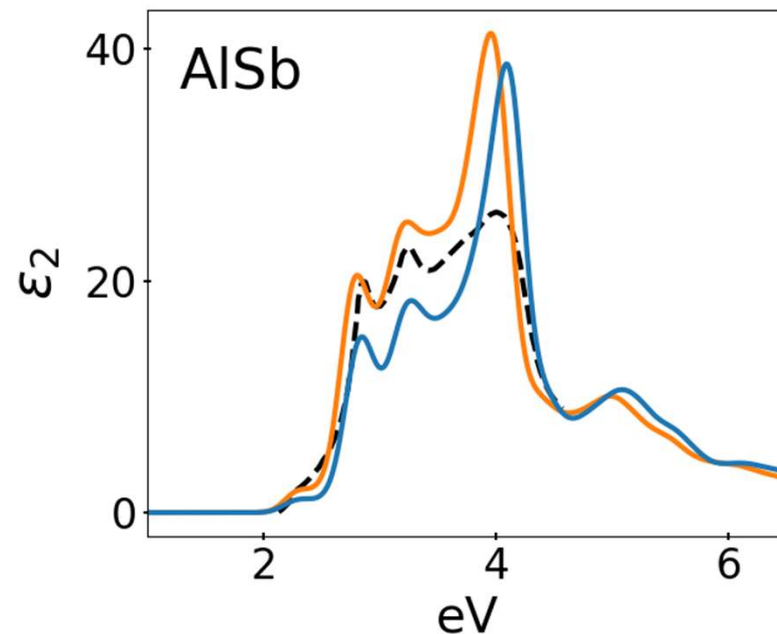


Spectroscopy with range-separated hybrid functionals

Leeor Kronik

*Department of Materials and Interfaces,
Weizmann Institute of Science, Rehovoth, Israel*



Workshop on Theoretical Chemistry, Austria, March 2020

Mind the gap

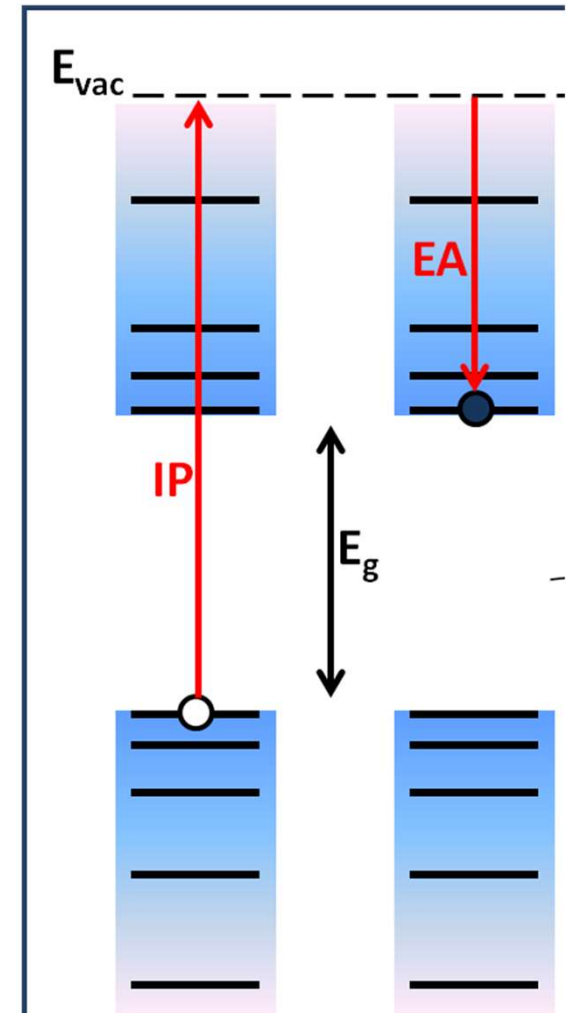
The Kohn-Sham gap underestimates the real gap

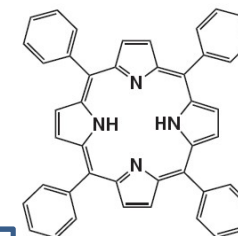
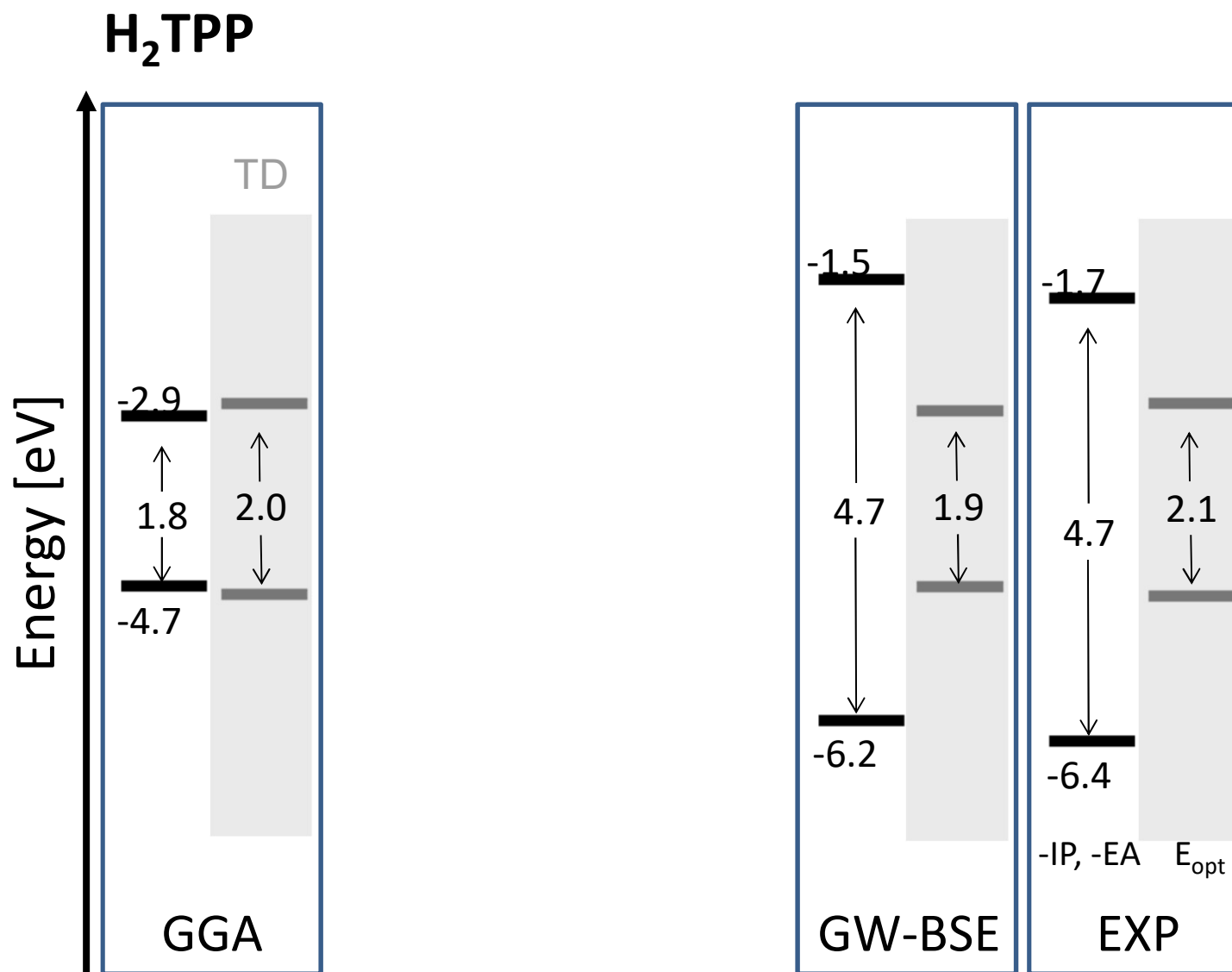
$$E_g = I - A = \epsilon_{KS}^{LUMO} - \epsilon_{KS}^{HOMO} + \Delta_{xc}$$

Perdew and Levy, *PRL* 1983;
Sham and Schlüter, *PRL* 1983

derivative
discontinuity!

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





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

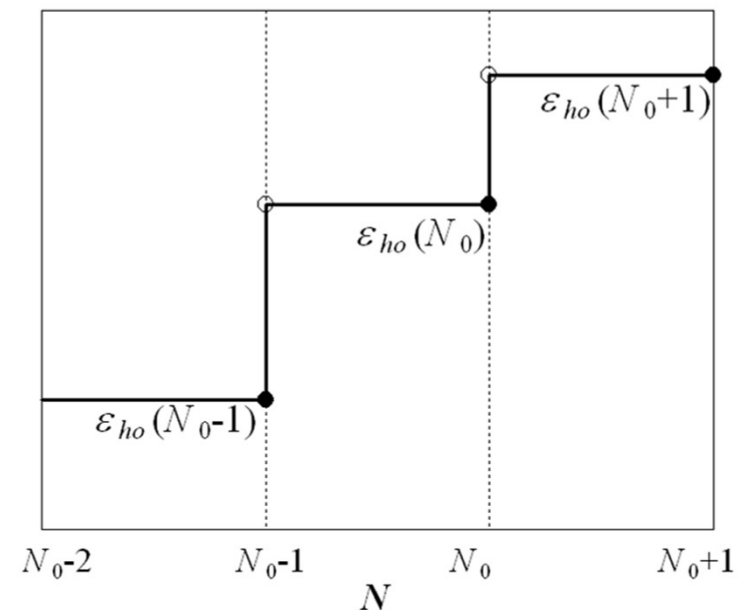
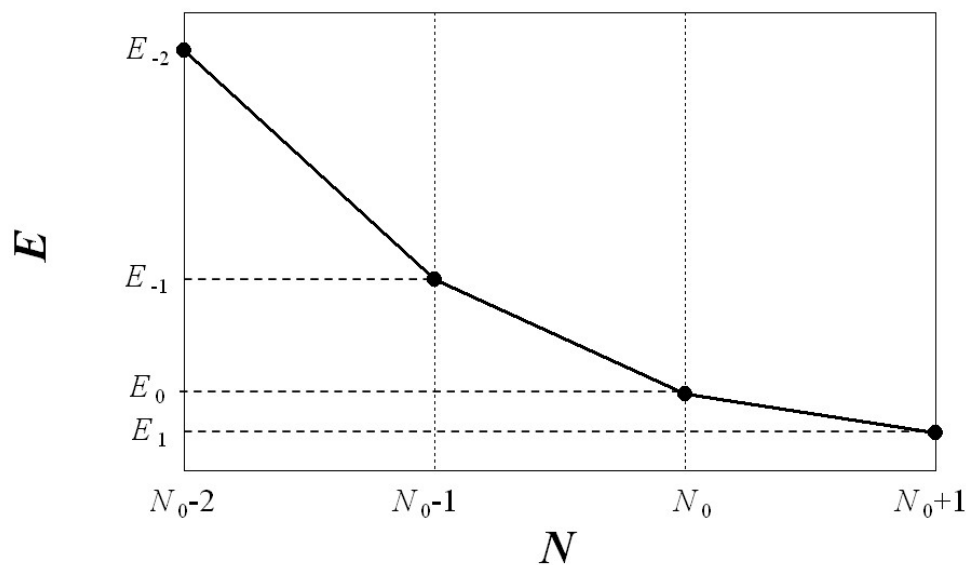
Piecewise linearity in DFT: Exact results from ensemble arguments

Fractional no. of electrons: $N = N_0 + \alpha$

- Piecewise-linearity
- The IP theorem

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

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



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

The Kohn-Sham equation

$$\left(\underbrace{-\frac{1}{2}\nabla^2}_{\text{kinetic}} + \underbrace{V_{ion}}_{\text{ion-e}} + \underbrace{V_{Hartree}}_{\text{e-e}} + \underbrace{V_{xc}}_{\text{many body}} \right) \psi_i(r) = E_i \psi_i(r)$$

$$\rho(r) = \sum_{\text{occupied states}} |\psi_i(r)|^2$$

$$V_{xc}([\rho]; r) = \frac{\delta E_{xc}[\rho]}{\delta \rho}$$

V_{xc} may “jump” by a spatially uniform constant across the integer point. A derivative discontinuity!

