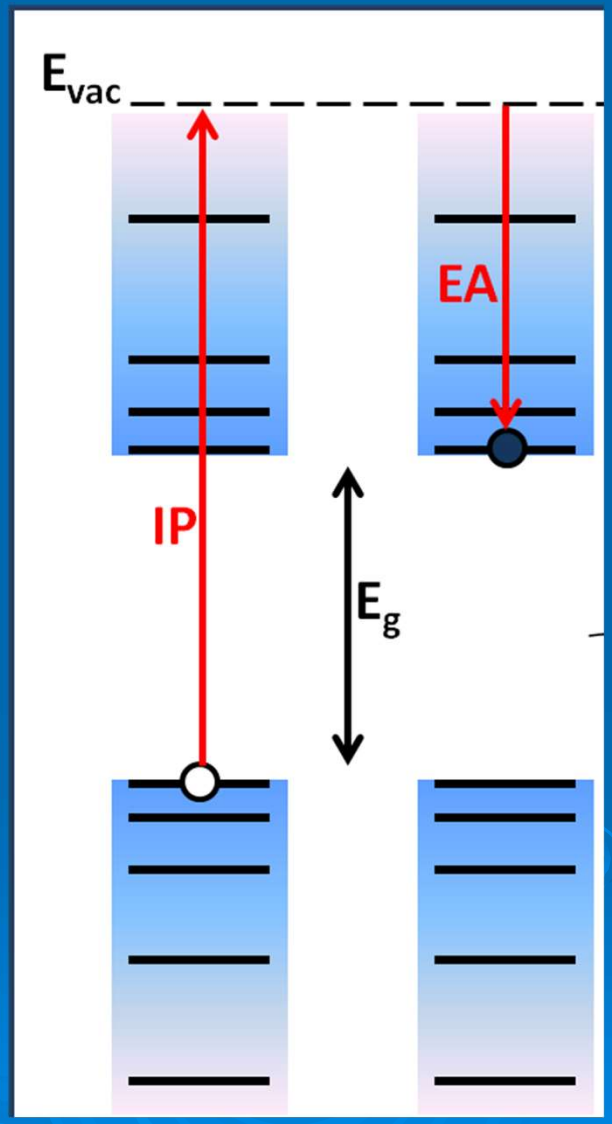
The Kohn-Sham gap underestimates the real gap

$$E_g = I - A = \varepsilon_{KS}^{LUMO} - \varepsilon_{KS}^{HOMO} + \Delta_{xc}$$

derivative discontinuity!

Perdew and Levy, *PRL* 1983;

Sham and Schlüter, *PRL* 1983



Kohn-Sham eigenvalues do not mimic the quasi-particle picture even in principle!

Confirmed by calculations:

Godby, Schlüter, Sham, Phys. Rev. Lett. 56, 2415 (1986).

Chan, J. Chem. Phys. 110, 4710 (1999).

Allen and Tozer, Mol. Phys. 100, 433 (2002).

Bandgaps and optical absorption spectrum of silicon

1. Wrong band gaps:

Indirect:

$E_{g,\mathrm{exp}} = 1.1$ eV

$E_{g,PBE} = 0.58$ eV

Direct:

$E_{g,\mathrm{exp}} = 3.35$ eV

$E_{g,PBE} = 2.6$ eV

HSE:

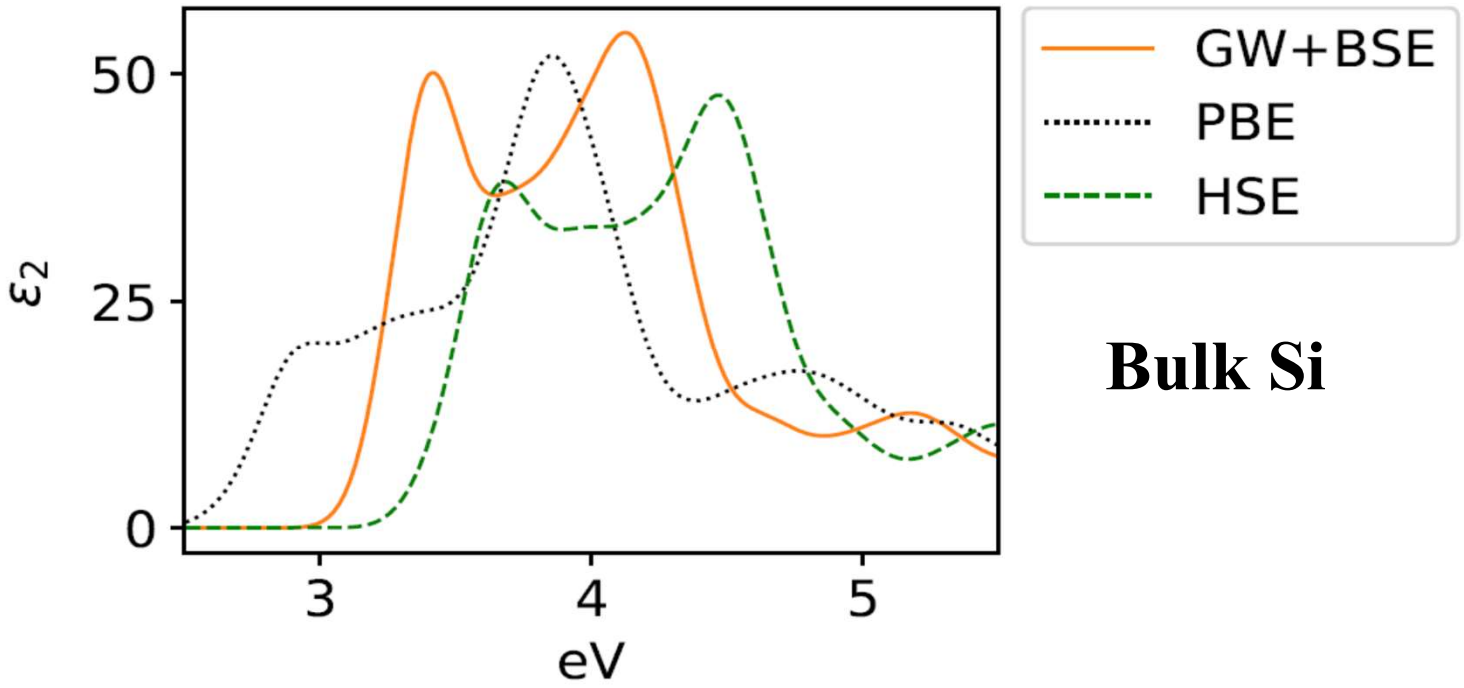
Indirect:

- $E_{g,exp} = 1.12\ eV$
- $E_{g,HSE} = 1.15\ eV$

Direct:

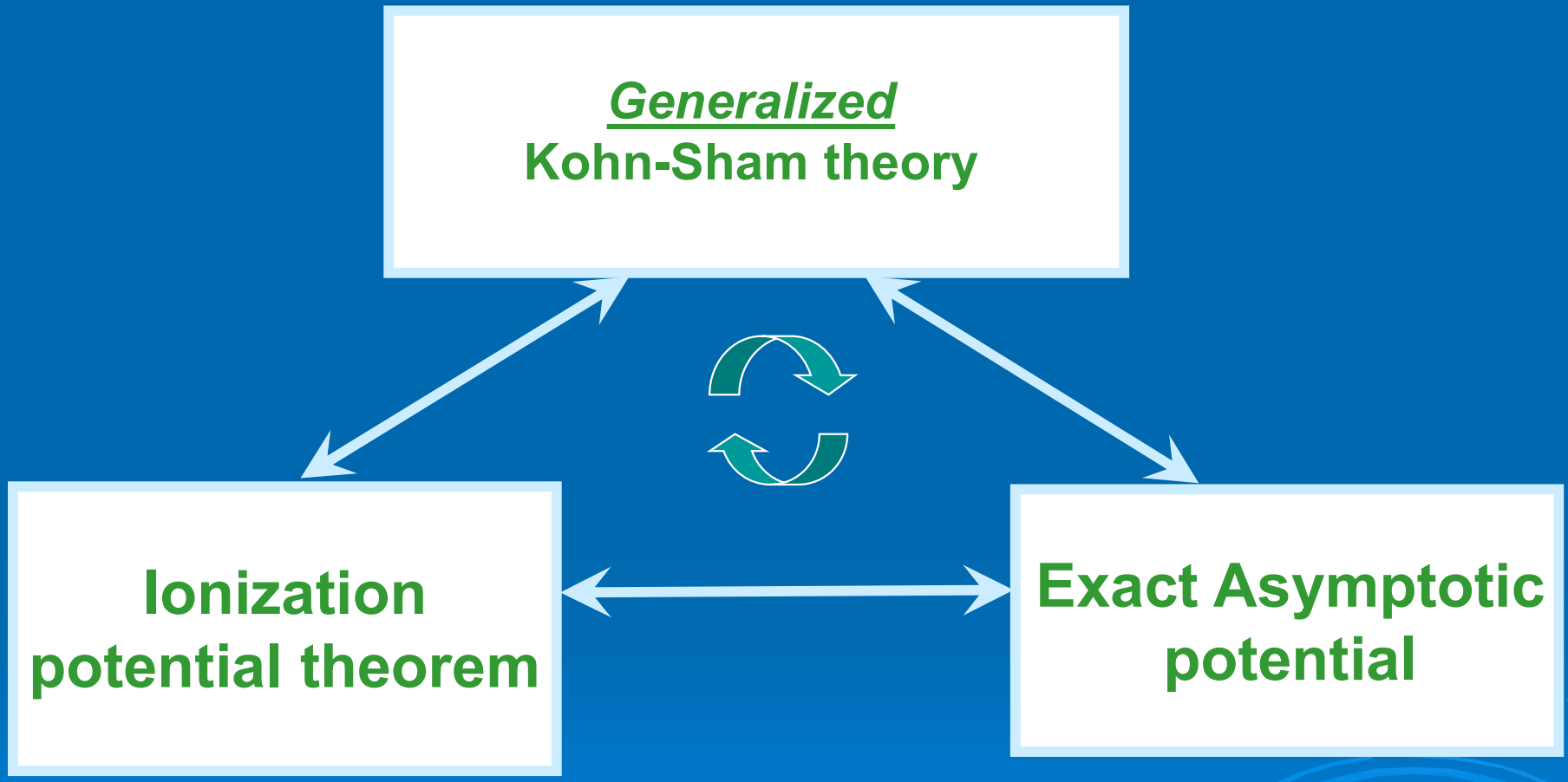
- $E_{g,exp} = 3.35\ eV$
- $E_{g,HSE} = 3.3\ eV$

2. Wrong optical absorption spectrum:



Bulk Si

Common origins
- *and unified approach to solution* -
of these and other failures



"The world stands on three principles"
- Simon the Righteous

"על שלשה דברים העולם עומד"
- שמעון הצדיק

Kronik, Stein, Refaely-Abramson, Baer, *J. Chem. Theo. Comp.* 8, 1515 (2012).

