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WEIZMANN INSTITUTE OF SCIENCE

Leeor Kronik
WIS

Solid-State Optical Absorption from Optimally-Tuned Time-Dependent Screened Range-Separated Hybrids

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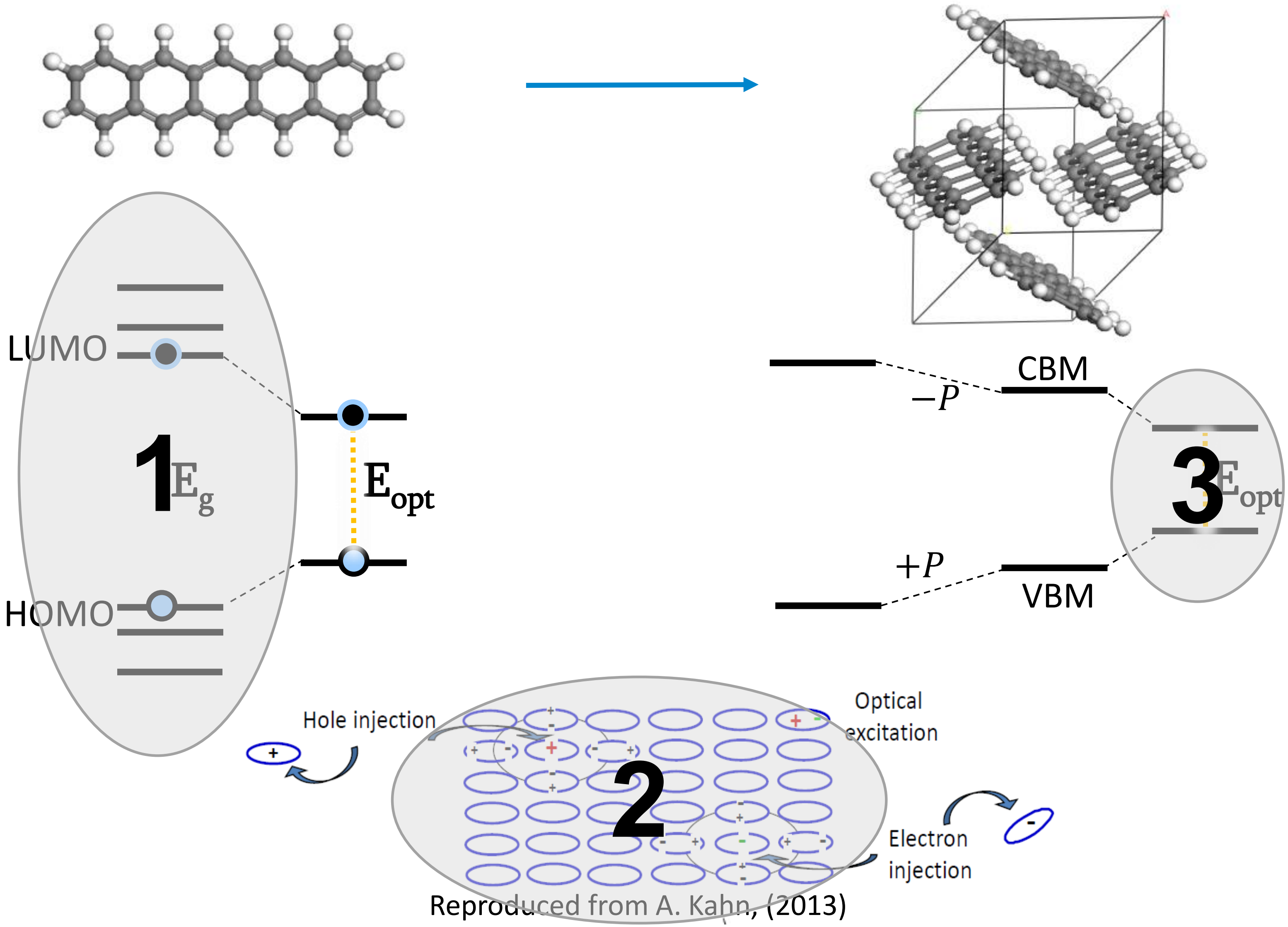
University of California, Berkeley;
Lawrence Berkeley National Laboratory

TDDFT Workshop, Benasque, September 2016

Solid-state excitations from TDDFT



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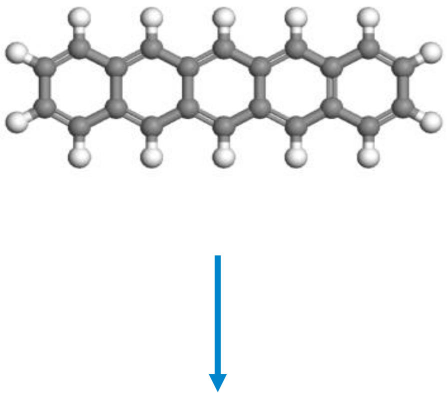
Excitations from TDDFT

1. Molecules:

   Calculating accurate energy levels and excitation gaps within Generalized-KS

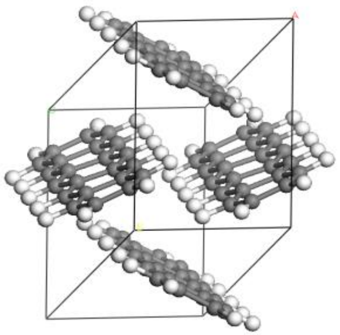
   with an optimally-tuned range-separated hybrid functional