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).

Generalized Kohn-Sham theory

Map to a *partially interacting* electron gas that is represented by a single Slater determinant.

- Seek Slater determinant that minimizes an energy functional $S[\{\varphi_i\}]$ while yielding the original density

- Type of mapping determines the functional form

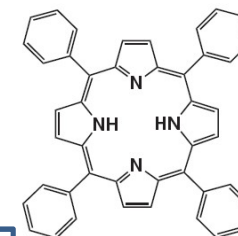
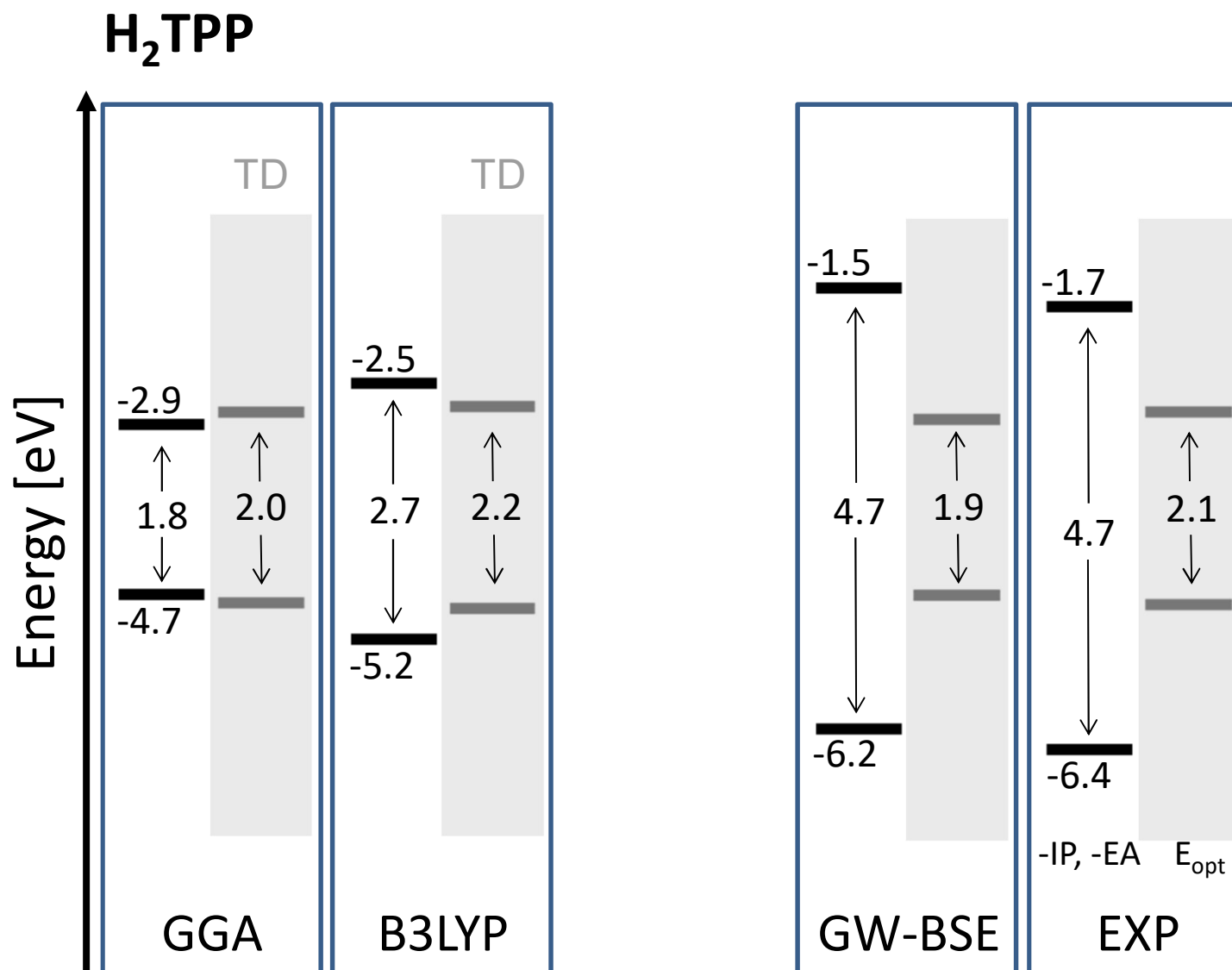
$$\left(\hat{O}_S[\{\varphi_j\}] + V_{ion}(r) + v_R([n]; r) \right) \varphi_i(r) = \varepsilon_i \varphi_i(r)$$

Seidl, Goerling, Vogl, Majeovski, Levy, *Phys. Rev. B* 53, 3764 (1996).

Kümmel & Kronik, *Rev. Mod. Phys.* 80, 3 (2008)

Baer, Livshits, Salzner, *Ann. Rev. Phys. Chem.* 61, 85 (2010).

- Derivative discontinuity problem possibly mitigated by non-local operator!!



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

Range-separated hybrid functionals

Coulomb operator decomposition:

$$r^{-1} = \underbrace{r^{-1} \operatorname{erfc}(\gamma r)}_{\text{Short Range}} + \underbrace{r^{-1} \operatorname{erf}(\gamma r)}_{\text{Long Range}}$$

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)

likura et al., *J. Chem. Phys.* **115**, 3540 (2001)

Yanai et al., *Chem. Phys. Lett.* **393**, 51 (2004)

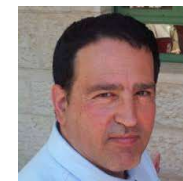
But how to choose the range??



Tamar
Stein

Optimal tuning of γ

Roi
Baer



**Ionization potential
theorem:**

$$-\varepsilon_{\text{HOMO}}^{\gamma} = E_{\text{gs}}(N-1; \gamma) - E_{\text{gs}}(N; \gamma)$$

Need both IP(D), EA(A) \Rightarrow choose γ to best obey the ionization potential theorem for both neutral donor and charged acceptor:

Minimize

$$J(\gamma) = \sum_{i=0,-} (\varepsilon_{\text{HOMO}}^{\gamma,i} + E_{\text{gs}}^i(N_i - 1; \gamma) - E_{\text{gs}}^i(N_i; \gamma))^2$$

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

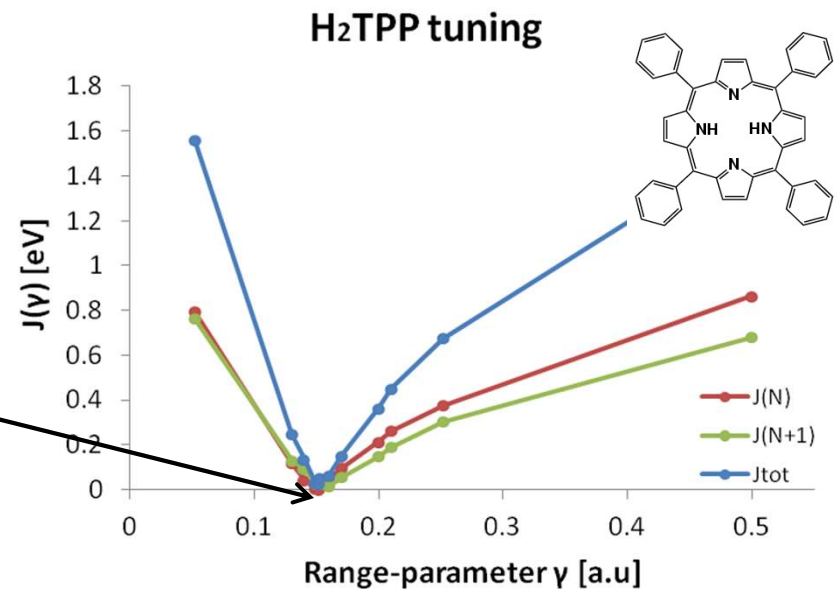
**Stein, Kronik, Baer, J. Am. Chem. Soc. (Comm.) 131, 2818 (2009).
Stein, Eisenberg, Kronik, Baer, Phys. Rev. Lett. 105, 266802 (2010).**

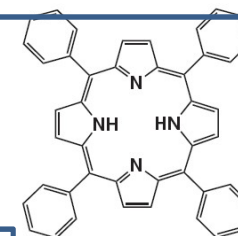
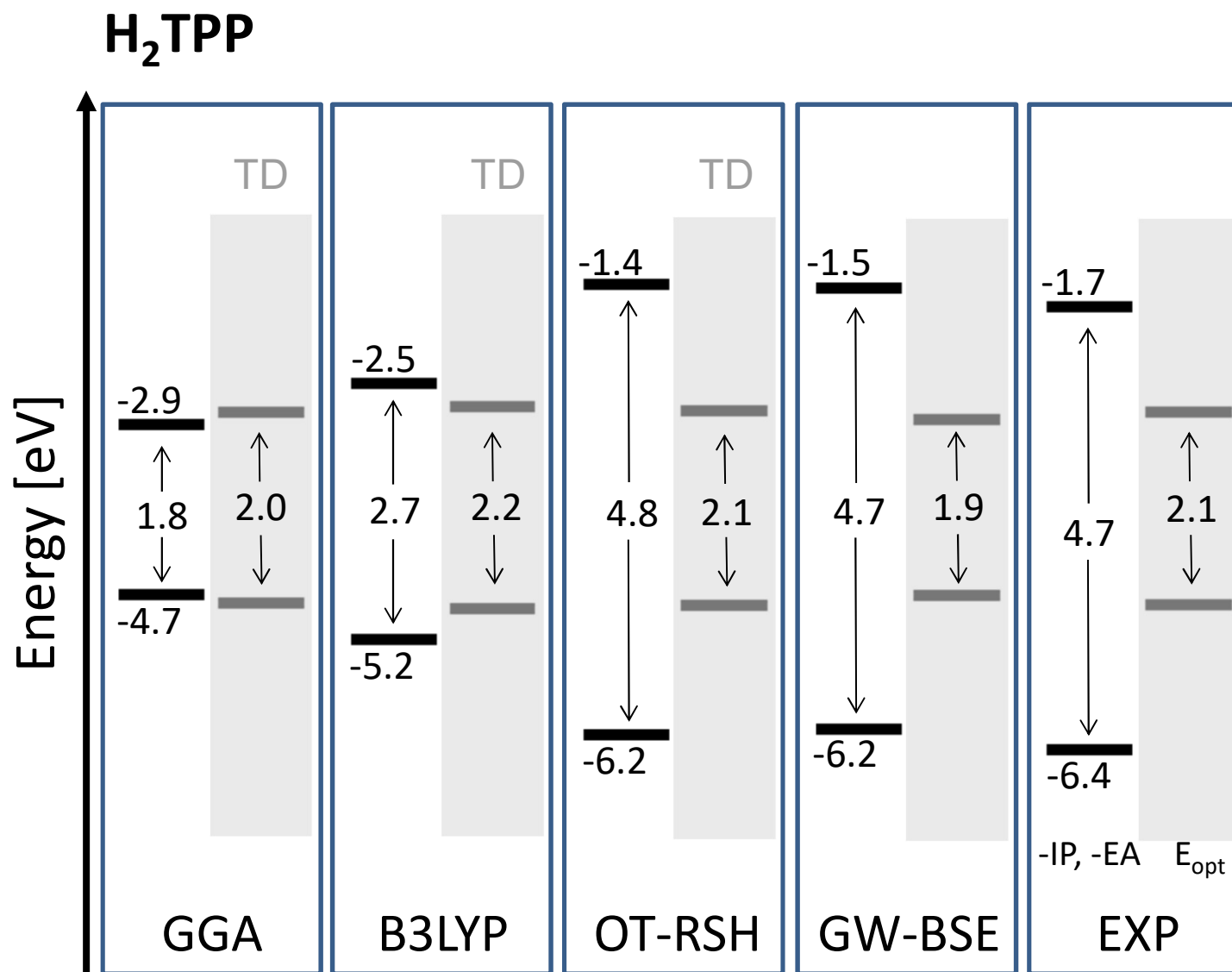
Tuning the range-separation parameter

$$J(\gamma) = \left| \epsilon_H^\gamma(N) + IP^\gamma(N) \right| + \left| \epsilon_H^\gamma(N+1) + IP^\gamma(N+1) \right|$$