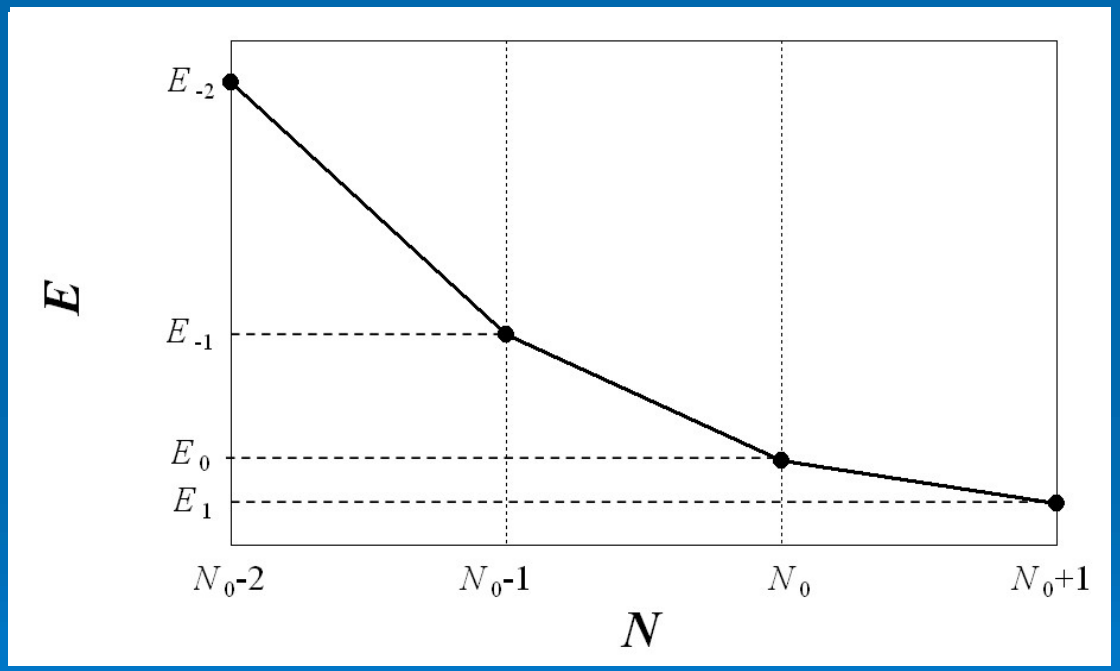
Piecewise linearity in DFT: Exact results from ensemble arguments

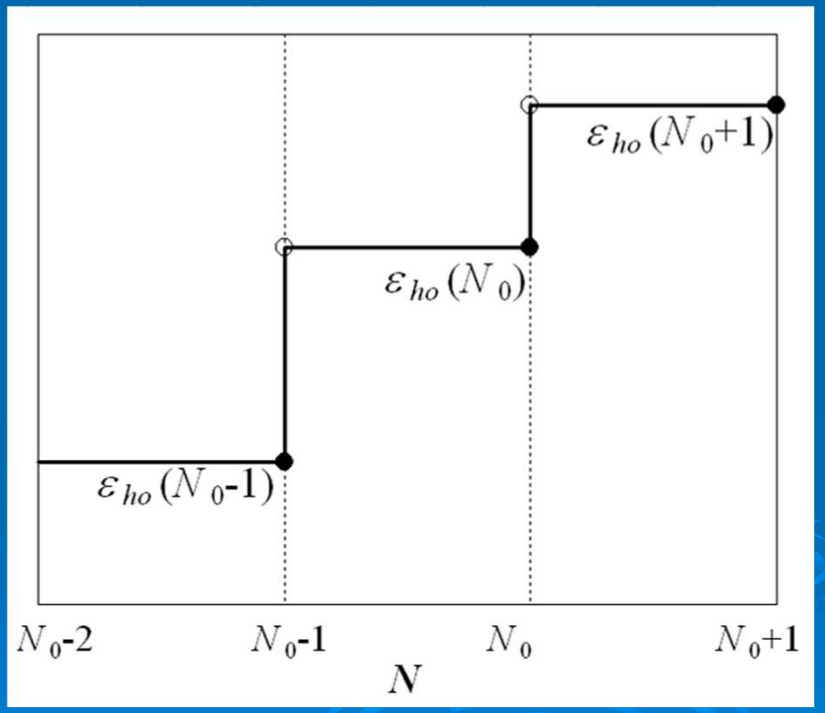
- Piecewise-linearity

$$E(N) = (1-\alpha)E_0 + \alpha E_1$$

- The IP theorem

$$\varepsilon_{ho}(N) = -I(N_0) =: E_0 - E_{-1}$$





Perdew, Parr, Levy, Balduz, PRL 49, 1691 (1982).

Pure state proof: Yang, Zhang, Ayers, PRL 84, 5172 (2000).

Hybrid functionals mix Fock and Kohn-Sham exchange

$$\left(-\frac{1}{2}\nabla^2 + V_{ion}(r) + V_H([n];r) + a\hat{V}_F + (1-a)v_x^{sl}([n];r) + v_c^{sl}([n];r)\right)\varphi_i(r) = \varepsilon_i\varphi_i(r)$$

They are ***outside*** Kohn-Sham theory
owing to the use of a non-multiplicative potential

But well within ***generalized*** Kohn-Sham theory, which maps to a *partially interacting* electron gas that is represented by a single Slater determinant.

DFT: Seidl, Goerling, Vogl, Majevski, Levy, *Phys. Rev. B* 53, 3764 (1996).

Multitude of exact maps:
Choose the one that eliminates the derivative discontinuity!

Kronik, Stein, Refaely-Abramson, Baer, *J. Chem. Theo. Comp.* 8, 1515 (2012).
Garrick, Natan, Gould, Kronik, *Phys. Rev. X* 10, 021040 (2020).
Kronik & Kümmel, *PCCP* 22, 16467 (2020).

Tim Gould

Generalized Kohn-Sham theory in action: global hybrid functionals

Rachel Garrick

Exact Hybrid Theory

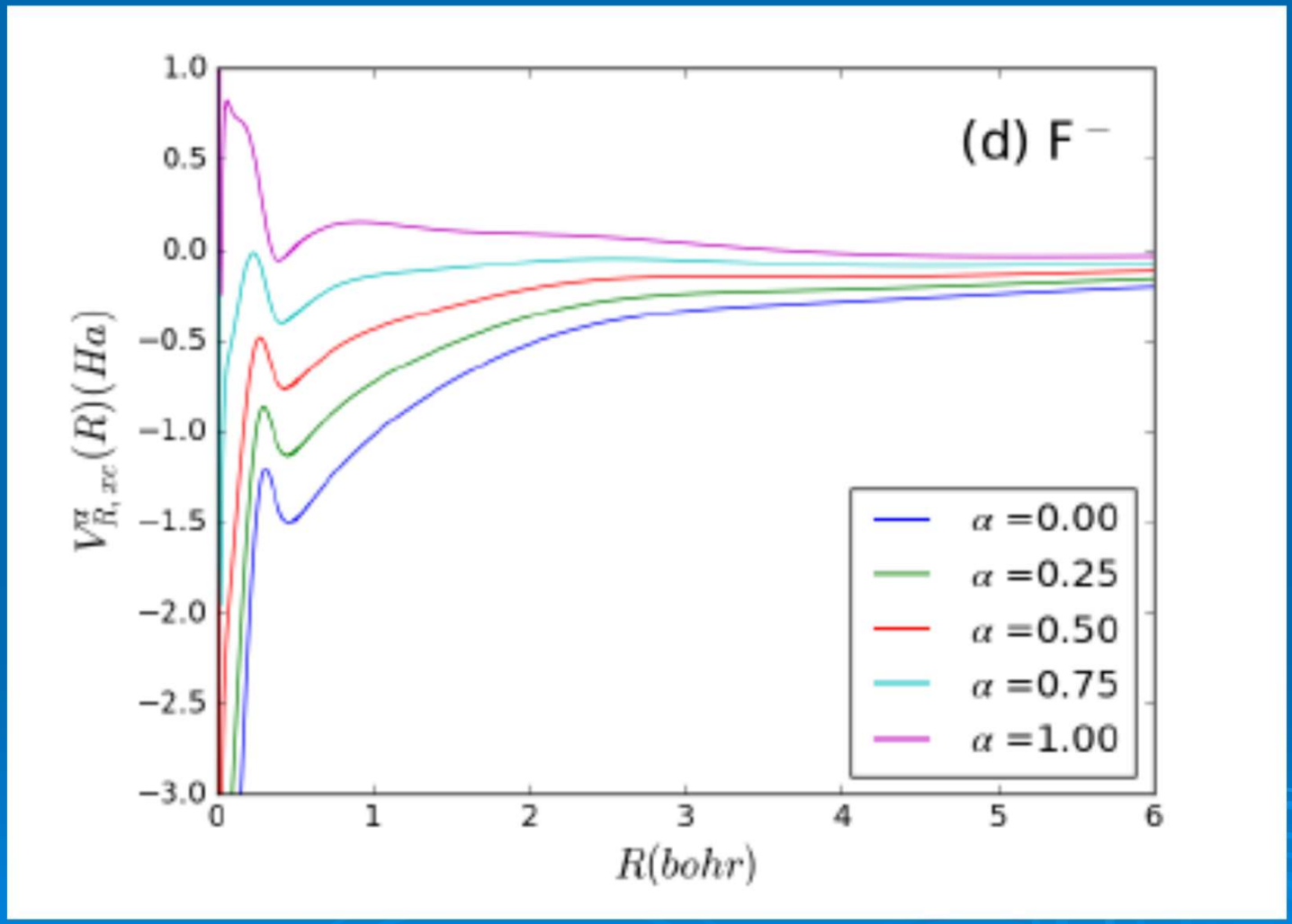
$$\left(-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + \alpha\hat{V}_F + \alpha V_{\text{H}}([n];\mathbf{r}) + V_R([n];\mathbf{r})\right)\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

Approximate Hybrid Theory

$$V_R^{\alpha}([n];\boldsymbol{r}) = (1-\alpha)V_{\text{H}}([n];\boldsymbol{r}) + (1-\alpha)V_{\text{x,SL}}([n];\boldsymbol{r}) + V_{\text{c,SL}}([n];\boldsymbol{r})$$

Görling, Levy, J. Chem. Phys. 106, 2675 (1997).
Garrick, Natan, Gould, Kronik, Phys. Rev. X 10, 021040 (2020).

Exact Generalized Kohn-Sham theory in action: The case of a hybrid functional



Garrick, Natan, Gould, Kronik, Phys. Rev. X 10, 021040 (2020)

Extending the Reach of Generalized Kohn-Sham Theory

Eur. Phys. J. B (2018) 91: 170
https://doi.org/10.1140/epjb/e2018-90103-0

THE EUROPEAN PHYSICAL JOURNAL B

Regular Article

Time-dependent generalized Kohn–Sham theory*

Roi Baer[1,a] and Leeor Kronik[2,b]

Ensemble generalized Kohn–Sham theory: The good, the bad, and the ugly

Cite as: J. Chem. Phys. **154**, 094125 (2021); https://doi.org/10.1063/5.0040447
Submitted: 13 December 2020 . Accepted: 11 February 2021 . Published Online: 05 March 2021

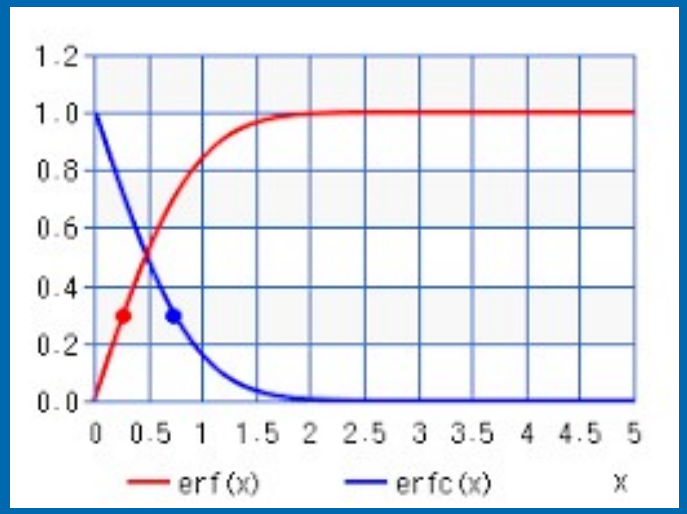
Tim Gould, and Leeor Kronik

Range-separated hybrid functionals

Coulomb operator decomposition:

$$r^{-1} = r^{-1}\mathrm{erfc}(\gamma r) + r^{-1}\mathrm{erf}(\gamma r)$$

Short Range **Long Range**



Emphasize long-range exchange, short-range exchange correlation!

$$\left(-\frac{1}{2}\nabla^2 + V_{ion}(r) + V_H([n];r) + \hat{V}_F^{lr,\gamma} + v_x^{sr,\gamma}([n];r) + v_c^{sl}([n];r)\right)\varphi_i(r) = \varepsilon_i\varphi_i(r)$$

See, e.g.: Leininger et al., *Chem. Phys. Lett.* 275, 151 (1997)
Iikura et al., J. *Chem. Phys.* 115, 3540 (2001)
Yanai et al., *Chem. Phys. Lett.* 393, 51 (2004)

But how to choose the range??

Tamar Stein

Gen 1: Optimal tuning !

Roi Baer

Ionization potential theorem:

$$-\varepsilon^{\gamma}_{\mathrm{HOMO}} = E_{gs}(N-1;\gamma) - E_{gs}(N;\gamma)$$

Tune, don't fit, the range-separation parameter!