2. Molecular crystals:

   Modeling the solid-state dielectric response into the xc functional

   Calculating accurate excitation gaps with an optimally-tuned **screened** range-separated hybrid functional



3. Other crystals:

   Investigating model abilities

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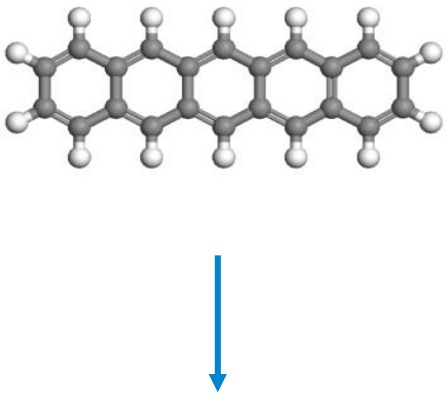

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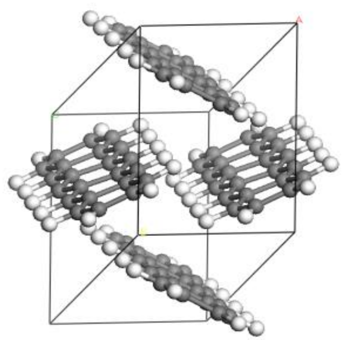

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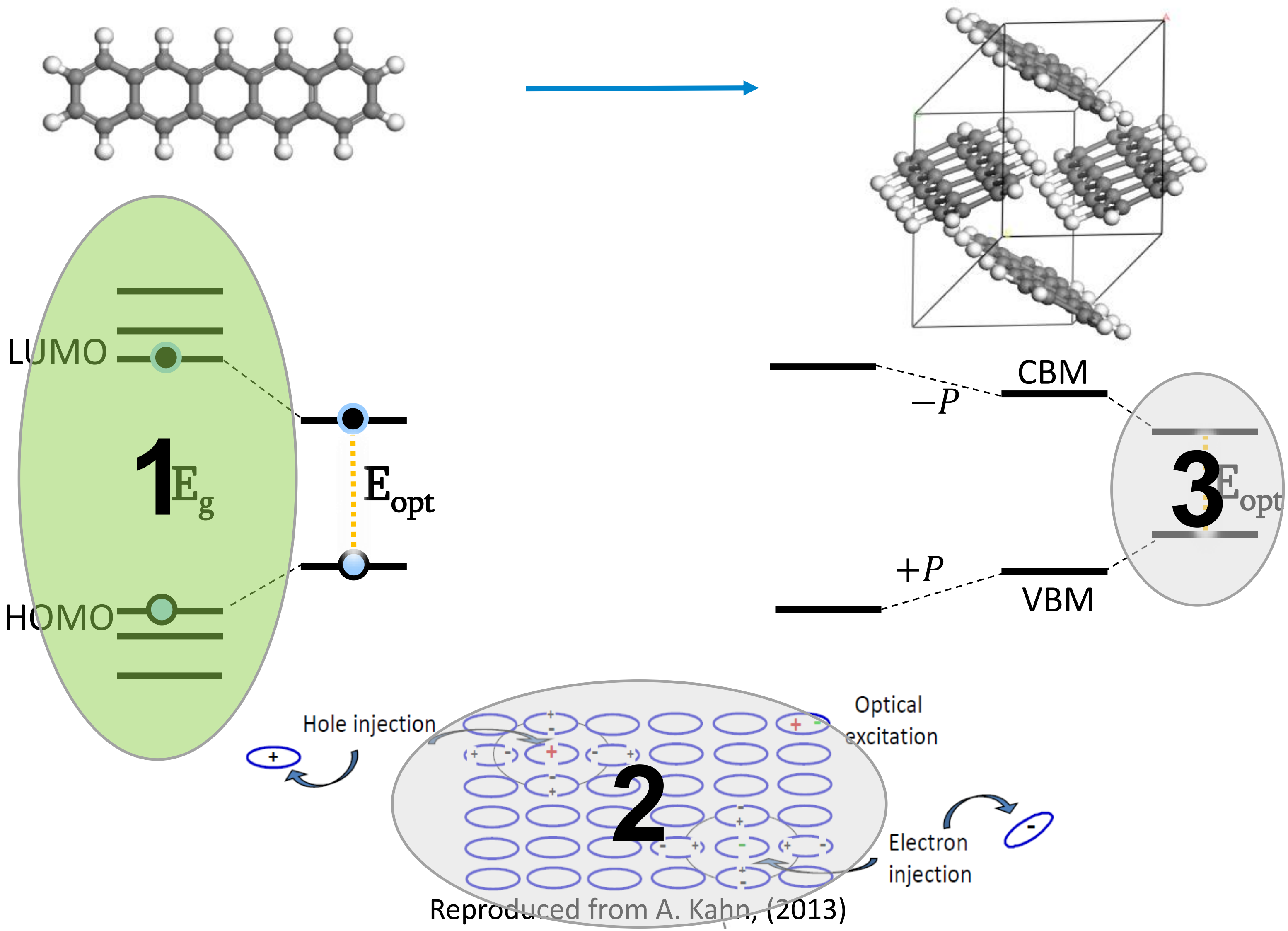