Neutral molecule (IP) Anion (EA)

$$J(\gamma_{opt}) = \min\{J(\gamma)\}$$





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

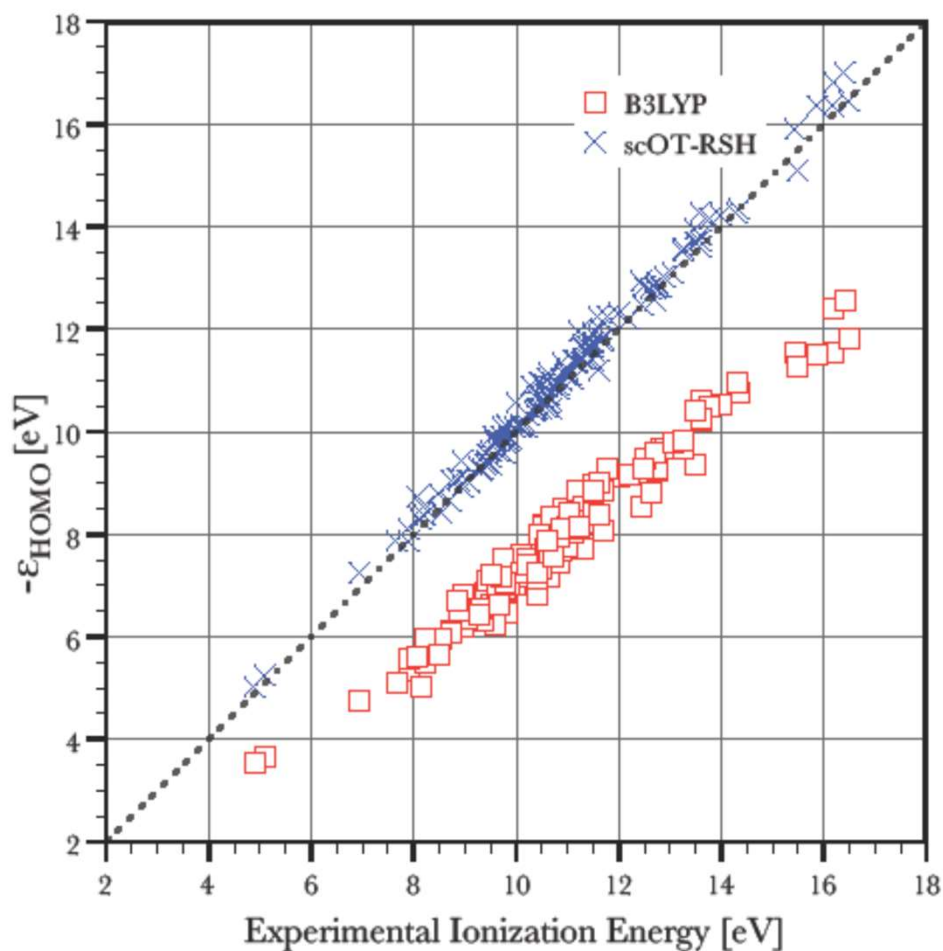


Isaac
Tamblyn



Jeff
Neaton

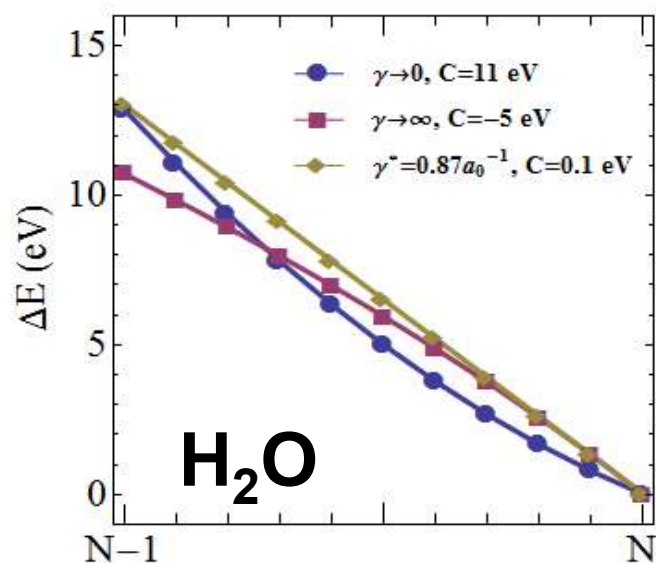
Ionization potential from the HOMO energy for all 148 molecules in the G2 set



Sivan Refaely-
Abramson

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

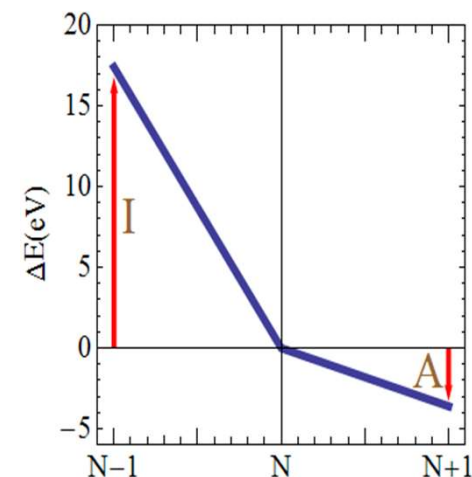
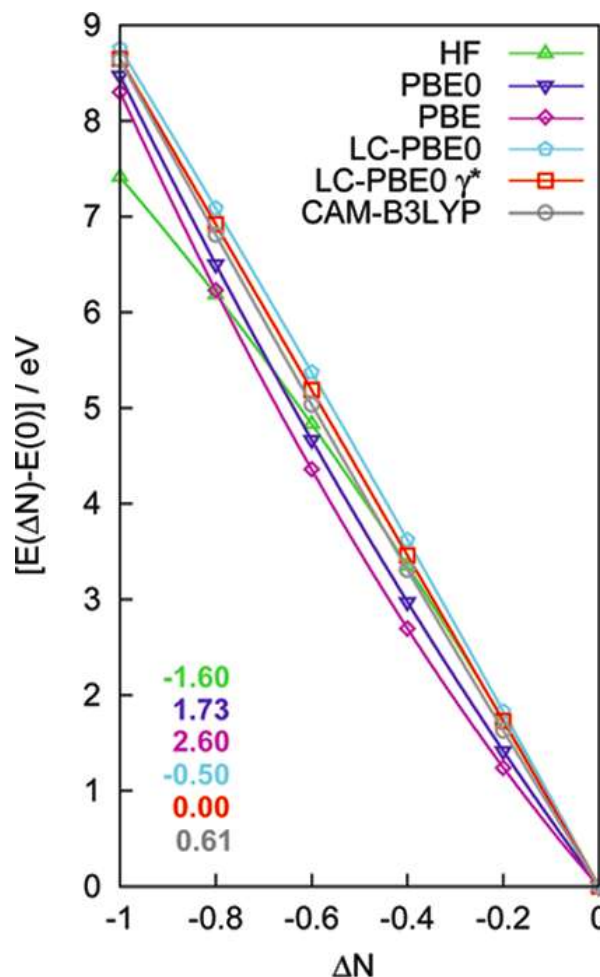
**Optimal tuning = negligible DD =>
Piecewise linearity!**



H₂O

**Kronik et al.
JCTC 8, 1515 (2012).**

**See also work
from Yang,
Marzari ,...**



β-Pinene

**Srebro & Autschbach
JCTC 8, 245 (2012).**

**Proof: Stein, Autschbach, Govind, Kronik, Baer,
J. Phys. Chem. Lett. 3, 3740 (2012).**

Curvature and missing DD: Doppelgänger!

Curvature $-1 \leq x \leq 0$

$$E^N(x) = \frac{1}{2} C^N x(x+1) + (1+x)E^N - xE^{N-1}.$$

$$\varepsilon_H^N = \left. \frac{dE^N(x)}{dx} \right|_{x=0} = E^N - E^{N-1} + \frac{1}{2} C^N$$

$$\begin{aligned} \varepsilon_L^{N-1} &= \varepsilon_H(x \rightarrow -1^+) = \left. \frac{dE^N(x)}{dx} \right|_{x=-1} \\ &= E^N - E^{N-1} - \frac{1}{2} C^N \end{aligned}$$

Curvature and missing DD: Doppelgänger!

$$I^N - I^{N+1} = \underbrace{\varepsilon_L^N - \varepsilon_H^N}_{\text{Kohn-Sham gap}} + \underbrace{\frac{1}{2} (C^N + C^{N+1})}_{\text{DD substitute!}}$$

Fundamental gap

**Missing DD and curvature:
You can't have one without the other**

Stein, Autschbach, Govind, Kronik, Baer,
J. Phys. Chem. Lett. 3, 3740 (2012).

Curvature-based eigenvalue corrections!

For PBE (in eV):



Jochen
Autschbach



Niri Govind

	$C^N(0)$	$C^N(-1)$	$-\varepsilon_H^N$	$-\varepsilon_L^{N-1}$	$I^N(H)$	$I_N(L)$	I^N
F_2	12.0	12.5	9.1	21.4	15.1	15.1	15.2
Anth.	4.3	4.2	5.0	9.2	7.1	7.1	7.1

Quantitative correction to ~0.1 eV!

Traditional point of view:

DD & curvature two separate but somewhat-related bugs

This point of view: DD & curvature quantitatively related

Missing DD is a bug ; Curvature is a feature

Generalized OT-RSH - formalism

$$\frac{1}{r} = \frac{\alpha + \beta \text{erf}(\gamma r)}{r} + \frac{1 - [\alpha + \beta \text{erf}(\gamma r)]}{r}$$

Yanai et al., *Chem. Phys. Lett.* **393**, 51 (2004)

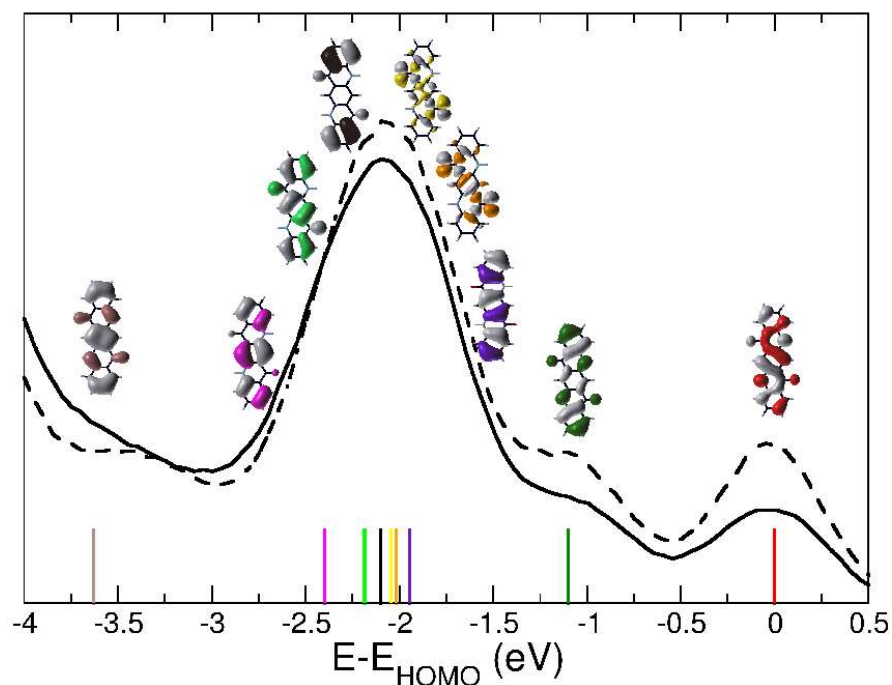
**Asymptotics: $\alpha + \beta = 1$ (Standard RSH limit: $\alpha = 0, \beta = 1$).
 γ still tuned from the ionization potential theorem**

$$J^2(\gamma; \alpha) = \sum_{i=-1,0,1} (\varepsilon_{H(N+i)}^{\gamma; \alpha} + IP^{\gamma; \alpha}(N+i))^2$$