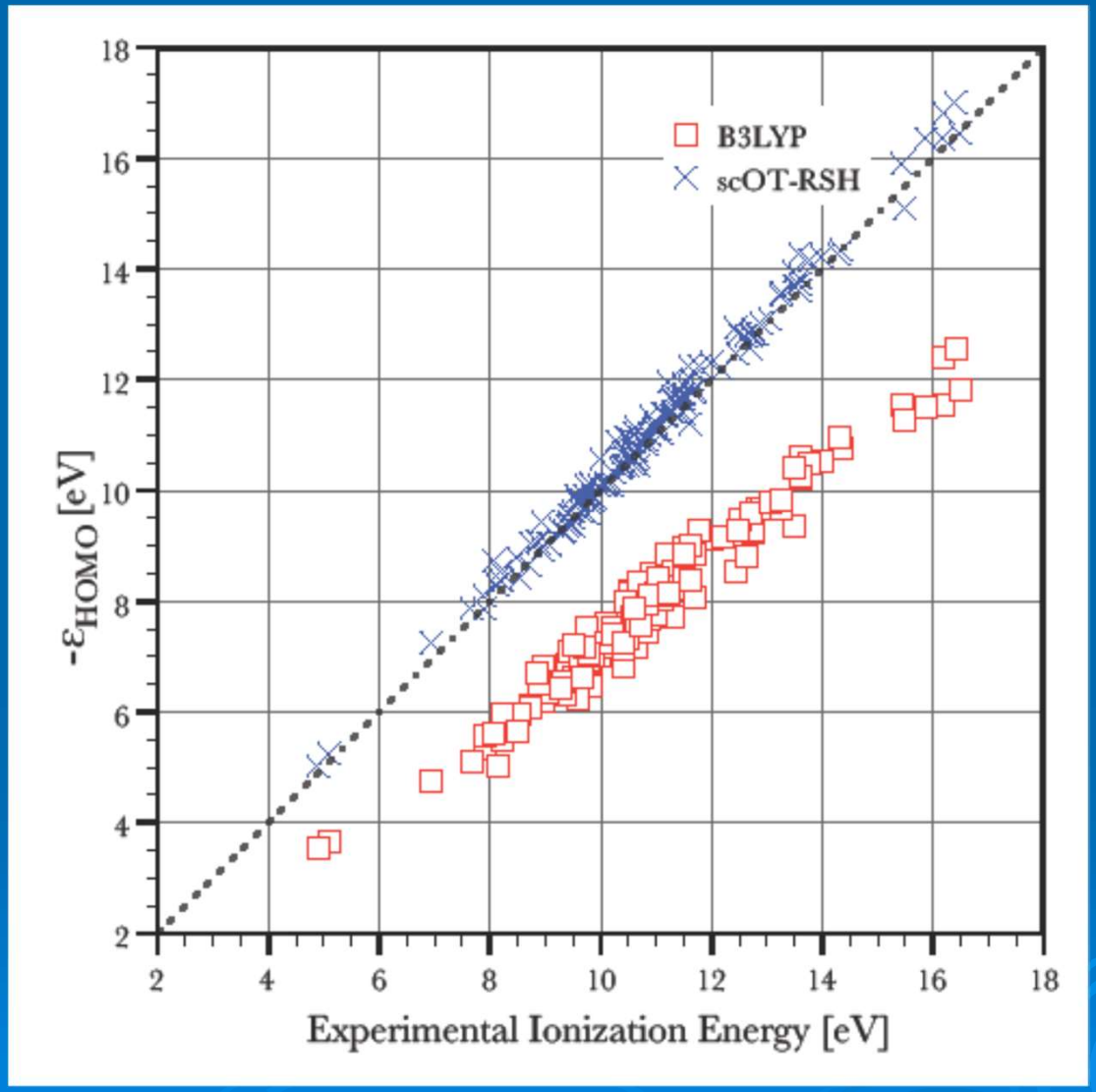
Stein, Kronik, Baer, J. Am. Chem. Soc. (Comm.) 131, 2818 (2009).
Stein, Eisenberg, Kronik, Baer, Phys. Rev. Lett. 105, 266802 (2010).

Ionization potential and geometry for all 148 molecules in the G2 set

Isaac Tamblyn

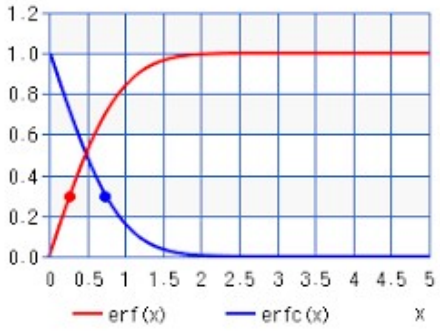
Jeff Neaton

Sivan Refaely-Abramson



Tamblyn, Refaely-Abramson, Neaton, Kronik, J. Phys. Chem. Lett. 5, 2734 (2014).

Gen 2: *Screened* range-separated hybrid (SRSH) functionals



$$\frac{1}{r} = \underbrace{\frac{\mathrm{erfc}(\gamma r)}{r}}_{\text{Short range}} + \underbrace{\frac{\mathrm{erf}(\gamma r)}{r}}_{\text{Long range}}$$

$$\frac{1}{r} = (1-\alpha)\frac{\mathrm{erfc}(\gamma r)}{r} + \alpha\frac{\mathrm{erfc}(\gamma r)}{r} + \left(1-\frac{1}{\epsilon}\right)\frac{\mathrm{erf}(\gamma r)}{r} + \frac{1}{\epsilon}\frac{\mathrm{erf}(\gamma r)}{r}$$

Semilocal exchange (PBE)

Exact exchange

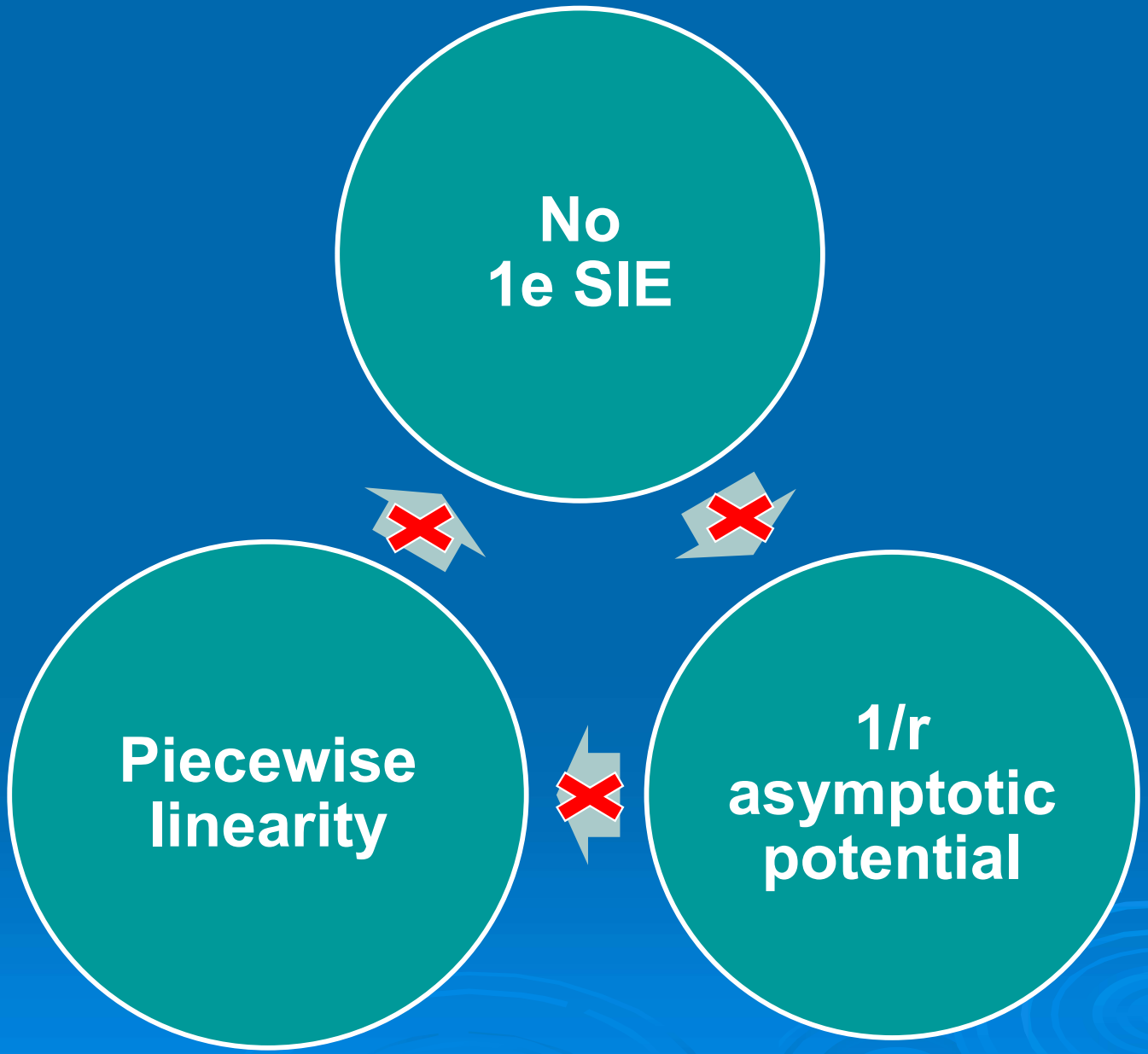
Refaely-Abramson et al., Phys. Rev. Lett. 109, 226405 (2012).
Refaely-Abramson et al., Phys. Rev. B (R) 88, 081204 (2013).

Overviews:

Kronik & Neaton, Annu. Rev. Phys. Chem. 67, 587 (2016).
Kronik & Kümmel, Adv. Materials 30, 1706560 (2018).

Three *inequivalent properties* of the exact functional

Stephan Kümmel



Kronik & Kümmel, PCCP 22, 16467 (2020).

Sahar Sharifzadeh

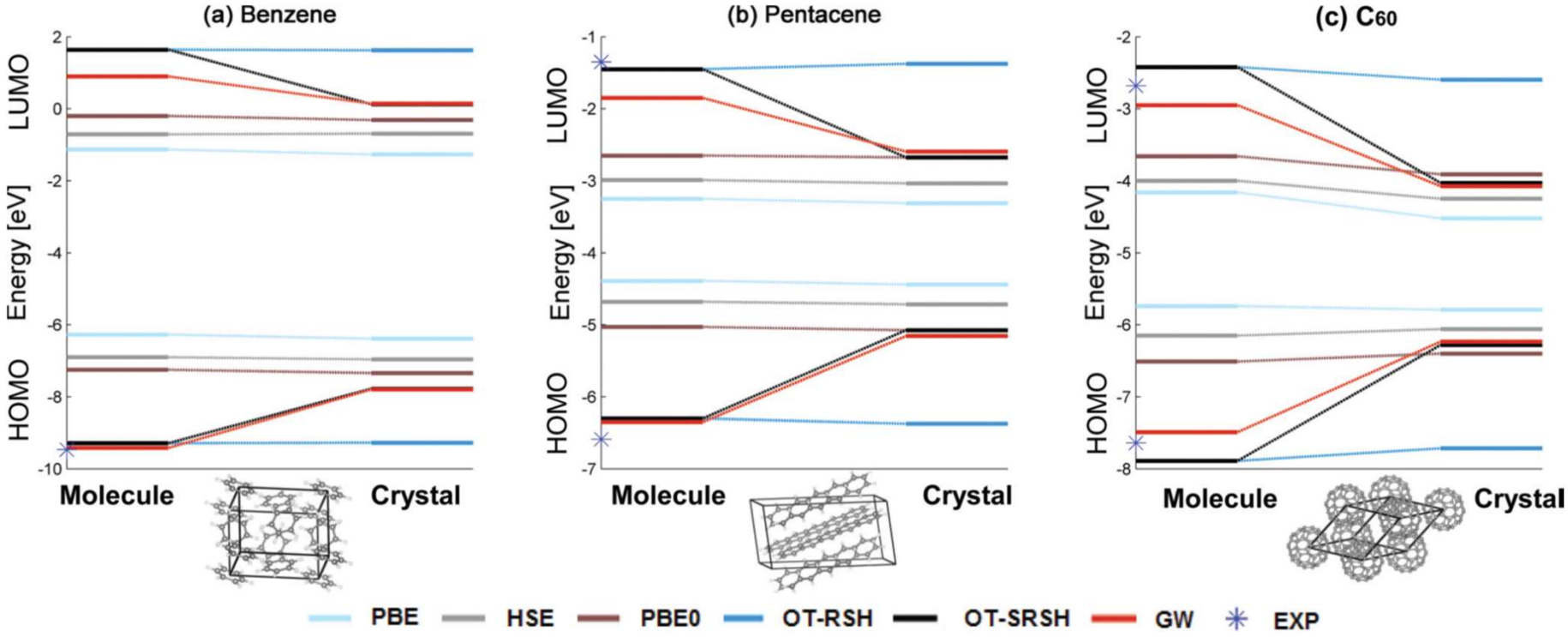
Jeff Neaton

Gap renormalization

Sivan Refaely-Abramson

SRSH — GW ✳ EXP

Just screen the long-range exchange!