Reproduced from A. Kahn, (2013)

Molecular Excitations

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

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

Generalized-KS:

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

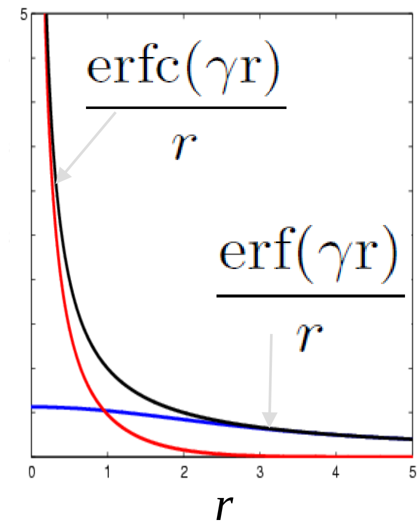
non-local, orbital specific **remainder local potential**

A. Seidl, A. Gorling, P. Vogl, J. A. Majewski, M. Levi, Phys. Rev. B 53, 3764 (1996)

Range-Separated Hybrid Functionals:

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

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



Toulouse et al., JQC 100, 1047 (2004); Leininger et al., CPL 275, 151 (1997); Yanai et al., CPL 393, 51 (2004)

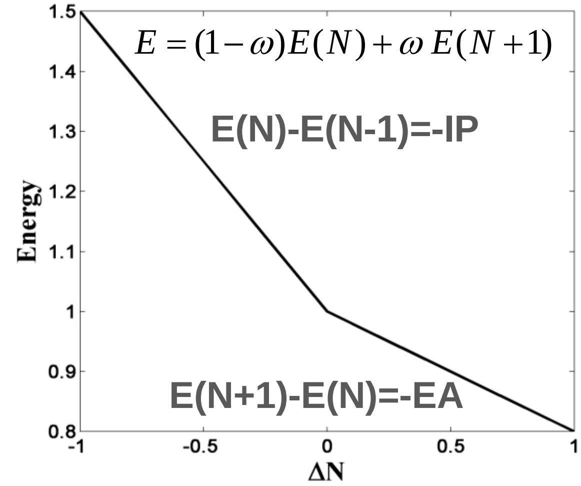
Tuned Range-Separated Hybrids

Optimal Parameter Tuning:

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

$\alpha+\beta \rightarrow 1$

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

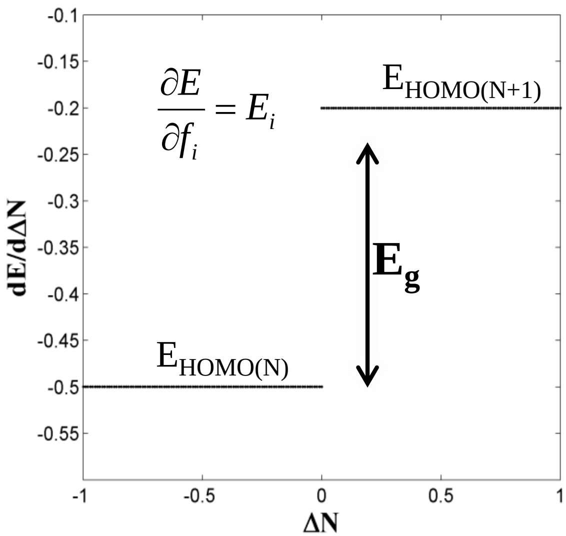


J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Phys. Rev. Lett. 49, 1691 (1982)

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

$$J^2(\gamma;\alpha) = J^2(N) + J^2(N+1)$$
$$= (\varepsilon_{HOMO(N)}^{\gamma;\alpha} + IP^{\gamma;\alpha}(N))^2 + (\varepsilon_{HOMO(N+1)}^{\gamma;\alpha} + IP^{\gamma;\alpha}(N+1))^2$$