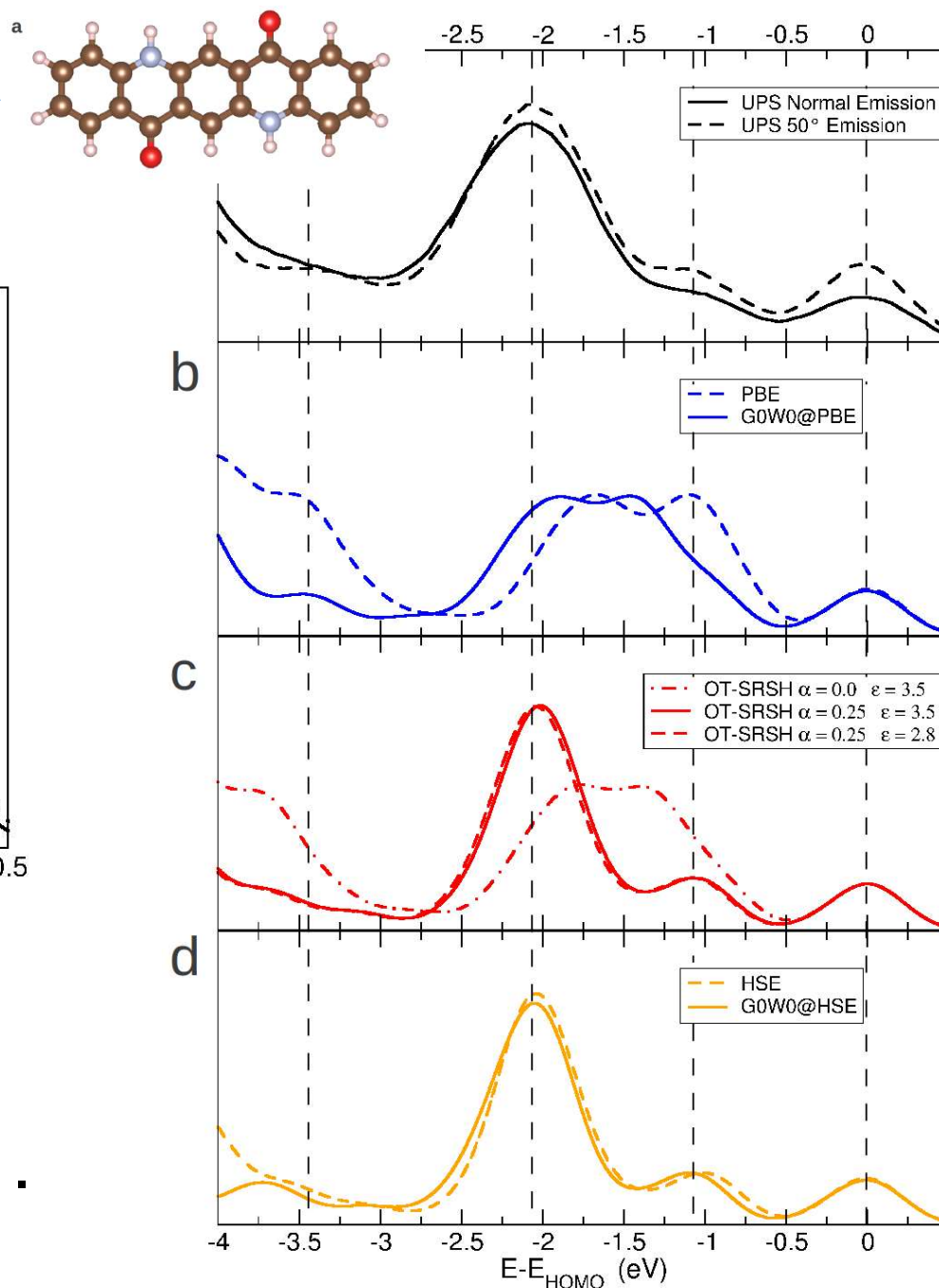
Refaely-Abramson, Sharifzadeh, Govind, Autschbach, Neaton, Baer, Kronik
Phys. Rev. Lett. **109**, 226405 (2012)

**For applications see also work from groups of, e.g.,
Brédas, Autschbach, Dunietz, Wong, ...**

Application: Photoemission spectroscopy of quinacridone



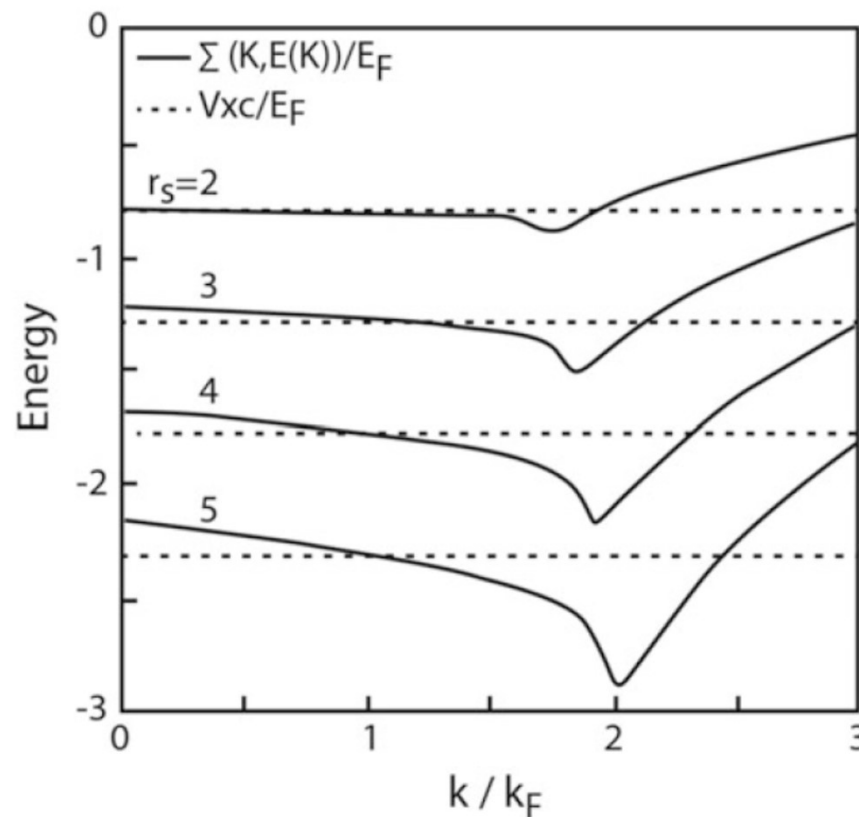
**Lüftner, Refaely-Abramson,
Pachler, Resel, Ramsey,
Kronik, Puschnig,
Phys. Rev. B 90, 075204 (2014) .**



Self energy versus Kohn-Sham potential in a uniform electron gas

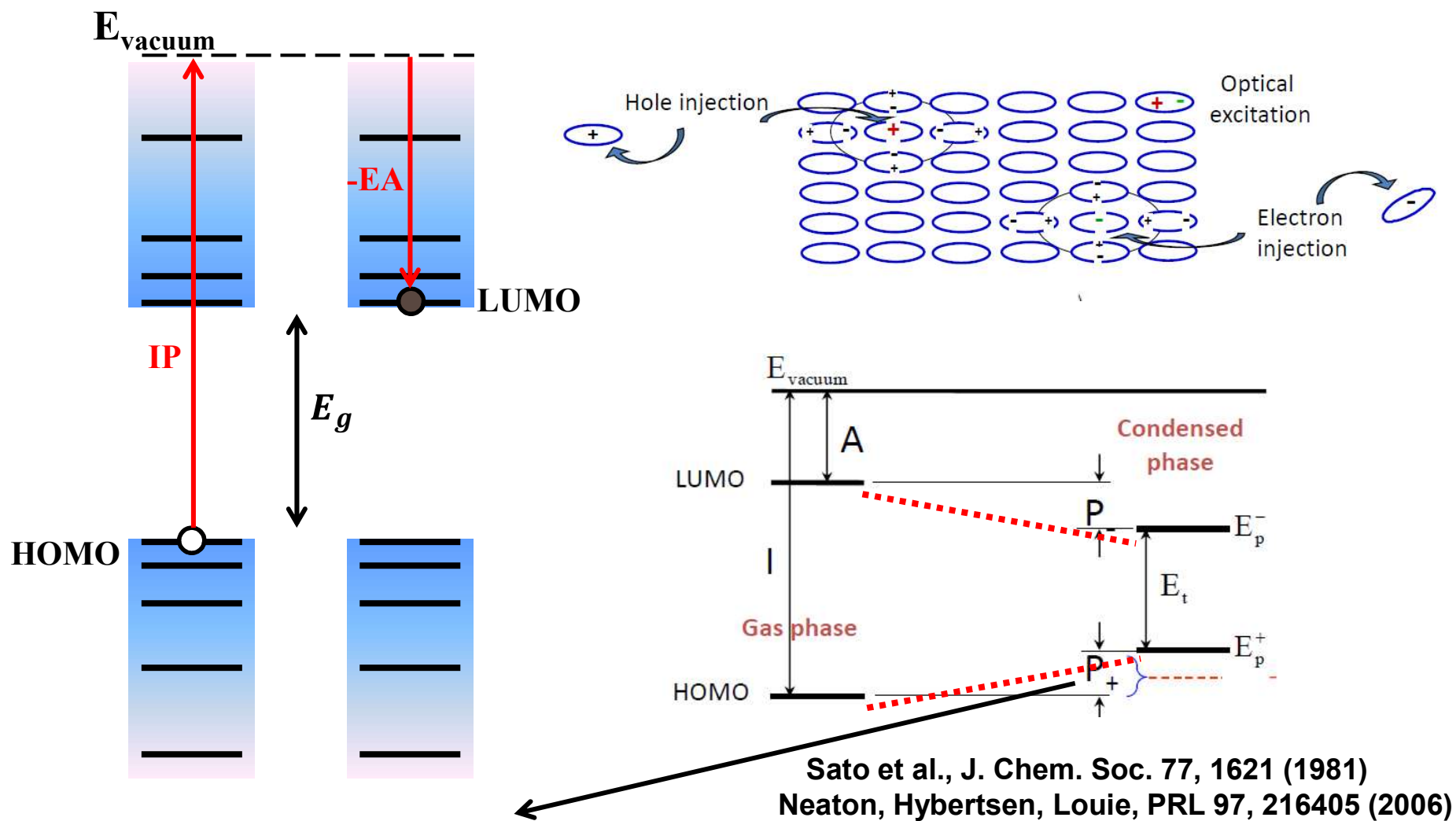
Kohn-Sham eigenvalues are not one-particle excitation energies.

Sham & Kohn, Phys. Rev. 145, 561 (1966)



Jones & Gunnarson, Rev. Mod. Phys. 61, 68 (1989).