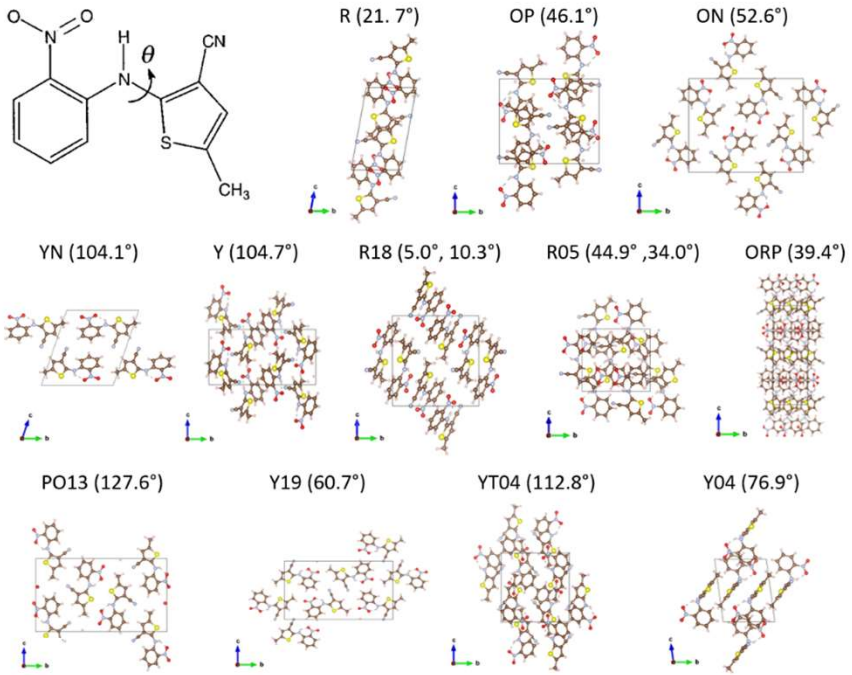
- ~~Molecular gaps are too small~~
- ~~No renormalization~~

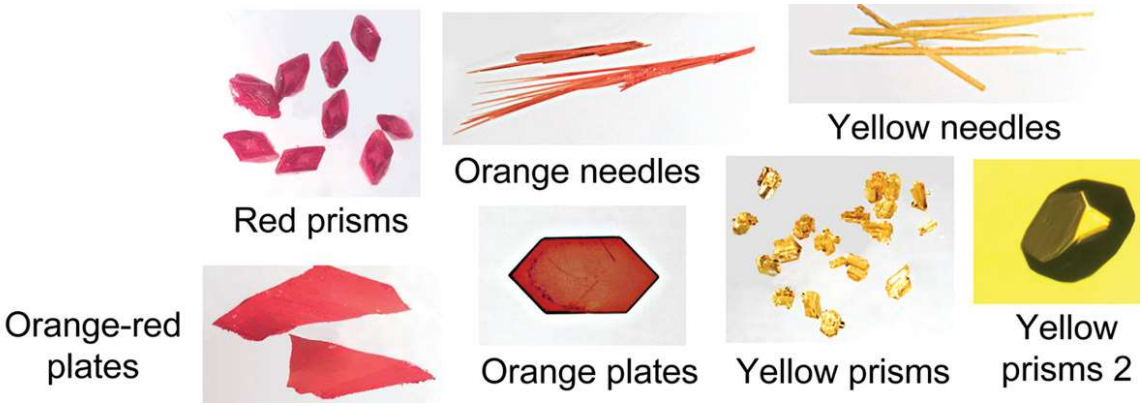
S. Refaely-Abramson, S. Sharifzadeh, M. Jain, R. Baer, J. B. Neaton and L. Kronik, Phys. Rev. B(R) 88, 081204 (2013).

Color Polymorphism

Different polymorphs of the same compound with different optical absorption in the visible range, which results in different colors

ROY (5-Methyl-2-[(2-nitrophenyl) amino]-3-thiophenecabonitrile**) – Red, Orange, Yellow**

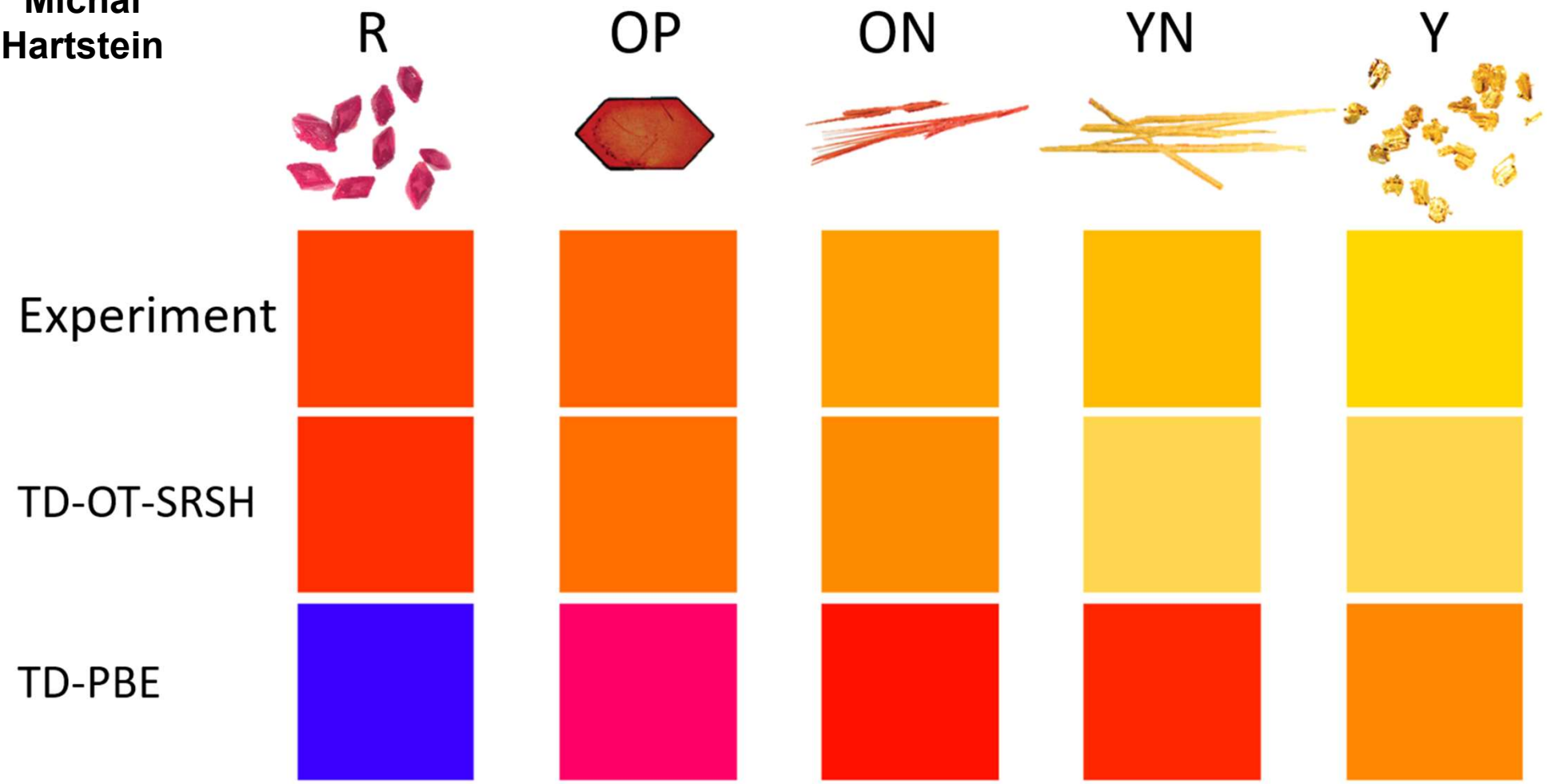




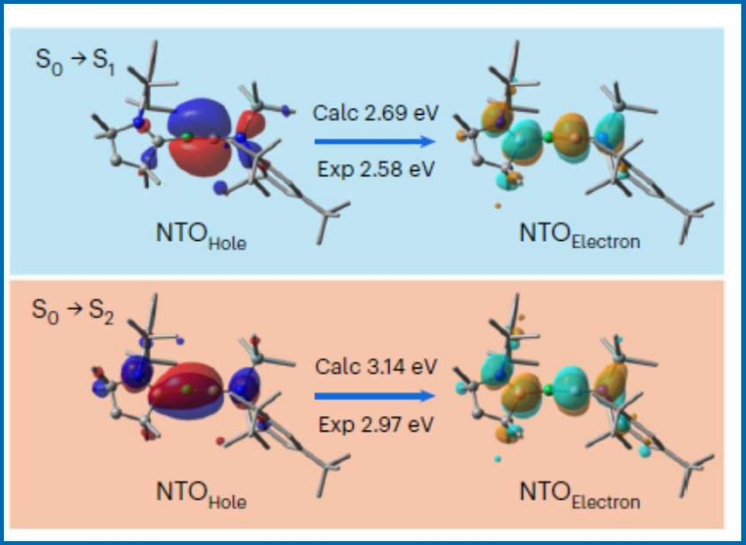
Yu, Lian, Accounts of chemical research 43, 1257 (2010).

Results: Colors of ROY Polymorphs

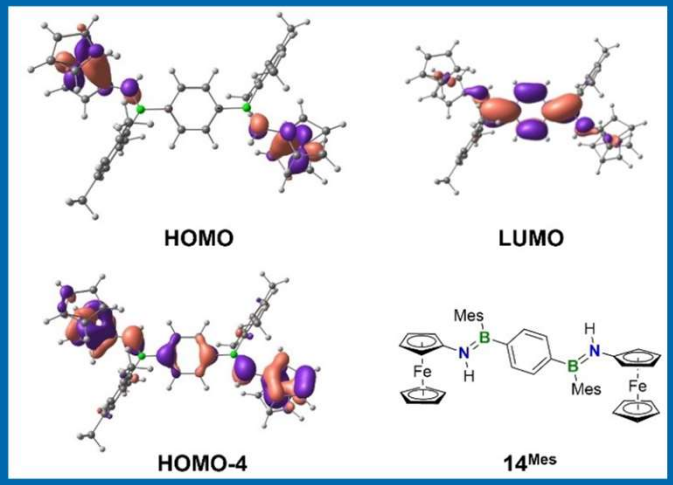
Michal Hartstein



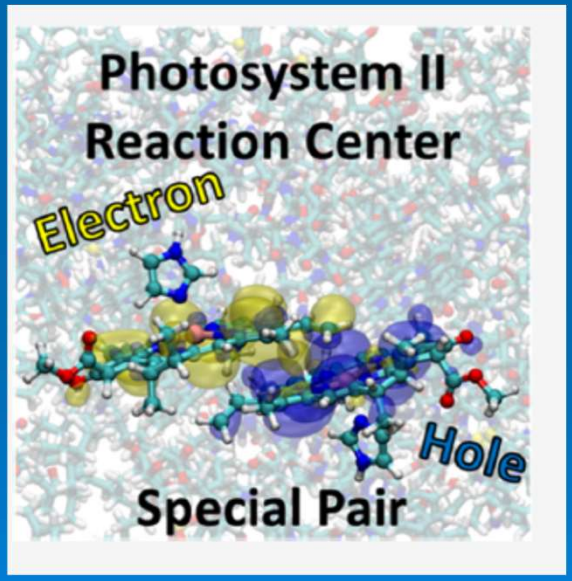
Hartstein, Ohad, Kronik, *J. Chem. Theory Comp.* 20, 5510 (2024)