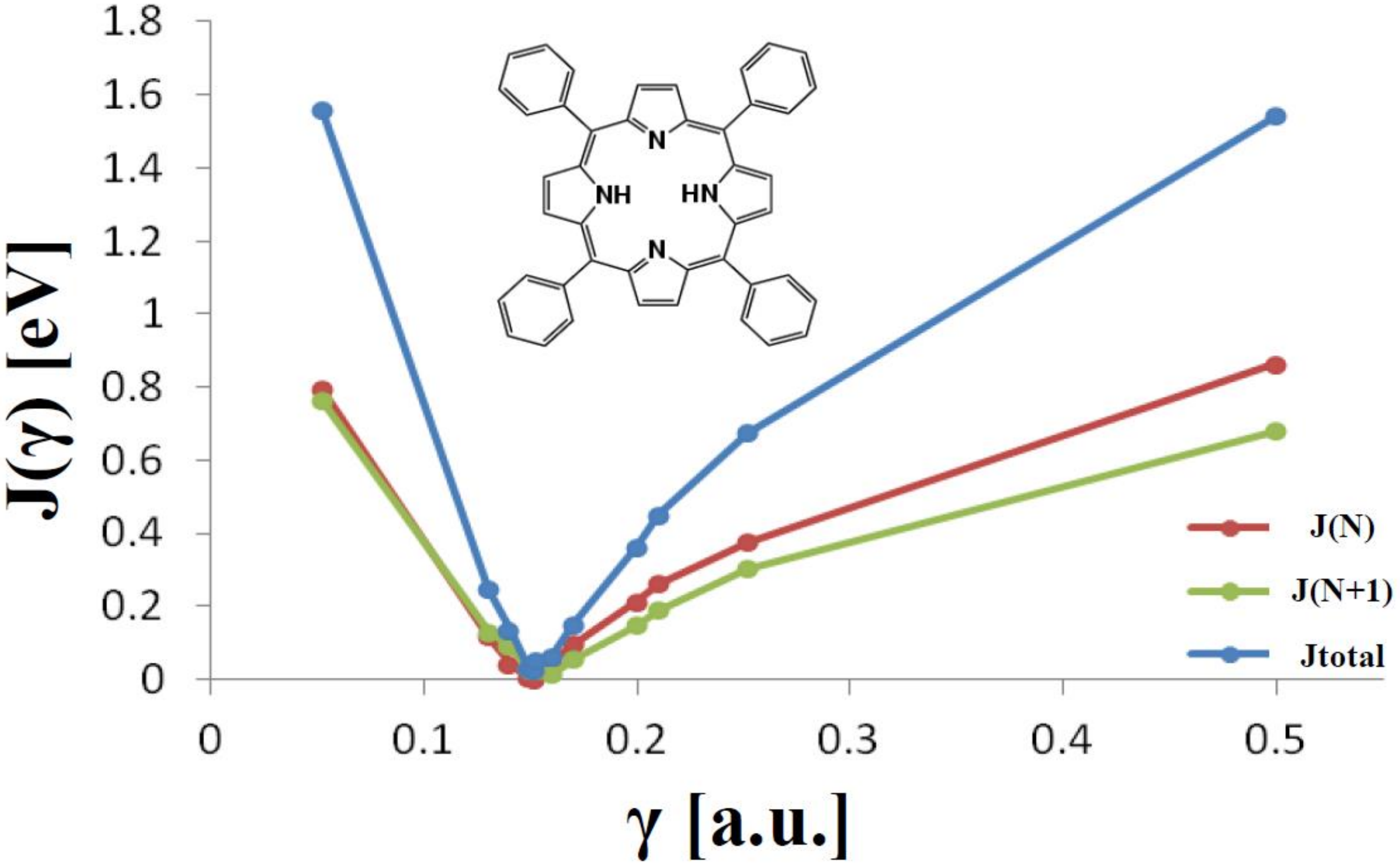
T. Stein, H. Eisenberg, L. Kronik, and R. Baer, PRL 105, 266802 (2010);
L. Kronik, T. Stein, SRA, and R. Baer, JCTC 8, 1515 (2012)



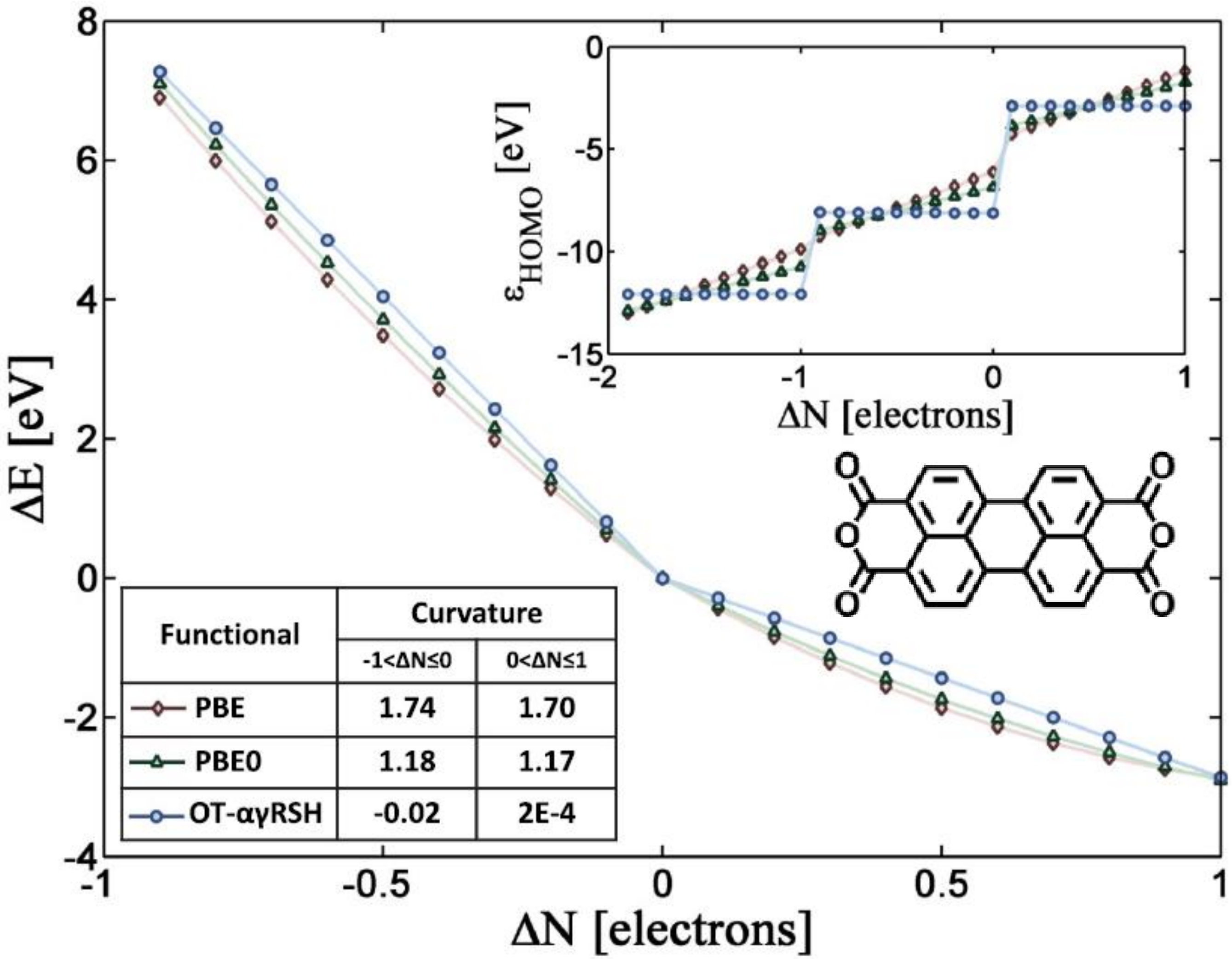
J. F. Janak, Phys. Rev. B 18, 7165 (1978)