Molecular crystals: Fundamental gap renormalization



Electronic Polarization \longleftrightarrow **Dielectric Response**

Dielectric response: gap renormalization of molecular crystals

Fundamental gaps



Sahar Sharifzadeh



Jeff Neaton

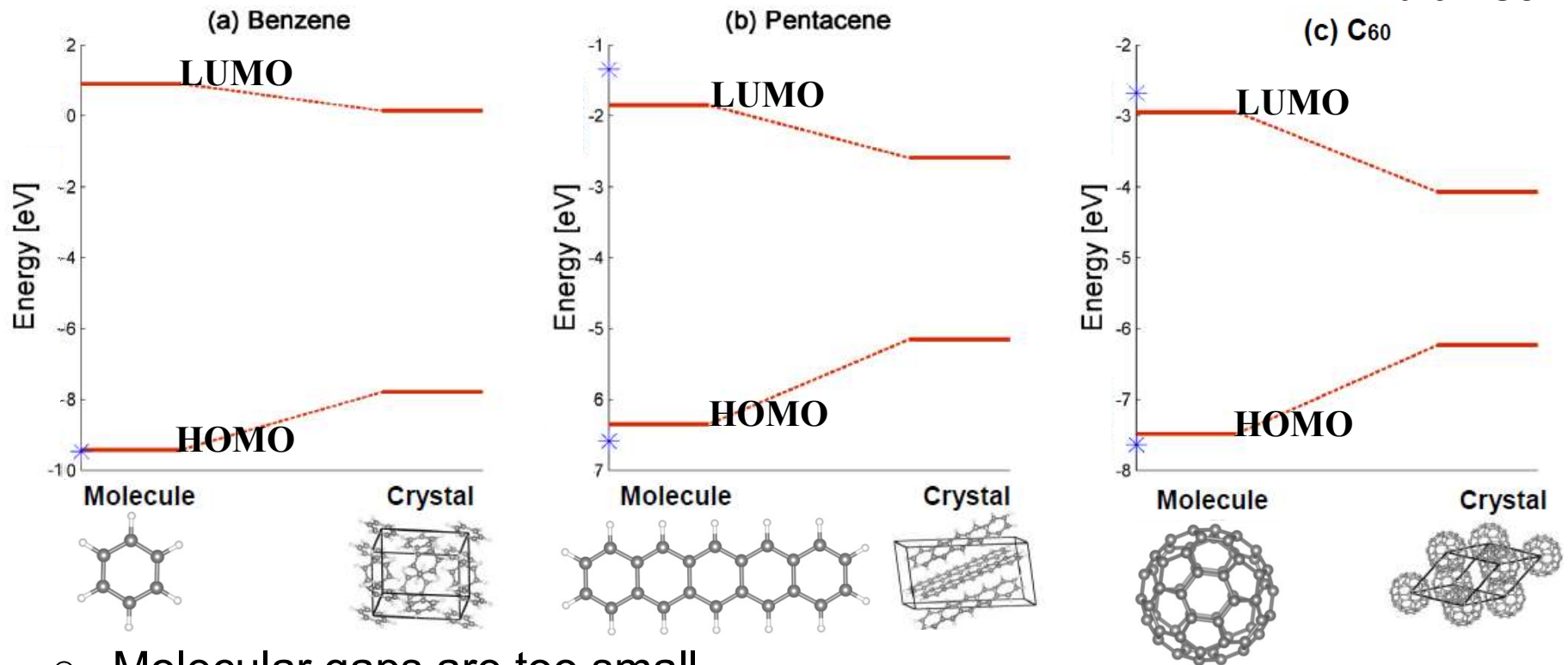


Sivan Refaely-Abramson

— PBE

— GW

* EXP



- Molecular gaps are too small
- No renormalization

Refaely-Abramson, Sharifzadeh, Jain, Baer, Neaton, Kronik, Phys. Rev. B (Rapid Comm.) 88, 081204, 2013

Gap renormalization of molecular crystals from density functional theory

Solid state screening: the OT-SRSH functional

- Optimally-tuned **screened** range-separated hybrids (**OT-SRSH**)

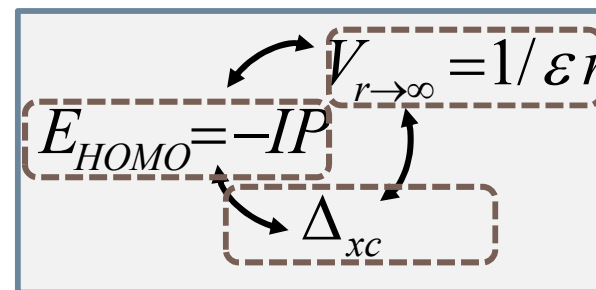
- Electron polarization \leftrightarrow dielectric screening

$$E_{xc} = \alpha E_{xx}^{SR,\gamma} + (1-\alpha) E_{lx}^{SR,\gamma} + \boxed{(\alpha + \beta) E_{xx}^{LR,\gamma}} + (1-\alpha-\beta) E_{lx}^{LR,\gamma} + E_{lc}$$

\swarrow
 $\frac{1}{\epsilon}$

Screened RSH:

$V \sim 1/\epsilon r$, not $1/r$



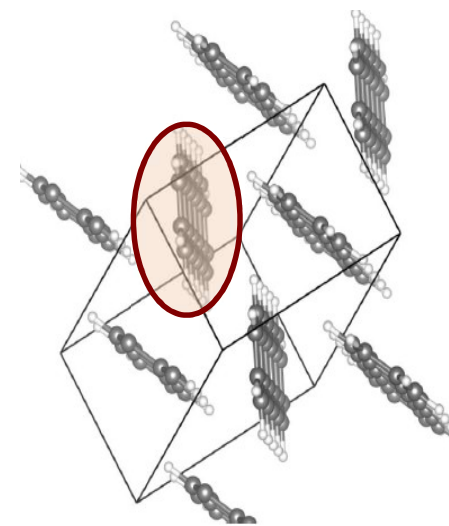
**Tuning parameters
fixed to
gas-phase values**

Overviews:

**Kronik & Neaton, Annu. Rev. Phys. Chem.,
67, 587 (2016).**

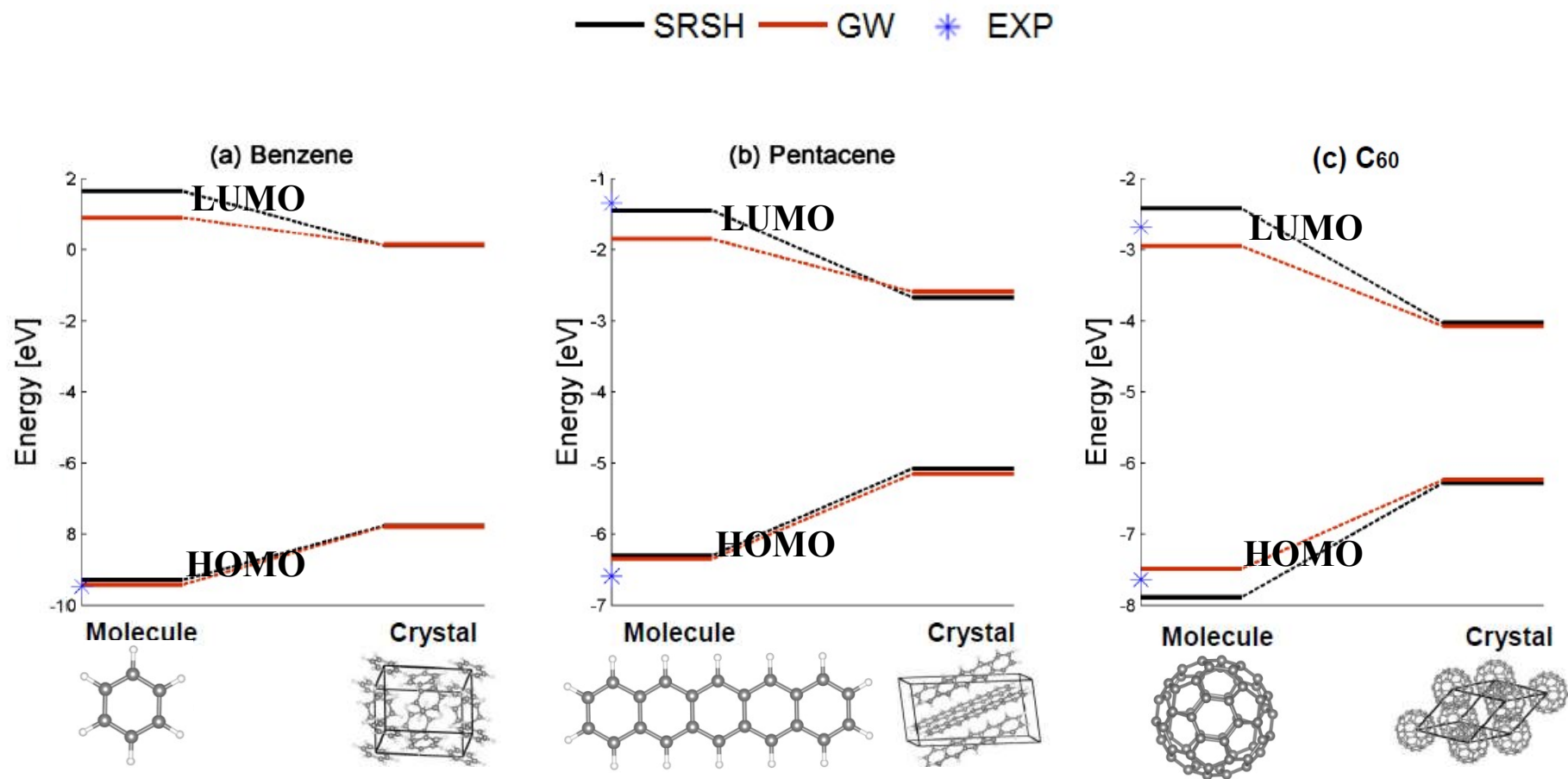
**Kronik & Kümmel, Adv. Materials,
30, 1706560 (2018).**

**See also work
from groups of
Shimazaki, Galli,
Ullrich...**



Gap renormalization of molecular crystals from density functional theory

Gap renormalization



- Molecular gaps are too small
- No renormalization

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

**“Tough cases” for TDDFT
with standard functionals**

Charge transfer excitations

Optical absorption in the solid state

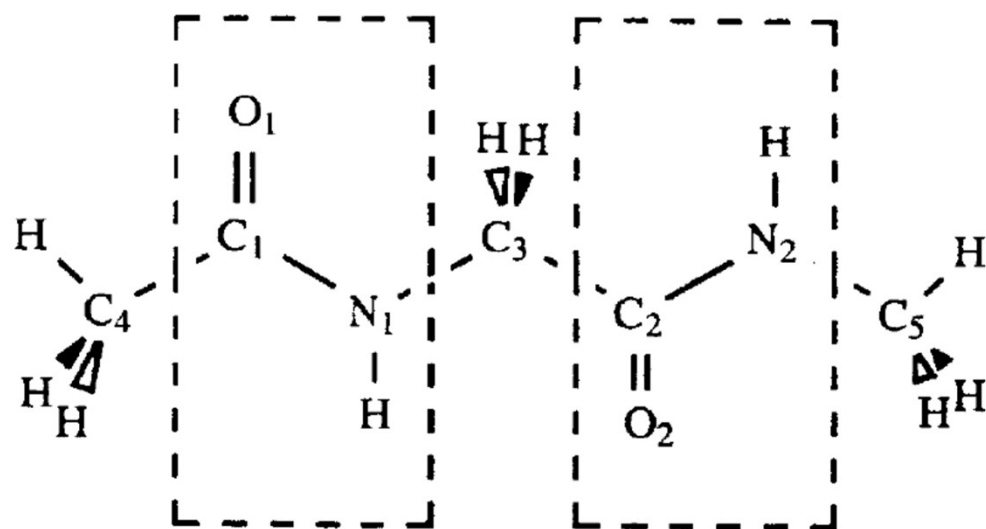
See, e.g.:

Maitra, J. Phys. Cond. Matter. 29, 423001 (2017).

Maitra, J. Chem. Phys. 144, 220901 (2016)

The charge transfer excitation problem

Linear-response time-dependent DFT, using either semi-local or standard hybrid functionals, seriously underestimates charge transfer excitation energies!



Charge transfer excitation:

BP86: 4.5 eV

CASPT2: 7.9 eV

**Tozer *et al.*, *Mol. Phys.*
97, 859 (1999).**

“Success consists of going from failure to failure without loss of enthusiasm.”