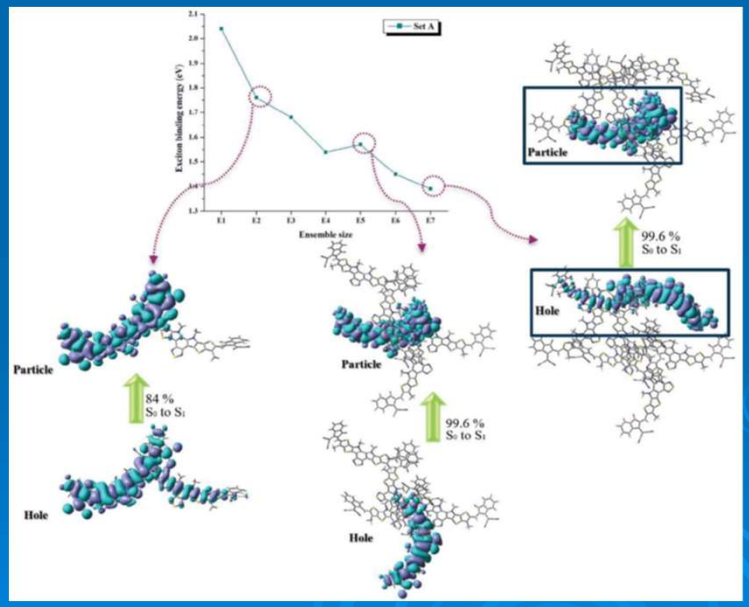
Novel Organic Molecules
Nature Synthesis (2025)



Metal-organic complexes
Schneider et al., Chem. Eur. J (2025)



Charge Transfer in biochemical systems
Forde et al., J. Phys. Chem. Lett. (2025)



Excitons in films for photovoltaics
Akram et al., Adv. Funct. Materials (2025)

The solid state quandary: $\Delta I \to 0$ because the VBM state is delocalized

Supercell (k unit cells)

$+\frac{1}{k}$	$+\frac{1}{k}$	$+\frac{1}{k}$
$+\frac{1}{k}$	$+\frac{1}{k}$	$+\frac{1}{k}$
$+\frac{1}{k}$	$+\frac{1}{k}$	$+\frac{1}{k}$

$$\Delta I = E(N-1) - E(N) + \epsilon_{VBM}$$

$$= kE_{cell}\left(N_{cell} - \frac{1}{k}\right) - kE_{cell}(N_{cell}) + \epsilon_{VBM}$$

$$= \lim_{k\to\infty} \frac{E_{cell}\left(N_{cell} - \frac{1}{k}\right) - E_{cell}(N_{cell})}{\frac{1}{k}} + \epsilon_{VBM}$$

$$= -\left.\frac{dE_{cell}}{dn}\right|_{N_{cell}} + \epsilon_{VBM}$$

Janak's theorem

$$\Delta I = -\epsilon_{VBM} + \epsilon_{VBM} = 0$$

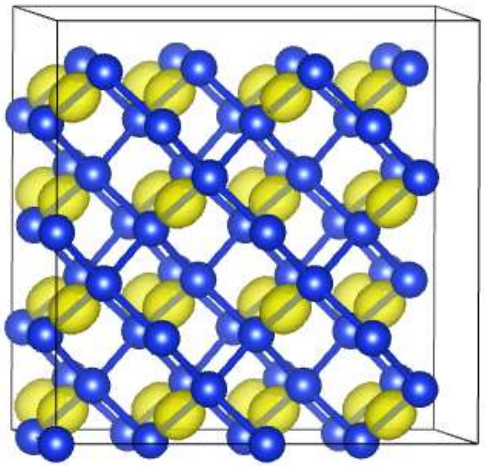
Mori-Sanchez, Cohen, and Yang, Phys. Rev. Lett. 100, 146401 (2008).
Kraisler & Kronik, J. Chem. Phys. 140, 18A540 (2014).
Vlcek et al., J. Chem. Phys. 142, 034107 (2015).

Dahvyd Wing **Guy Ohad**

Use constrained DFT to compute ΔI upon enforcing charge removal from a maximally localized Wannier function

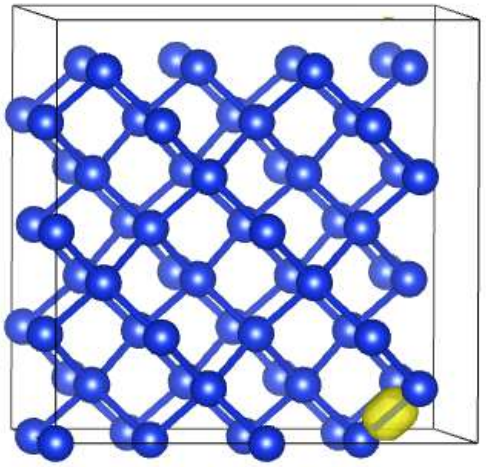
Marzari *et al.*, "Maximally localized Wannier functions: Theory and applications"
Rev. Mod. Phys. 84, 1419 (2012)

VBM Wavefunction of Silicon



See also work from groups of Marzari, Pasquarello, Yang, Wang, Galli, Ullrich, O'Reagan…

Maximally localized Wannier function of Silicon



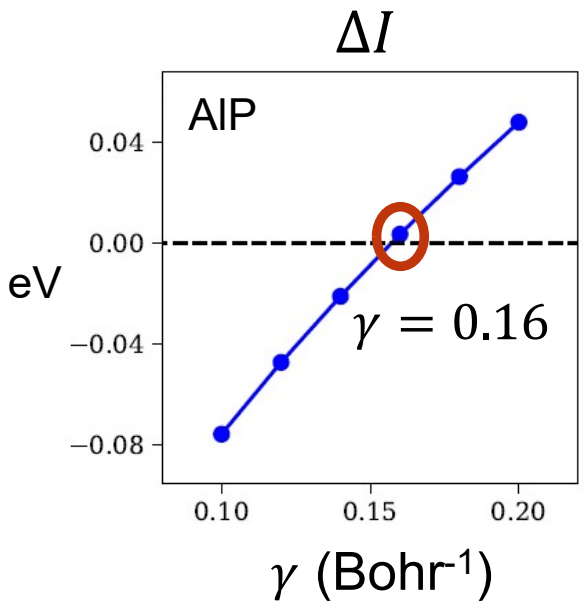
$$E_{\text{constr}}[\phi](N-1) = \min_{\psi}\left\{E_{\text{tot}}^{\text{SRSH}}(N-1) + \lambda\left(\sum_{i=1}^{N-1}|\langle\psi_i|\phi\rangle|^2 - f_\phi\right)\right\}$$

Ma and Wang,
Sci. Rep. 6, 24924 (2016)

$$\hat{H}_{\text{SRSH}}|\psi_i\rangle + \lambda|\phi\rangle\langle\phi|\psi_i\rangle = \epsilon_i|\psi_i\rangle$$

Gen 3: The Wannier-localized, optimally-tuned screened range-separated hybrid (WOT-SRSH) functional

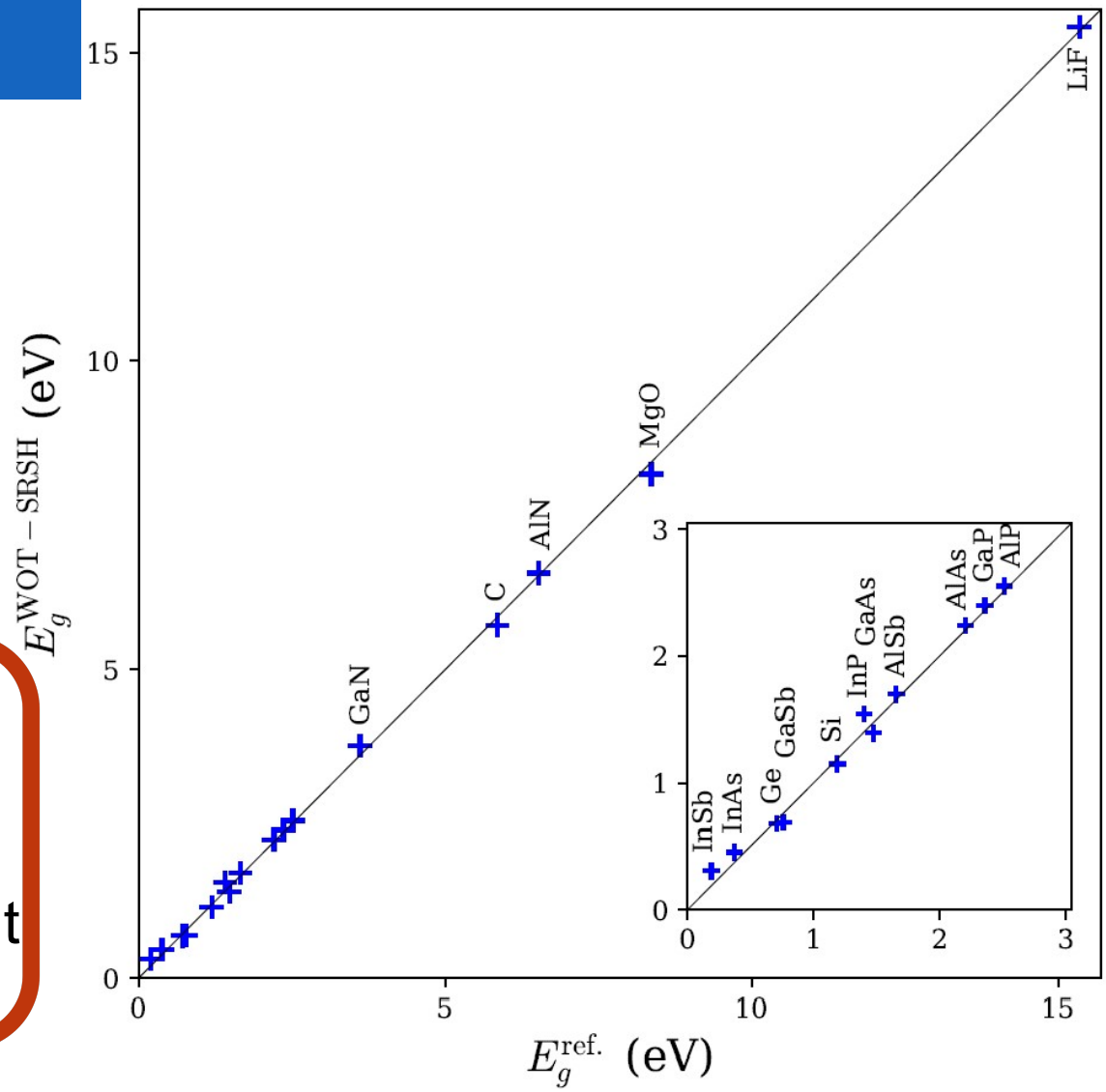
Ansatz: $\Delta I = E_{\text{constr}}[\phi](N-1) - E(N) + \langle \phi | \hat{H}_{\text{SRSH}} | \phi \rangle = 0$



Wing, Ohad, Haber, Filip, Gant, Neaton, Kronik, PNAS 118, e2104556118 (2021)

Testing WOT-SRSH on 16 well-studied materials

Reference band gaps, $E_g^{\mathrm{ref.}}$, are the experimental band gap plus the zero point renormalization (ZPR) energy



- Mean absolute error: ~0.1 eV
  - Largest error is 0.2 eV
- G_0W_0 with a PBE starting point has MAE of 0.4 eV

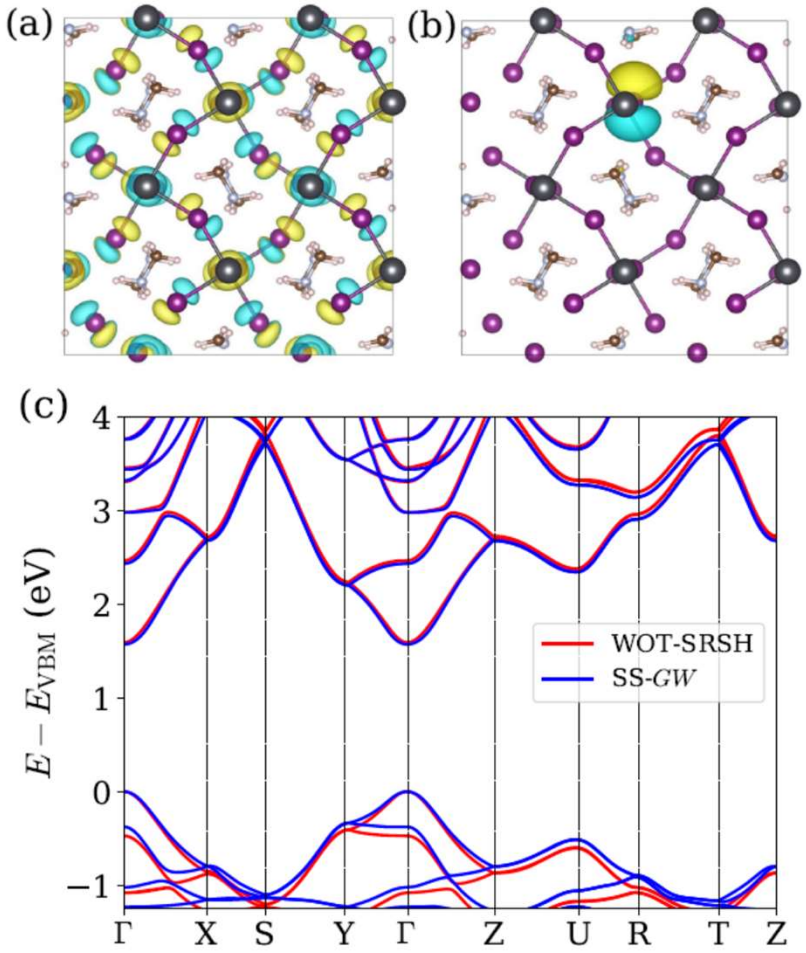
Wing, Ohad, Haber, Filip, Gant, Neaton, Kronik, PNAS 118, e2104556118 (2021)

Highlight: Scuseria, PNAS 118, e2113648118 (2021).