Relation between tuning and curvature linearity: Stein et al., JPCL 3, 3740 (2012)

Tuned Range-Separated Hybrids



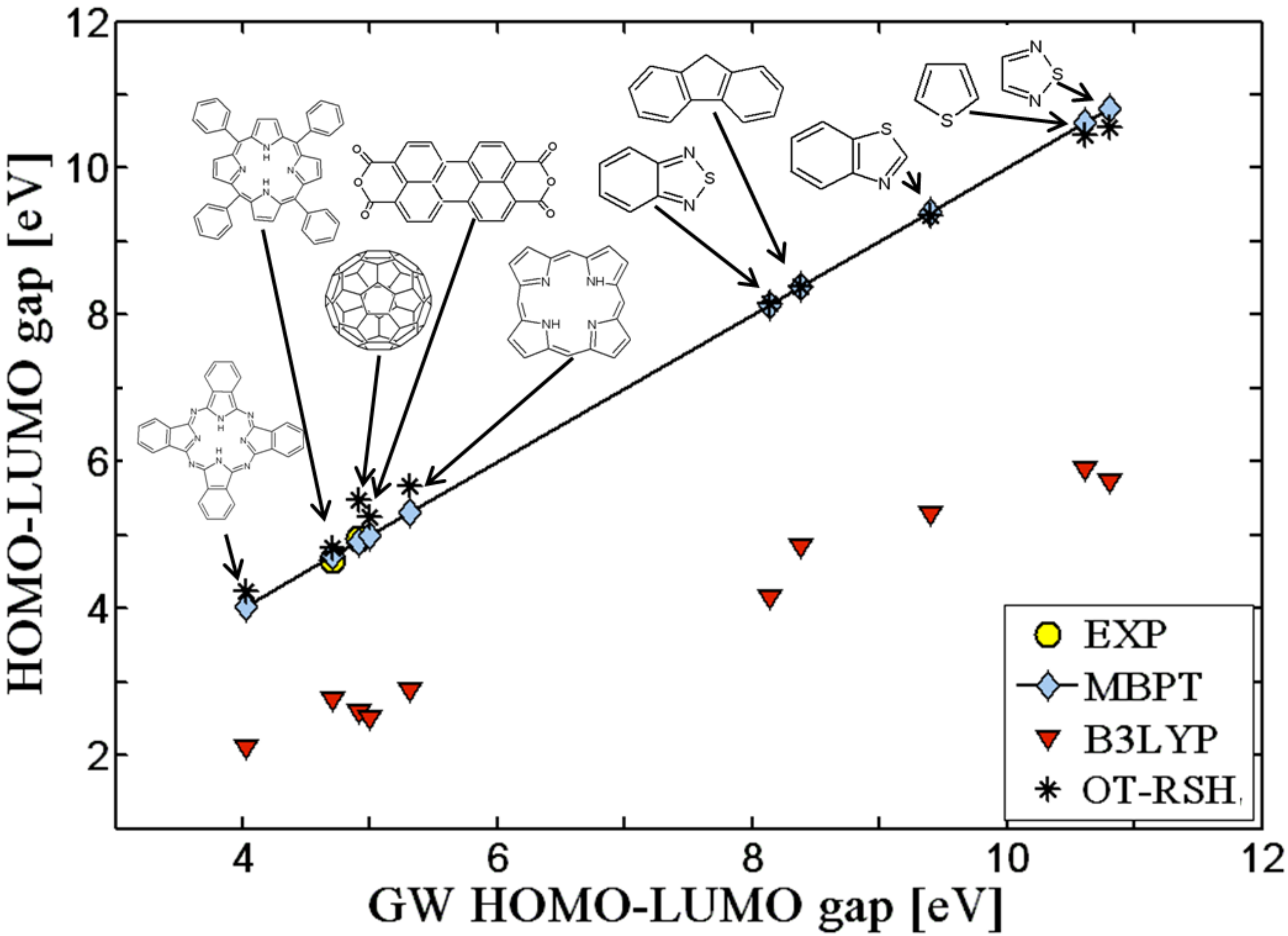
Tuned Range-Separated Hybrids



Functional	Curvature	
	-1<ΔN≤0	0<ΔN≤1
PBE	1.74	1.70
PBE0	1.18	1.17
OT-αγRSH	-0.02	2E-4