- Winston Churchill

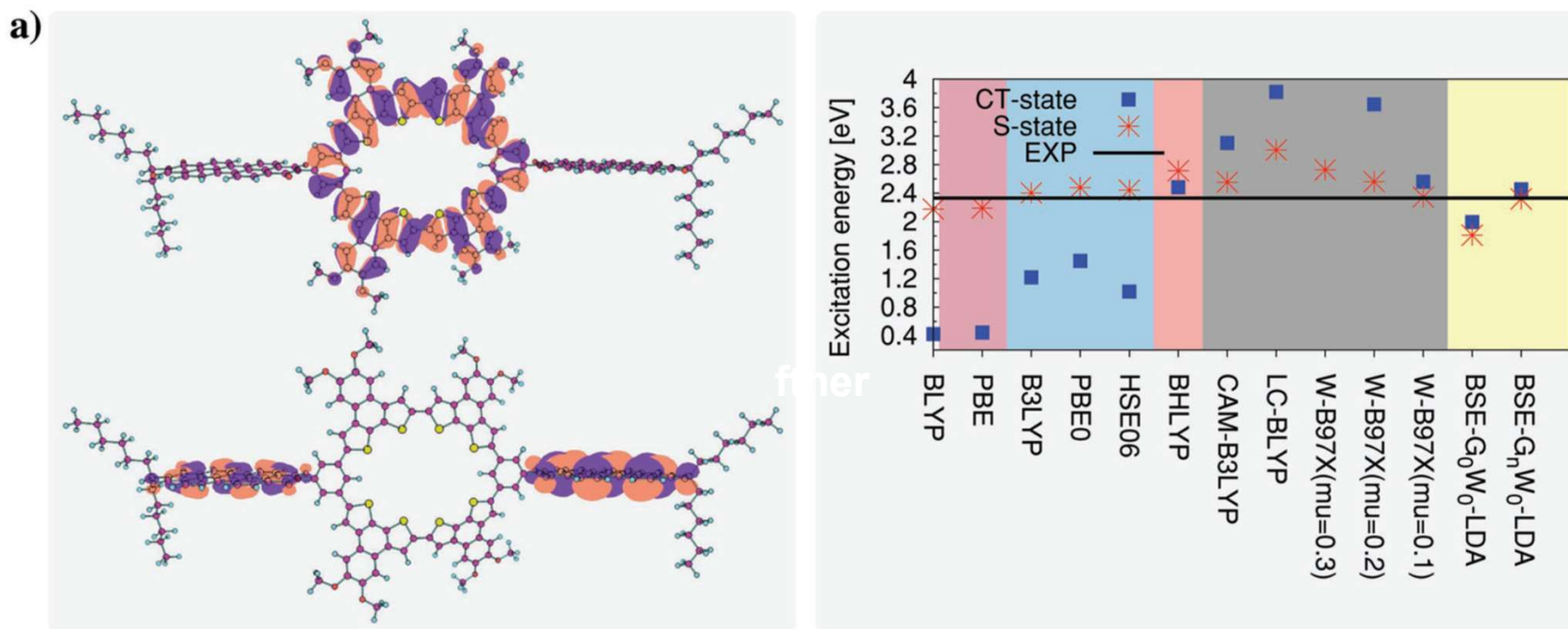
Results – gas phase Ar-TCNE

Donor	TD-PBE	TD-B3LYP	TD-BNL $\gamma=0.5$	TD-BNL Best γ	Exp	G_0W_0 - BSE	GW- BSE (psc)
benzene	1.6	2.1	4.4	3.8	3.59	3.2	3.6
toluene	1.4	1.8	4.0	3.4	3.36	2.8	3.3
o-xylene	1.0	1.5	3.7	3.0	3.15	2.7	2.9
Naphthalene	0.4	0.9	3.3	2.7	2.60	2.4	2.6
MAE	2.1	1.7	0.8	0.1	---	0.4	0.1

Thygesen PRL '11
Blase APL '11

Stein, Kronik, Baer, J. Am. Chem. Soc. (Comm.) 131, 2818 (2009).

Optimal tuning is excellent for predicting inter- and intra-molecular charge transfer excitations!



Ziaei & Bredow, *ChemPhysChem* 18, 579 (2017).

For the Theory See:

Stein, Kronik, Baer, *J. Am. Chem. Soc. (Comm.)* **131**, 2818 (2009).

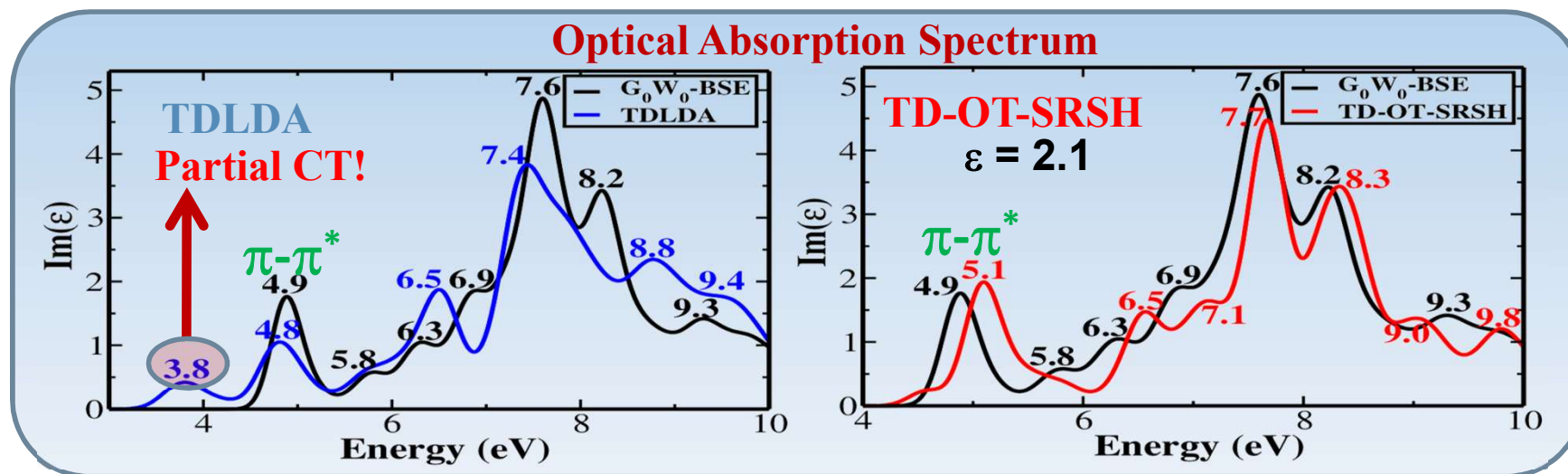
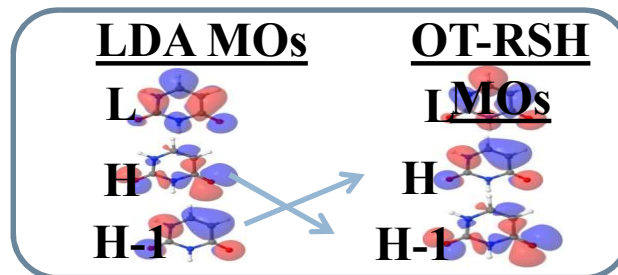
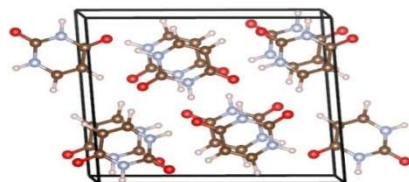
Stein, Kronik, Baer, *J. Chem. Phys.* **131**, 244119 (2009).

Allows solid-state optical absorption with TDDFT!



Arun Manna

Example: The Uracil Solid

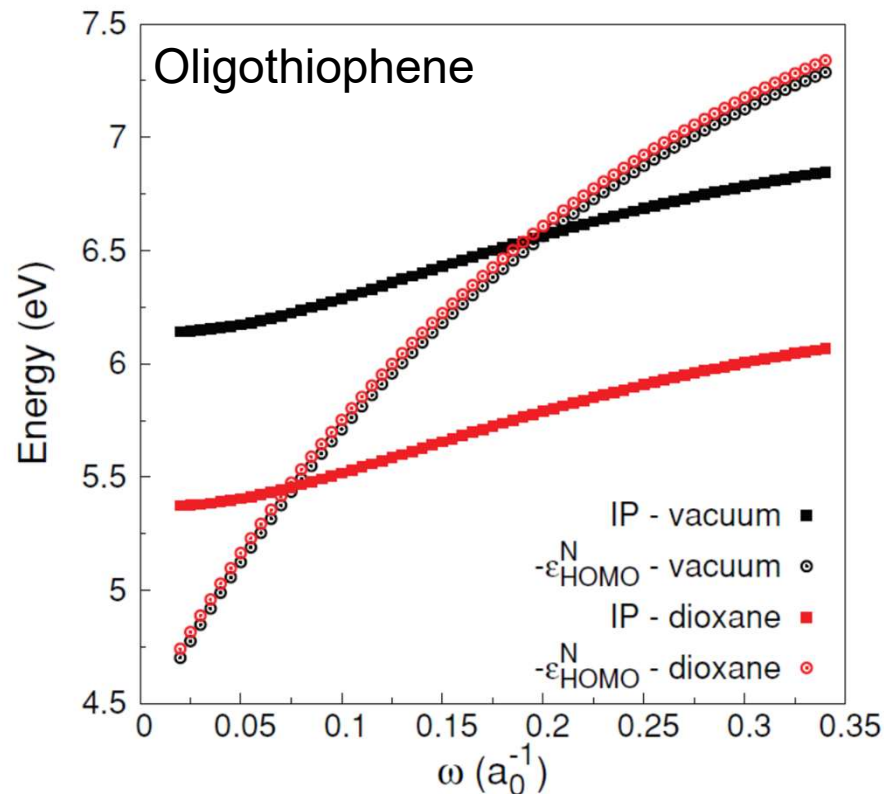


Manna, Refaely-Abramson, Reilly, Tkatchenko, Neaton, Kronik, *J. Chem. Theo. Comp.*, 14, 2919 (2018)

Combine OT-RSH with a polarizable continuum model (PCM)?

PCM = a molecule resides within a cavity in a dielectric medium and interacts with it coulombically.

Unphysical collapse of the range-separation parameter!



Stephan
Kümmel

De Queiroz and Kümmel, *J. Chem. Phys.* **141**, 084303 (2014).
Kronik & Kümmel, *Advanced Materials* **30**, 1706560 (2018).

Solid-state interface charge transfer excitations?