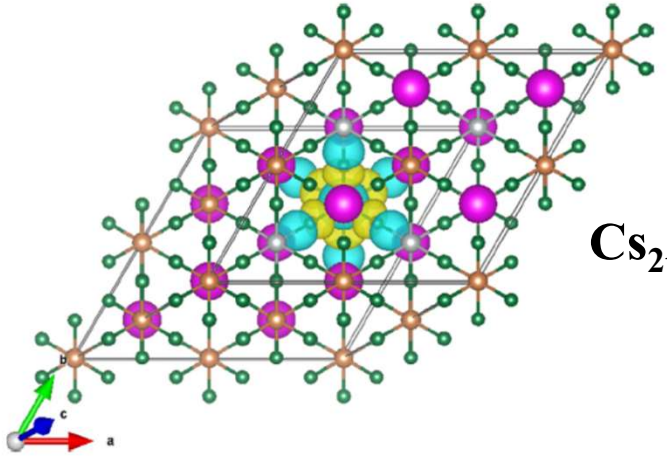
Guy Ohad

Francisca Sagredo

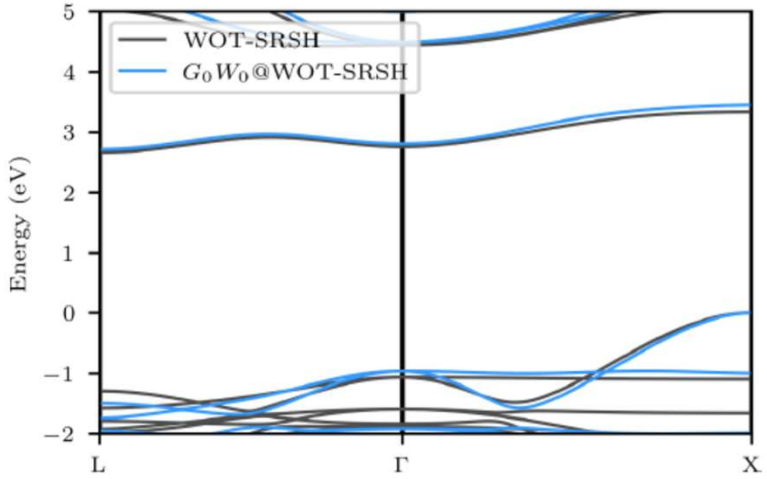
WOT-SRSH of Halide (single and double) Perovskites



$MAPbI_3$



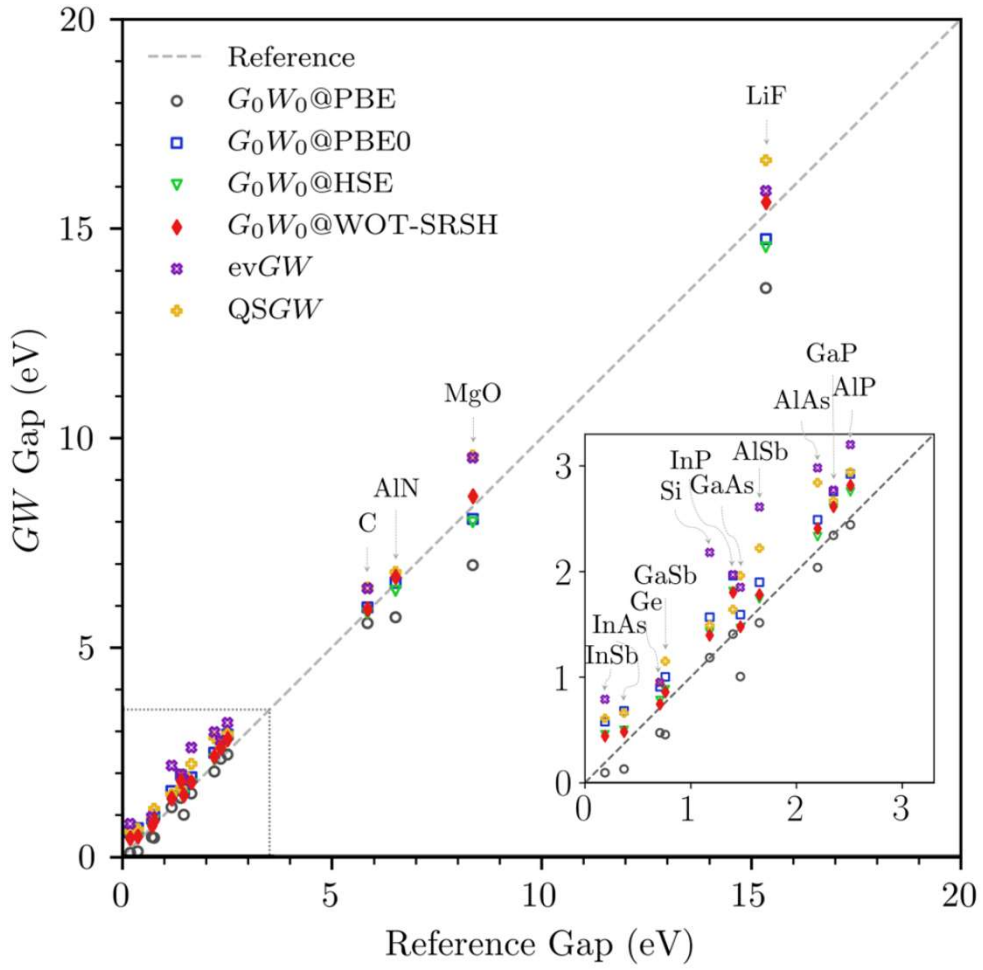
$Cs_2AgSbBr_6$



Ohad, Wing, Gant, Cohen, Haber, Sagredo, Filip, Neaton, Kronik
Phys. Rev. Materials 6, 104606 (2022).

Sagredo, Gant, Ohad, Haber, Filip, Kronik, Neaton
Phys. Rev. Materials 8, 105401 (2024).

WOT-SRSH is an optimal starting point for GW calculations



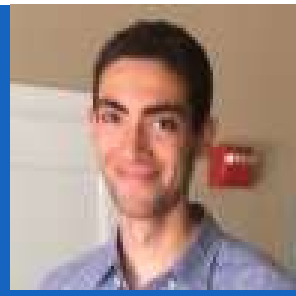
Stephen Gant

Gant, Haber, Filip, Sagredo, Wing, Ohad, Kronik, Neaton, Phys. Rev. Materials 6, 053802 (2022)

Dahvyd Wing

Optical absorption spectra from linear response time-dependent DFT

Jonah Haber



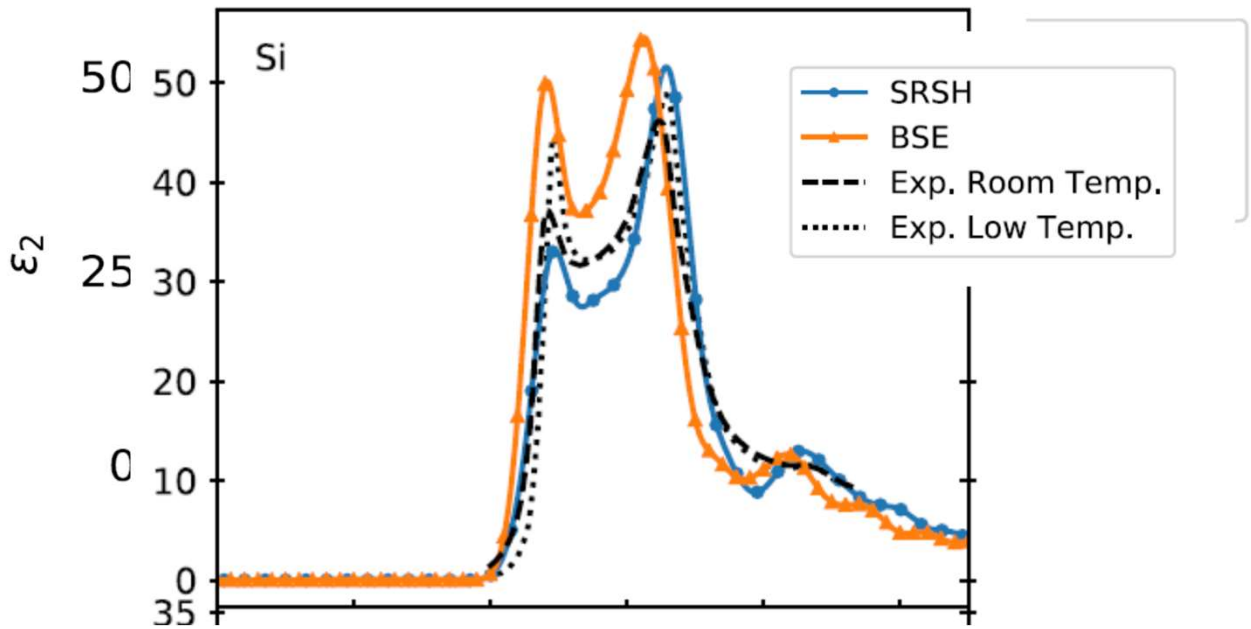
Three major challenges:

- (Semi)-local functionals underestimate the band gap – the spectrum is red shifted.
- Standard functionals do not have the correct asymptotic behavior, an essential property to accurately describe excitonic peaks.
- The xc kernel cannot be derived from approaches that use correction terms

OT-SRSH:

- Has the correct band gap.
- Has the correct long-range behavior.
- Proper density functional.