SRA, S. Sharifzadeh, N. Govind, J. Autschbach, J. B. Neaton, R. Baer, and L. Kronik, PRL 109, 226405 (2012)

Tuned Range-Separated Hybrids



SRA, R. Baer and L. Kronik, PRB 84, 075144 (2011)

Tuned Range-Separated Hybrids

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

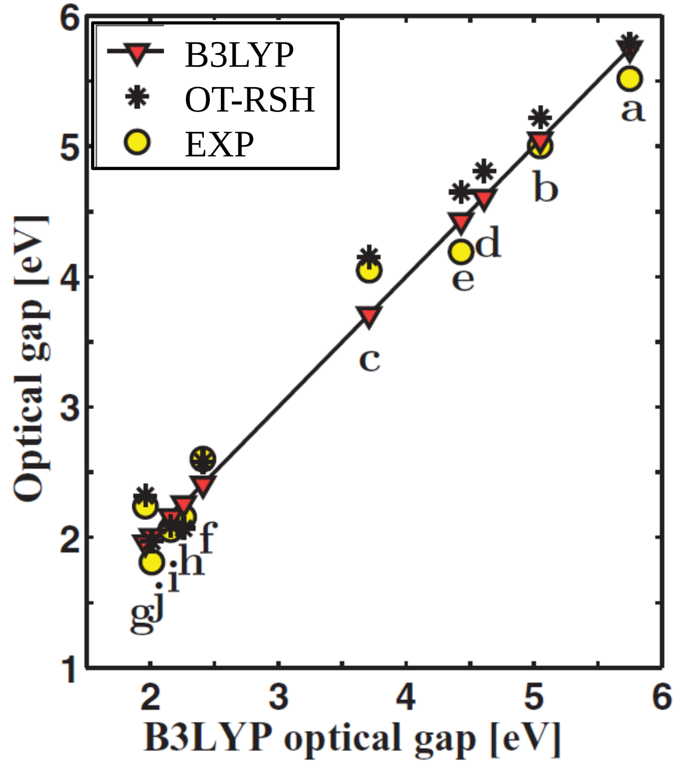
$$E_x^{SR} = -\frac{1}{4}\int\int \frac{|\rho(r,r')|^2}{|r-r'|}\mathrm{erfc}(\gamma(r-r'))\mathrm{d}^3r\mathrm{d}^3r'$$

$$v_x^{SR}[n(r')] = \frac{\delta E_x^{SR}[n]}{\delta n(r')}$$

$$f_x^{SR}[n(r)] = \frac{\delta v_x^{SR}[n(r)]}{\delta n(r')}$$

$$\langle ai|\left[\frac{1}{|r-r'|} + (1-\alpha)f_x^{SR} + f_c\right]|bj\rangle$$

$$-\langle ab|\left[\alpha\frac{\mathrm{erfc}(\gamma(|\mathrm{r}-\mathrm{r}'|)}{|r-r'|} + \frac{\mathrm{erf}(\gamma(|\mathrm{r}-\mathrm{r}'|)}{|r-r'|}\right]|ij\rangle$$

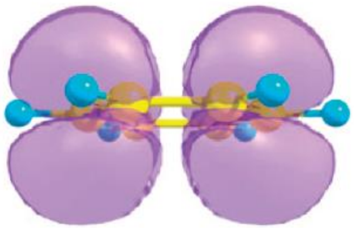


SRA, R. Baer and L. Kronik, PRB 84, 075144 (2011)

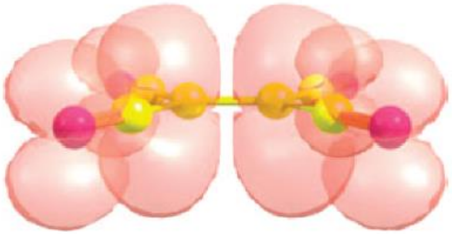
L. Kronik, T. Stein, SRA, and R. Baer, JCTC 8, 1515 (2012)

OT-RSH for CT excitations

$$E_{CT} = I_D - A_A - 1/R$$



$$\varepsilon_{\mathrm{H}} - \varepsilon_{\mathrm{L}} - \int\int |\phi_{\mathrm{H}}(r)|^2 u_\gamma(|r - r'|) |\phi_{\mathrm{L}}(r')|^2 \, \mathrm{d}^3r \, \mathrm{d}^3r'.$$



$\varepsilon_H - \varepsilon_L$ SL

$\varepsilon_H - \varepsilon_L - \alpha / R$ Conventional hybrid

$\varepsilon_H - \varepsilon_L - 1/R$ Range-separated hybrid

	B3LYP			BNL γ^*			exp[27]	
Ar	E	f	BNL $\gamma = 0.5$	γ^*		f	E	f
benzene	2.1	0.03	4.4	0.33	3.8	0.03	3.59	0.02
toluene	1.8	0.04	4.0	0.32	3.4	0.03	3.36	0.03
o-xylene	1.5	~0	3.7	0.31	3.0	0.01	3.15	0.05
naphthalene	0.9	~0	3.3	0.32	2.7	~0	2.60	0.01