	Theo – gas-phase (eV)		Expmt (eV)
Pn/C ₆₀	2.5		1.2-1.3
P3HT/PCBM	2.1		1.4-1.7



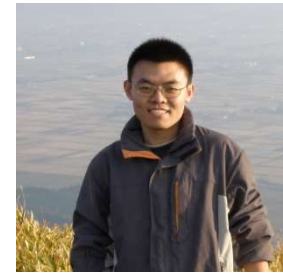
**David
Egger**



**Jean-Luc
Brédas**



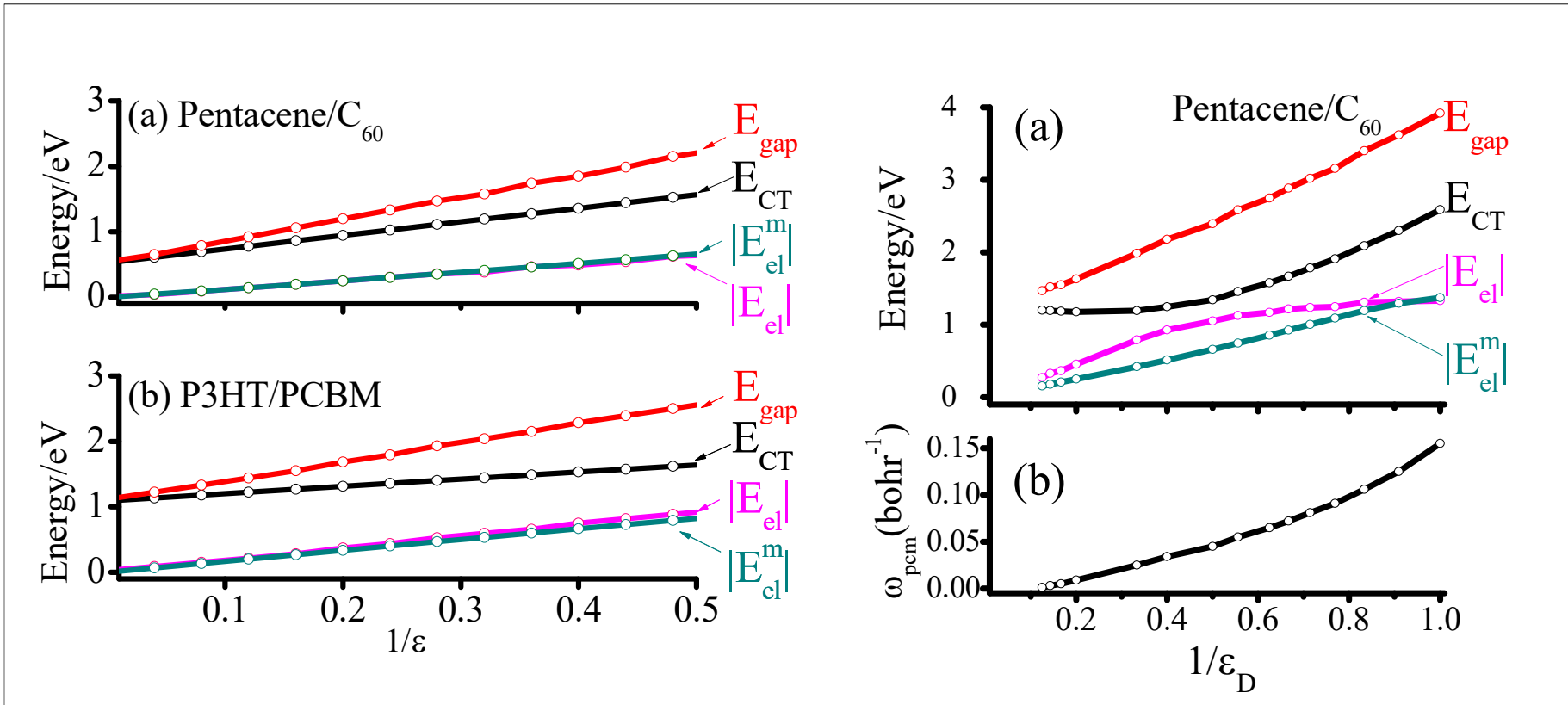
**Slava
Coropceanu**



**Zilong
Zheng**

**Zheng, Egger, Brédas, Kronik, Coropceanu,
J. Phys. Chem. Lett. 8, 3277 (2017).**

ϵ -tuning versus γ -tuning: The importance of screening



Proper Screening

Improper Screening

Zheng et al., *J. Phys. Chem. Lett.* **8**, 3277 (2017).

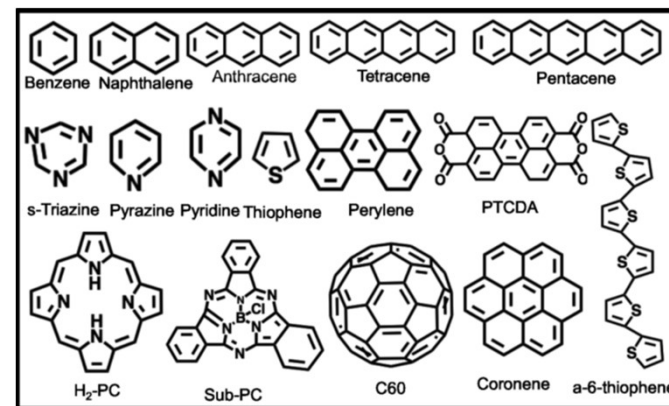
Kronik & Kümmel, *Advanced Materials* **30**, 1706560 (2018).

Solid-state interface charge transfer excitations

	Theo – gas-phase (eV)	Theo – screened (eV)	Expmt (eV)
Pn/C ₆₀	2.5	1.2	1.2-1.3
P3HT/PCB M	2.1	1.45	1.4-1.7

**Zheng, Egger, Brédas, Kronik, Coropceanu,
J. Phys. Chem. Lett. 8, 3277 (2017).**

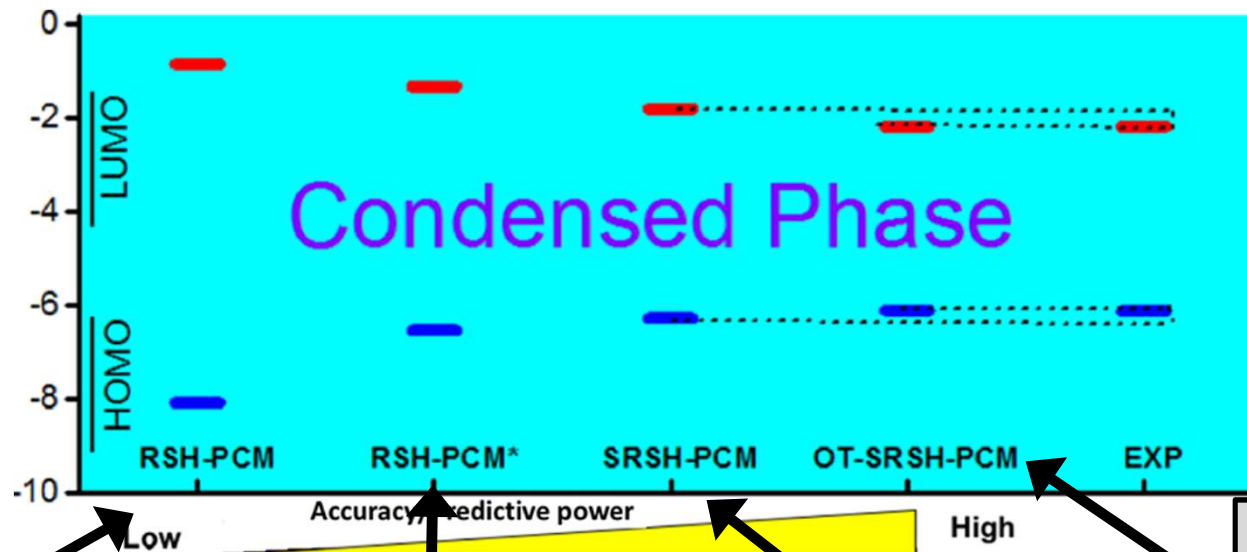
Solid-state gaps from single molecule calculations with PCM



Srijana Bhandari



Barry Dunietz



PCM, gas-phase optimal-tuning

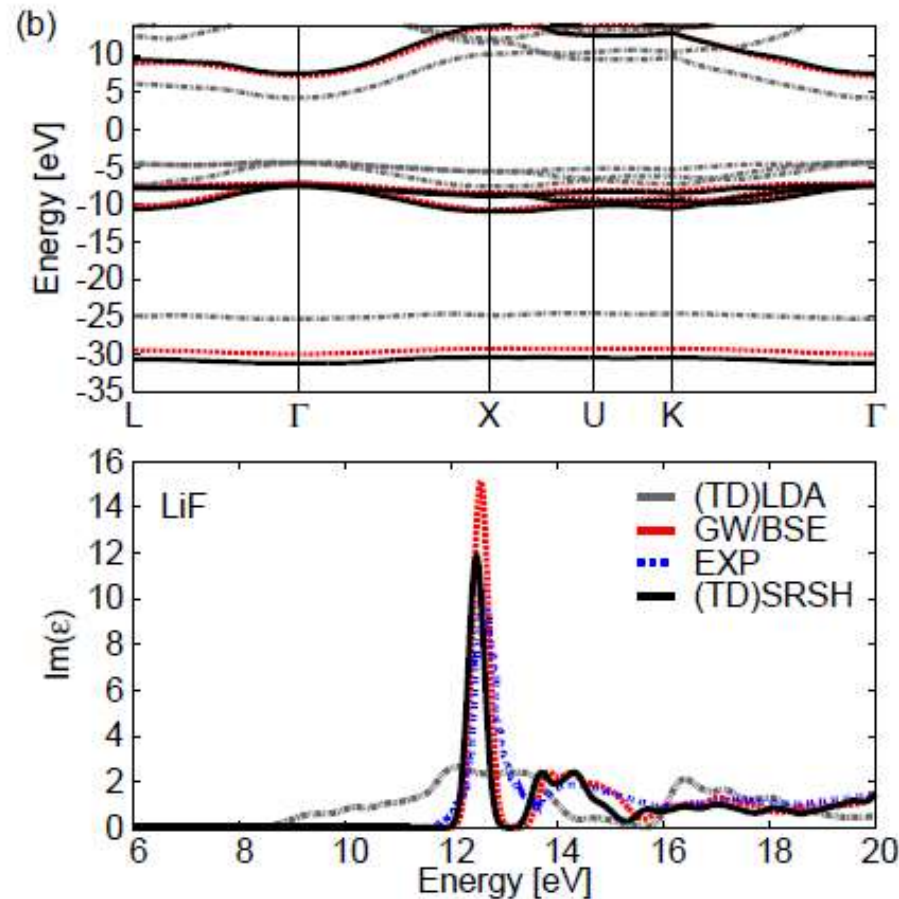
PCM-based optimal tuning

PCM + dielectric screening

PCM + dielectric screening + retuning

Bhandari, Cheung, Geva, Kronik, Dunietz, *JCTC* 14, 6287 (2018)

Extended to non-molecular solids with one empirical parameter

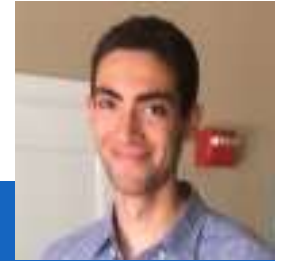


Refaely-Abramson, Jain, Sharifzadeh, Neaton, Kronik,
Phys. Rev. B (Rapid Comm.) **92**, 081204 (2015).