Optical absorption spectrum of silicon

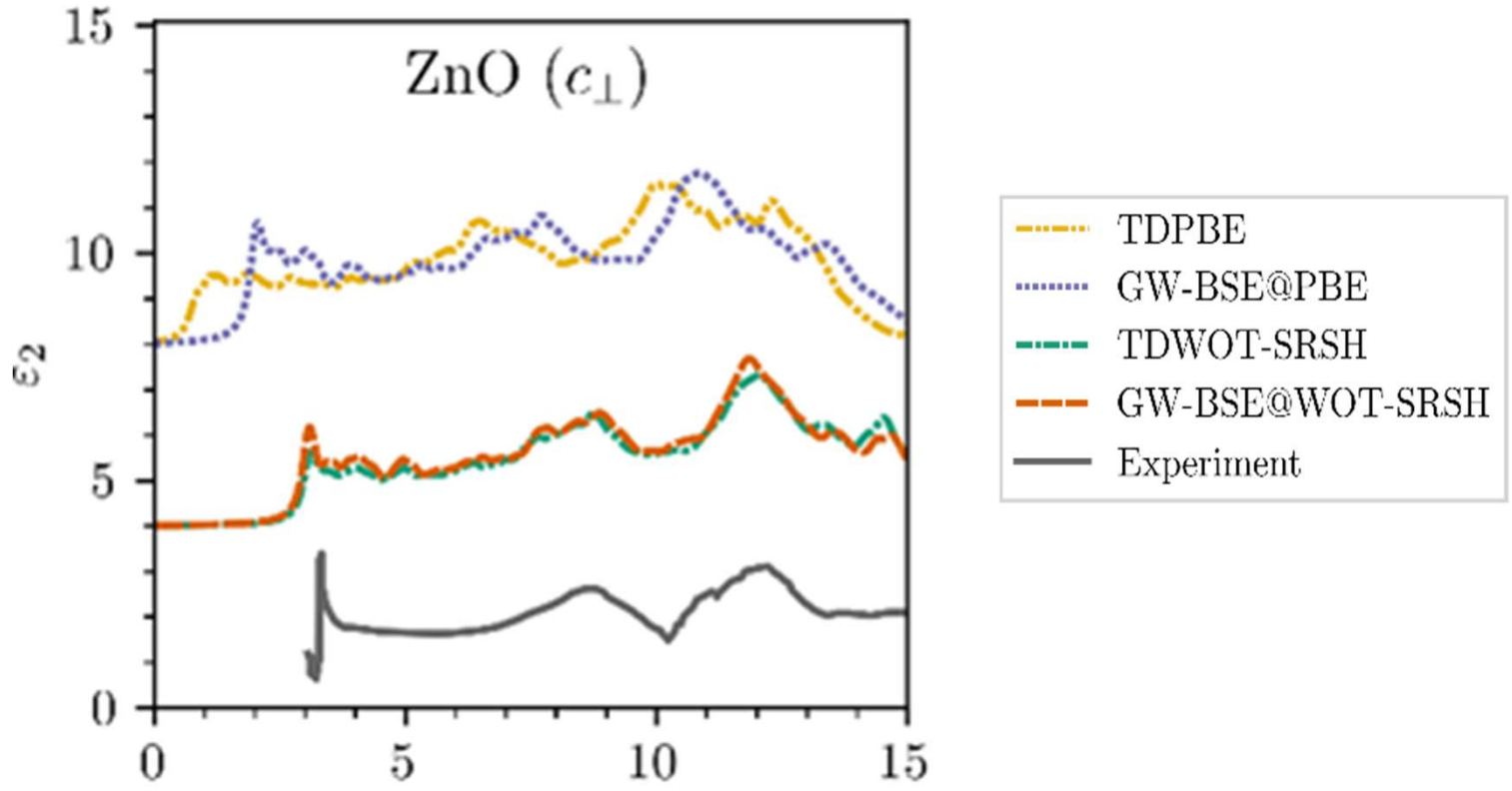


Wing, Haber, Noff, Barker, Egger, Ramasubramaniam, Louie, Neaton, Kronik, Phys. Rev. Materials 3, 064603 (2019).

WOT-SRSH is excellent for absorption spectra in closed-shell transition metal oxides

Guy Ohad

"ZnO — an extreme case for GW calculations"
in Friedrich et al. J. Phys.: Condens. Matter 24, 293201 (2012).



Stephen Gant

Ohad, Gant, Wing, Haber, Camarasa-Gomez, Sagredo, Filip, Neaton, Kronik
Phys. Rev. Materials 7, 123803 (2023).

Maria
Camarasa-Gómez

WOT-SRSH for 2d Materials

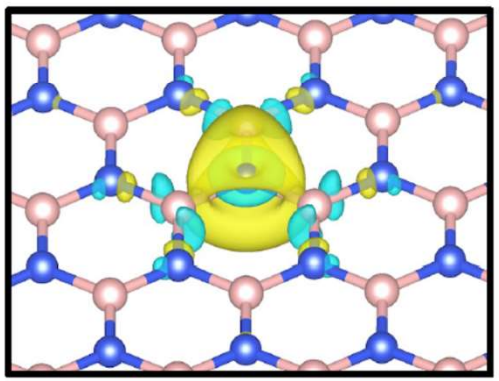
Ashwin
Ramasubramaniam

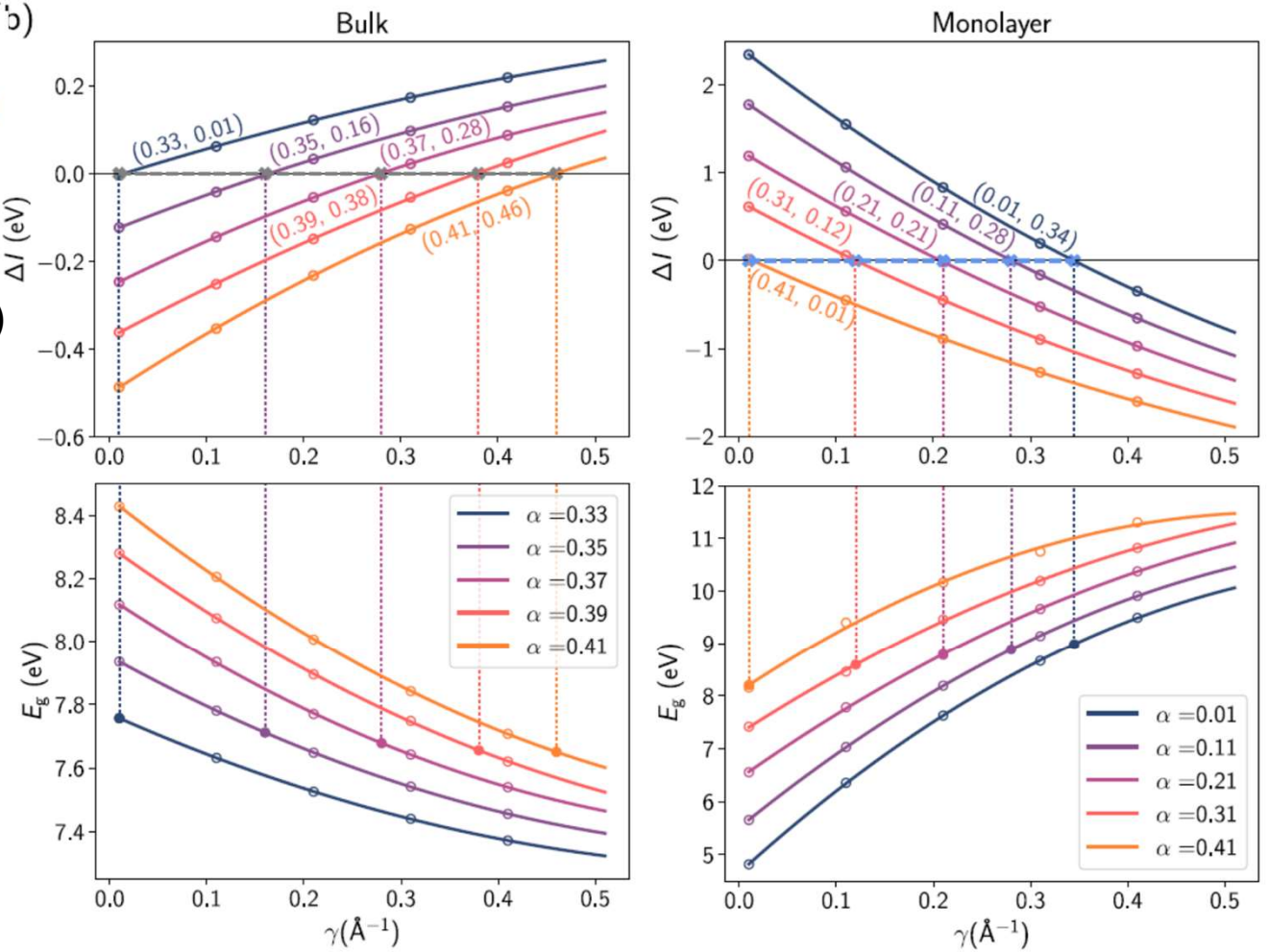
$$\epsilon_\infty = \mathrm{Tr}[\epsilon_\infty]/3 \quad \text{(Bulk)}$$
$$\epsilon_\infty = 1 \quad \text{(Monolayer)}$$

Cudazzo et al., PRB (2011)
Andresen et al., Nano Lett. (2015)
Qiu et al., PRB (2016)

h-BN

$|\phi|^2$

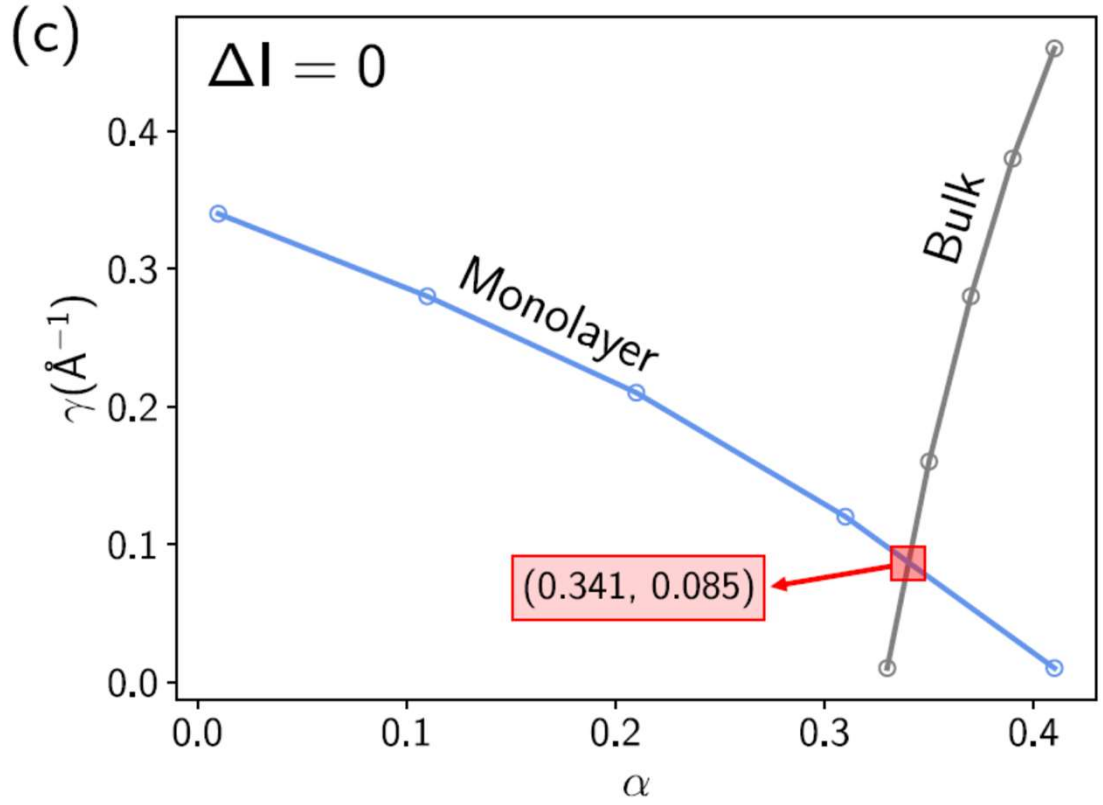




Camarasa-Gómez, Gant, Ohad, Neaton, Ramasubramaniam, Kronik, npj Comput. Materials 10, 288 (2024).

WOT-SRSH for 2d Materials

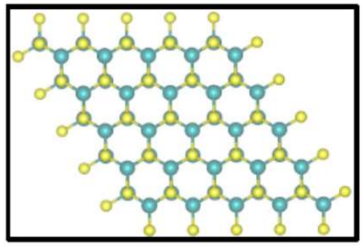
$$\epsilon_\infty = \mathrm{Tr}[\boldsymbol{\epsilon}_\infty]/3 \quad \text{(Bulk)}$$
$$\epsilon_\infty = 1 \quad \text{(Monolayer)}$$



Camarasa-Gómez, Gant, Ohad, Neaton, Ramasubramaniam, Kronik, npj Comput. Materials 10, 288 (2024).

One example

Molybdenum disulfide

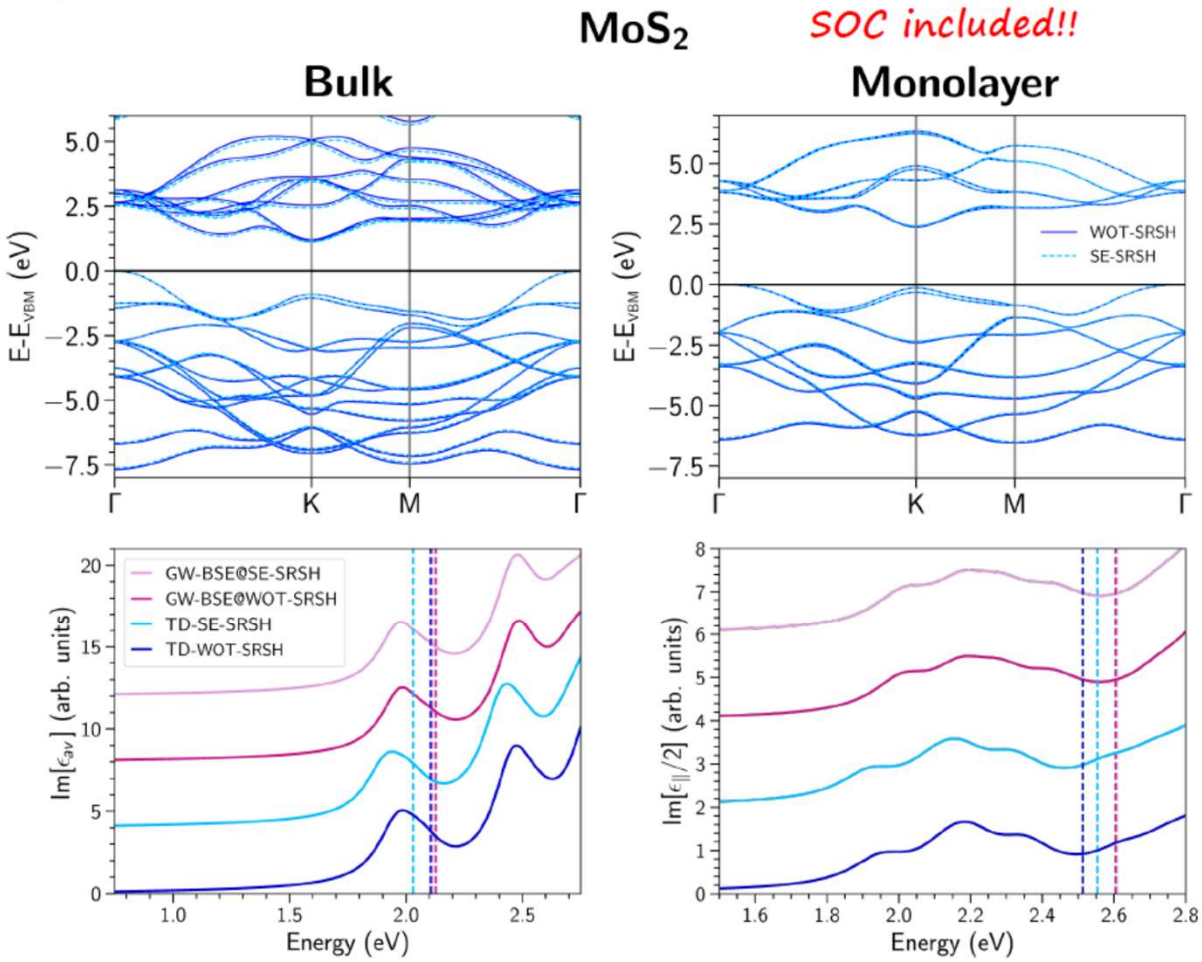


Monolayer & bulk
medium band gap

WOT-SRSH functional yields
good band structure !!

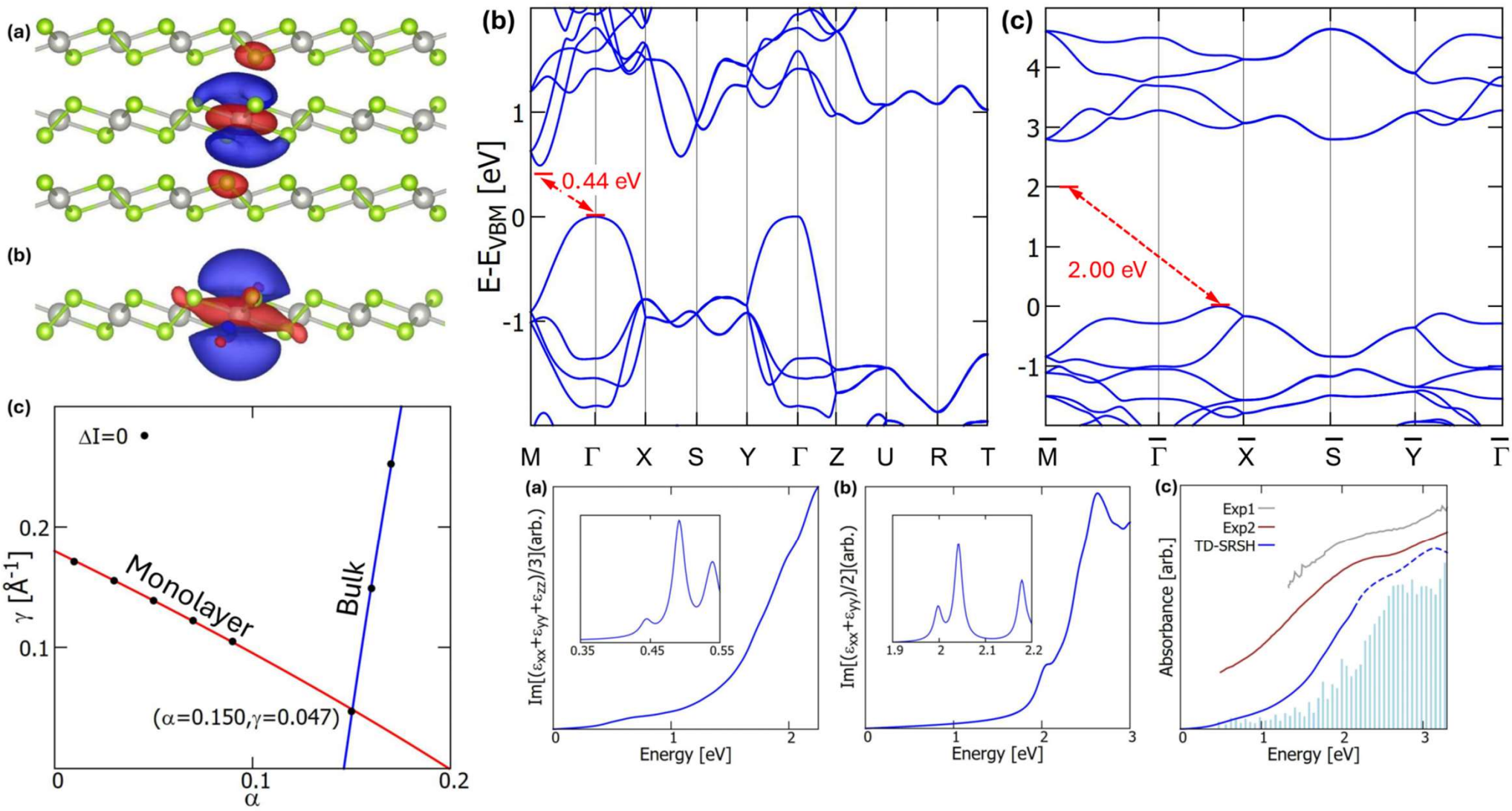
WOT-SRSH functional
yields excellent spectrum
eliminating empiricism!!

WOT-SRSH functional yields
good starting point for GW-BSE!!



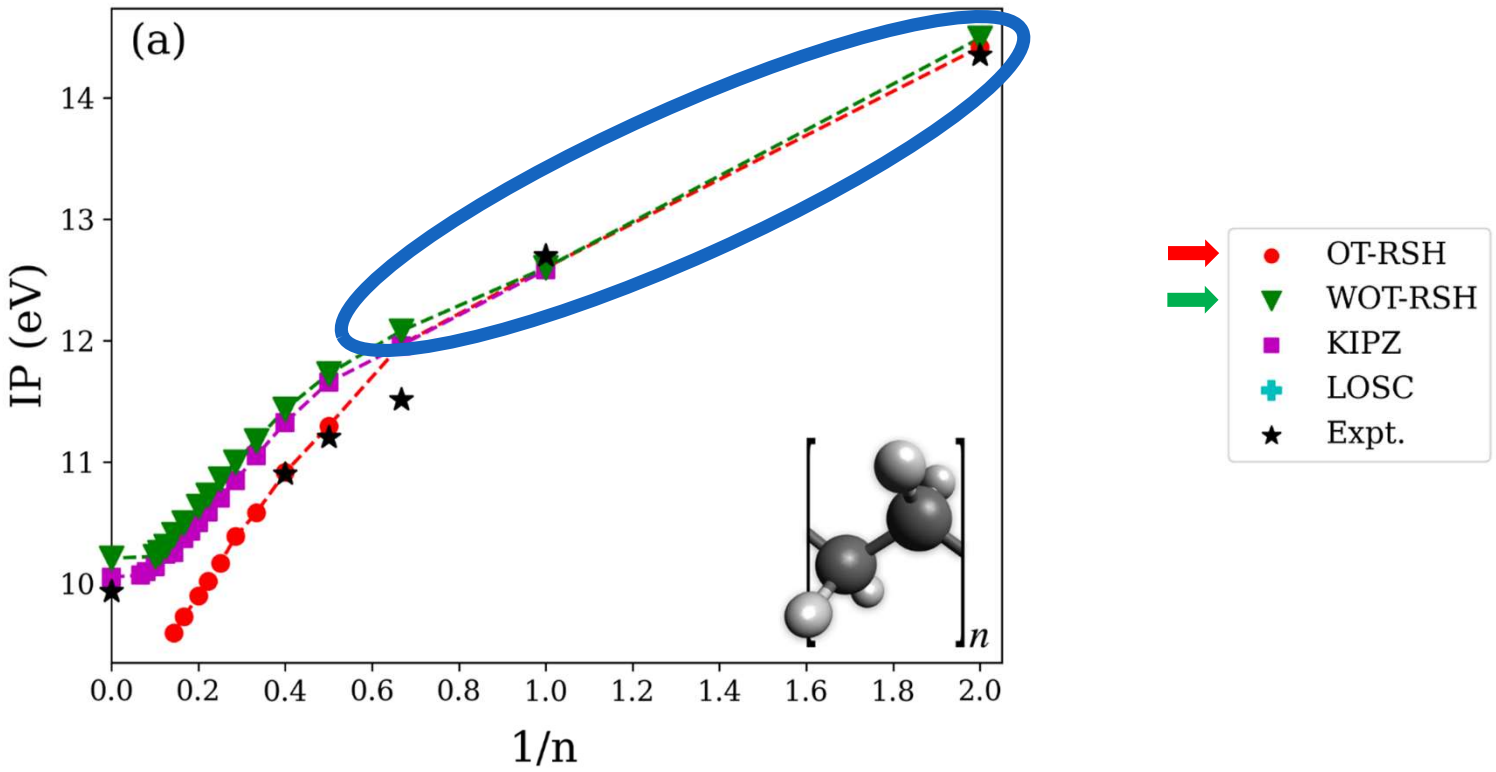
Camarasa-Gómez, Gant, Ohad, Neaton, Ramasubramaniam, Kronik, npj Comput. Materials 10, 288 (2024).

Resolving contradictory estimates of band gaps of bulk $PdSe_2$ for IR detection: 0 to 0.5 eV



Florio, Camarasa-Gómez, Ohad, Naveh, Kronik, Ramasubramaniam
Appl. Phys. Lett. 126, 143191 (2025).

Approaching the solid-state limit



OT and WOT agree well for small systems!
Can WOT be interpreted as a generalized optimal tuning strategy?

Ohad, Hartstein, Gould, Neaton, and Kronik, J. Chem. Theory Comput., 20(16), 7168 (2024).

Limitations of the approach

- Strong heterogeneity

Stretched heterodimers:

Karolewski, Kronik, and Kümmel, J. Chem. Phys. 138, 204115 (2013).

Molecule/metal interface:

Egger, Liu, Neaton, Kronik, Nano Lett. 15, 2448 (2015);
Liu, Egger, Refaely-Abramson, Kronik, Neaton,
J. Chem. Phys. 146, 092326 (2017).

- Strong correlation

Small copper oxide clusters:

Shi, Weissman, Bruneval, Kronik, Öğüt,
J. Chem. Phys. 149, 064306 (2018).

Spin cross-over complexes:

Prokopiou & Kronik, Eur. J. Chem. 24, 5173 (2018).

Optimal tuning of a double hybrid:

Prokopiou, Hartstein, Govind, Kronik, J. Chem. Theo. Comp. 18, 2331 (2022).

Conclusions

- WOT-SRSH: Wannier-localized optimal tuning of a screened range-separated hybrid functional

- A systematic, non-empirical solution for the long-standing challenges of the bandgap problem in DFT and solid-state excitonic effects in TDDFT