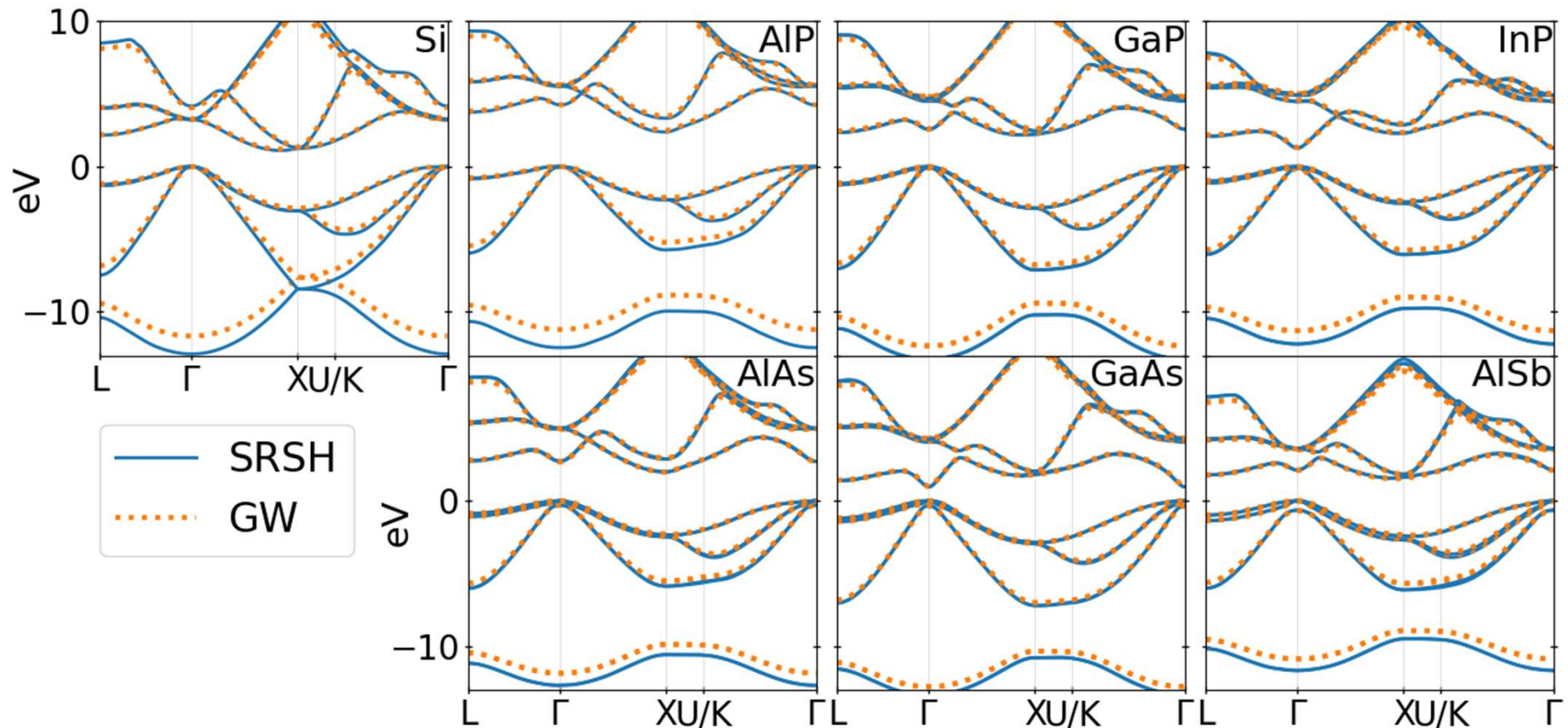


Dahvyd
Wing

Jonah Haber

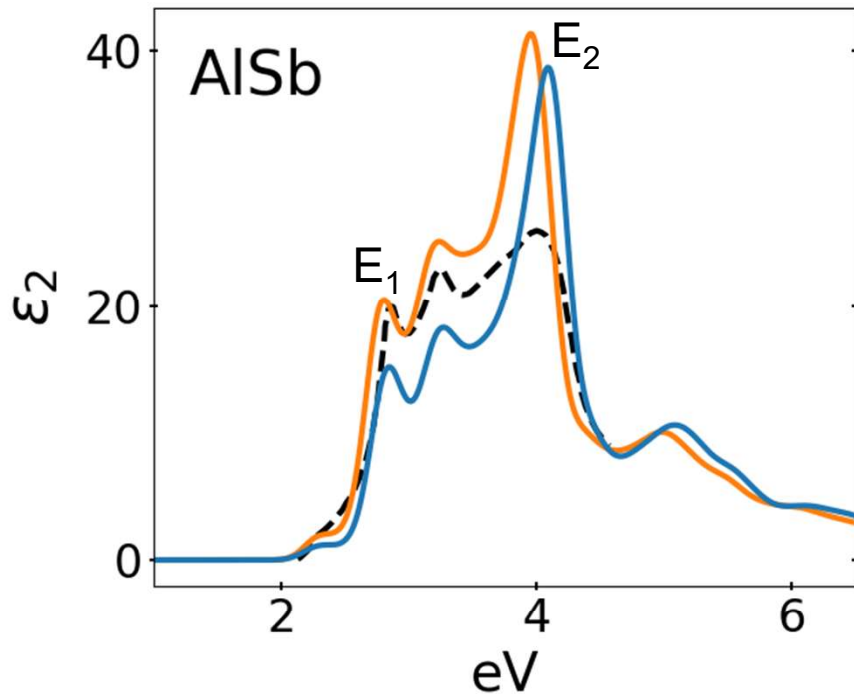


Band structures – incl. spin-orbit coupling



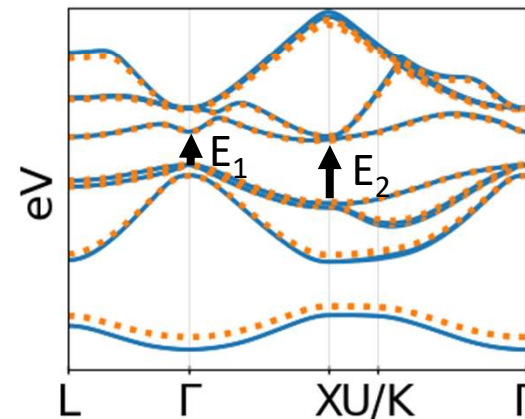
Wing, Haber, Noff, Barker, Egger, Ramasubramaniam,
Louie, Neaton, Kronik, *Phys. Rev. Materials* **3**, 064603 (2019).

Optical Absorption



Mean error of peak position :

- 0.03 eV for E_1
- 0.11 eV for E_2



— TDDFT (SRSH)

— GW+BSE

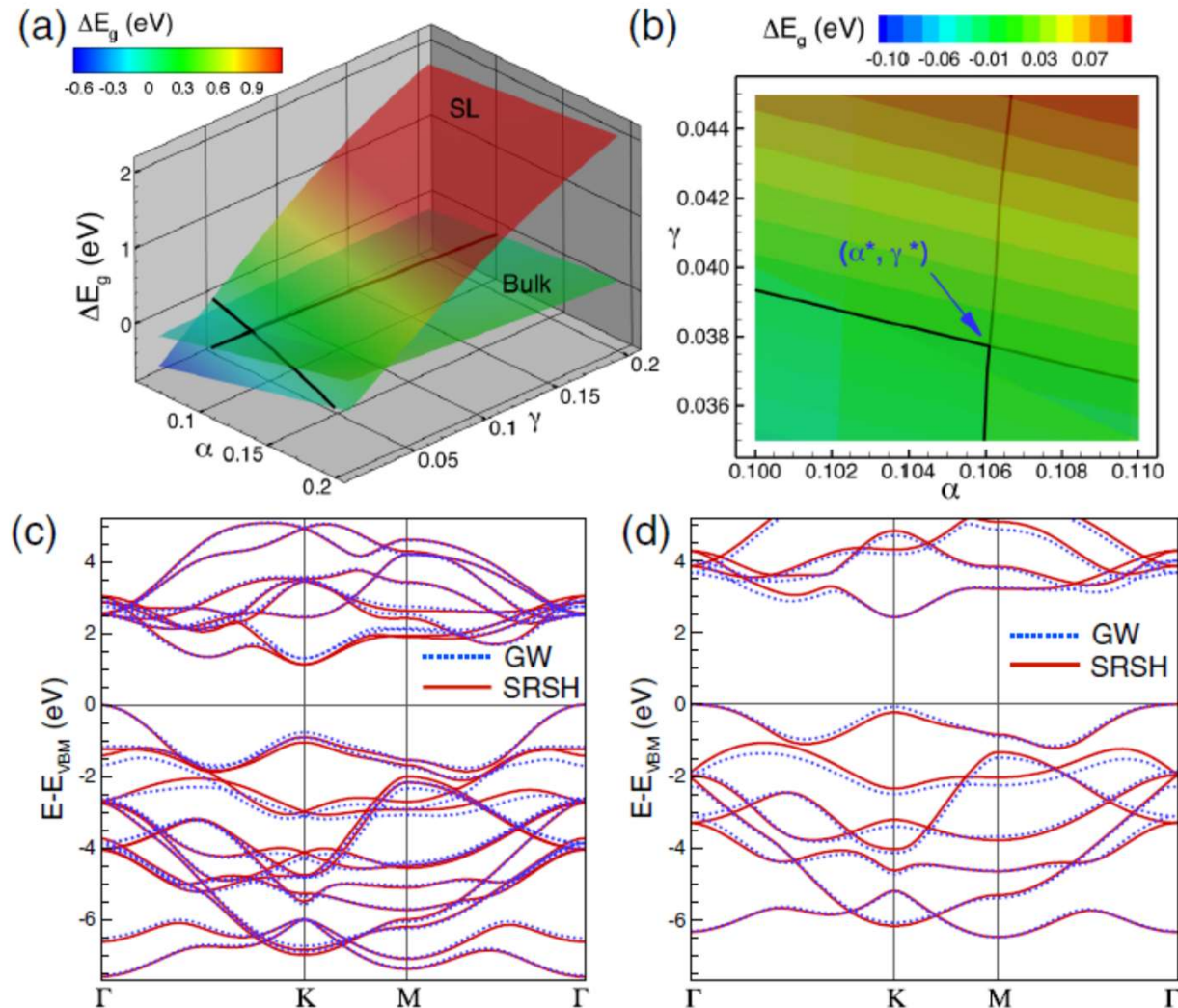
----- Exp. Room Temp.

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

Simultaneous RSH and SRSH tuning for 2d and layered materials: MoS₂

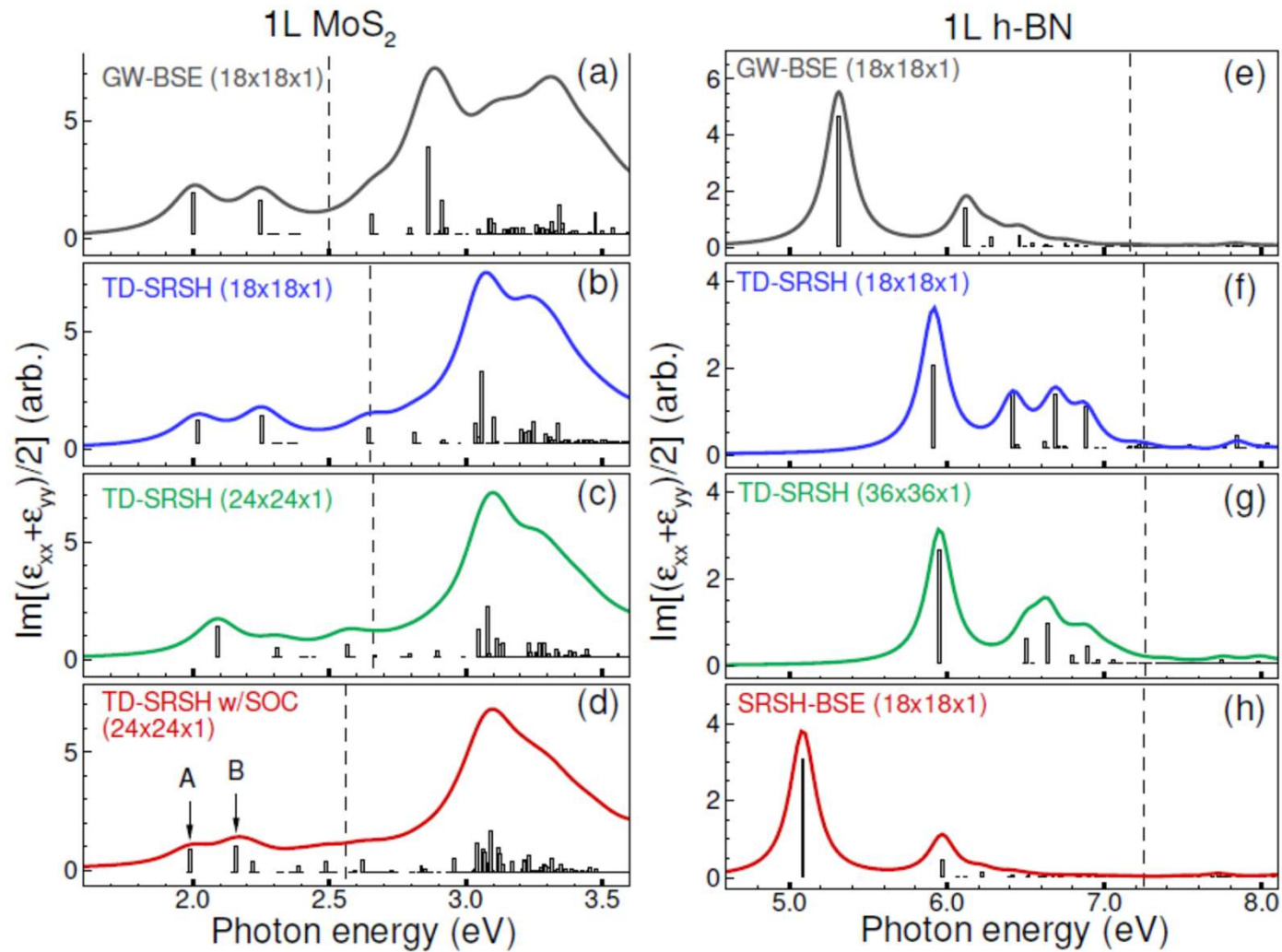


Ashwin
Ramasubramanian



Ramasubramanian, Wing, Kronik, 3, 084007 (2019).

Optical Absorption: Beyond a dielectric constant ?



Ramasubramaniam, Wing, Kronik, 3, 084007 (2019).

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, Ögüt,
J. Chem. Phys. 149, 064306 (2018).**

Spin cross-over complexes:

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

(TD)DFT can ~~not~~ quantitatively predict:

- **molecular gaps**
- **charge-transfer excitation energies**
- **photoemission spectra**
- **gap renormalization of molecular solids**
- **band structure and excitonic lineshapes in solids**