T. Stein, L. Kronik, and R. Baer, JACS 131, 2818 (2009)

Excitations from TDDFT

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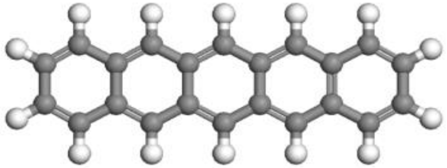

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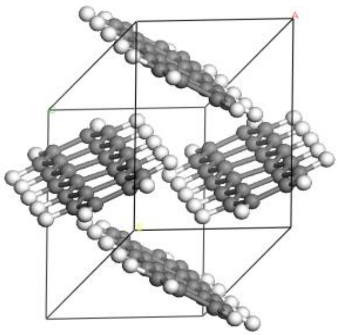

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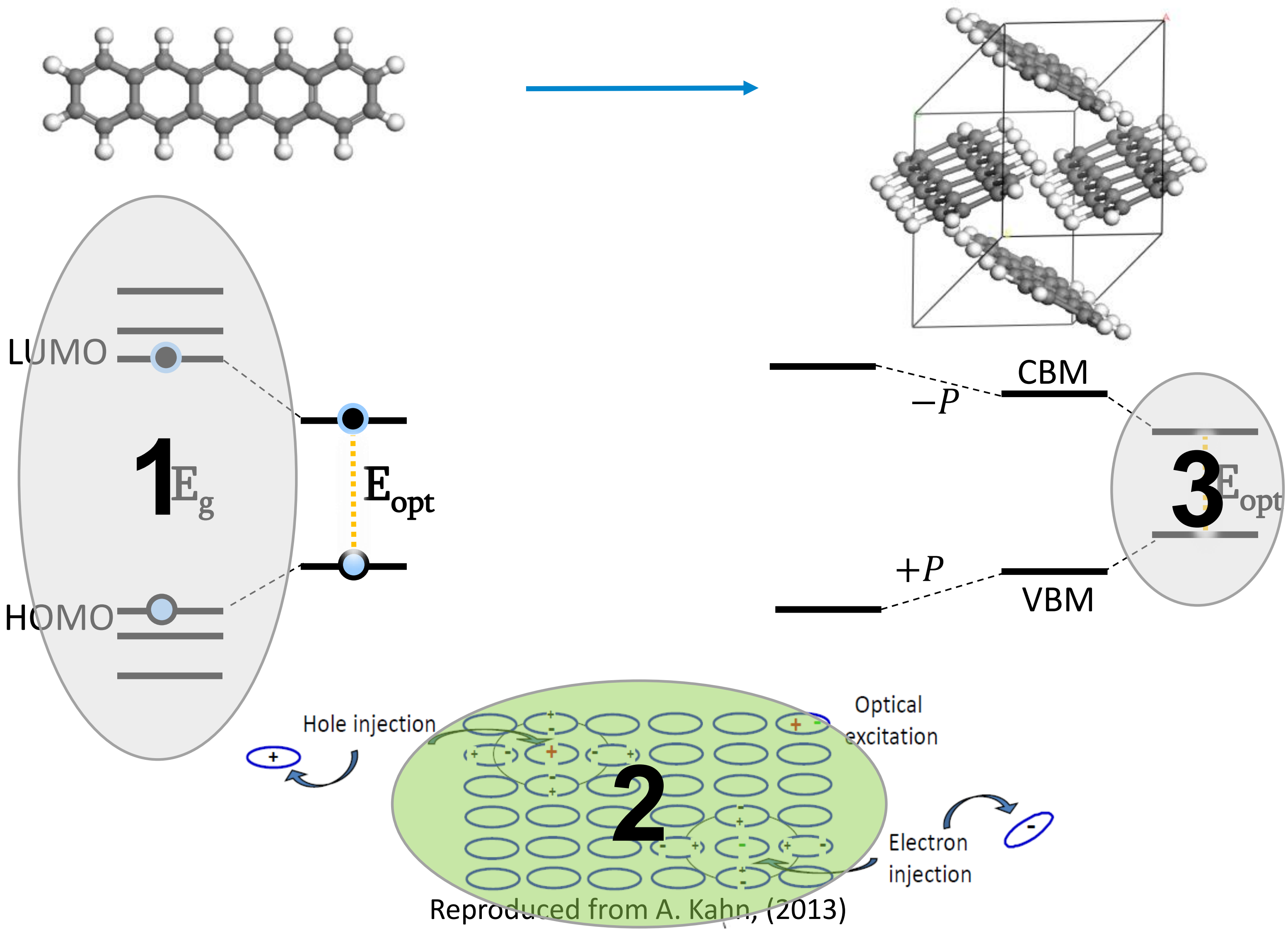
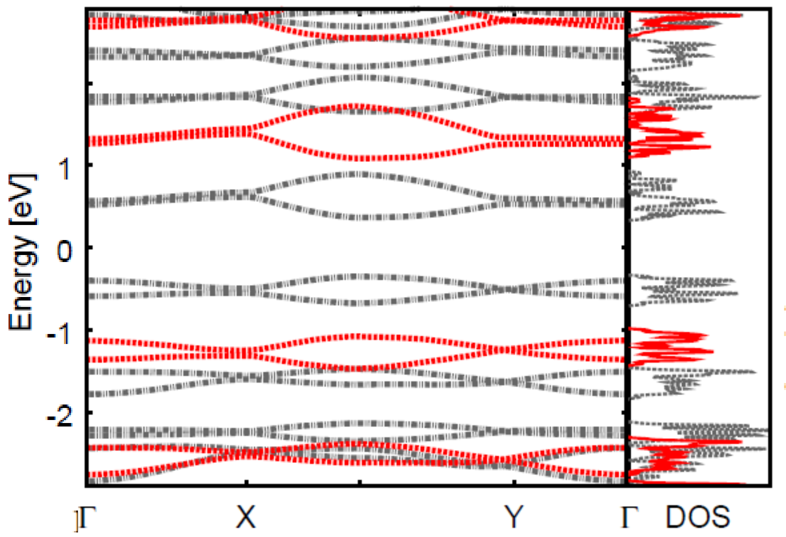
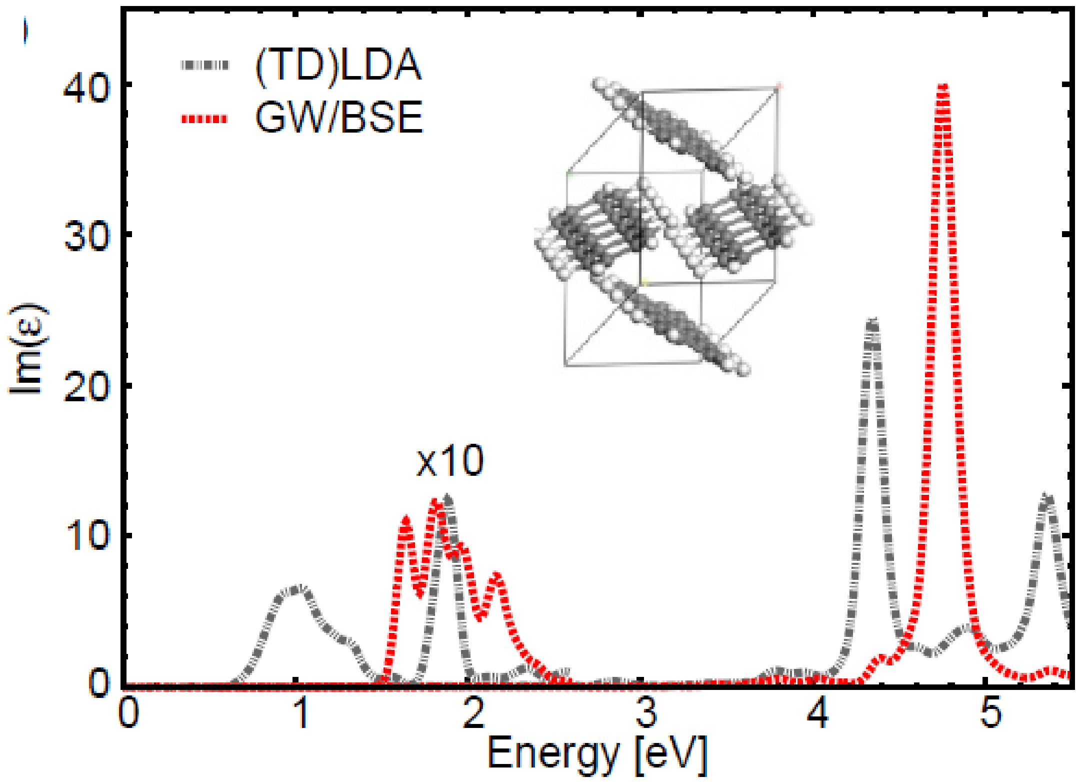
Excitations from TDDFT



Reproduced from A. Kahn, (2013)

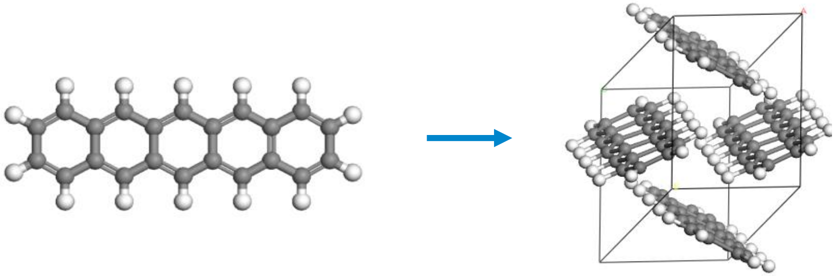
Optical Spectra- Molecular Crystals

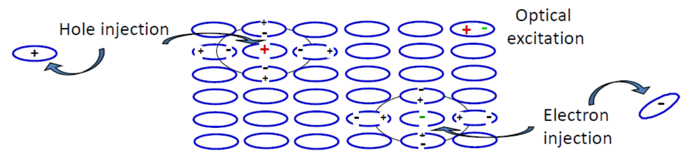


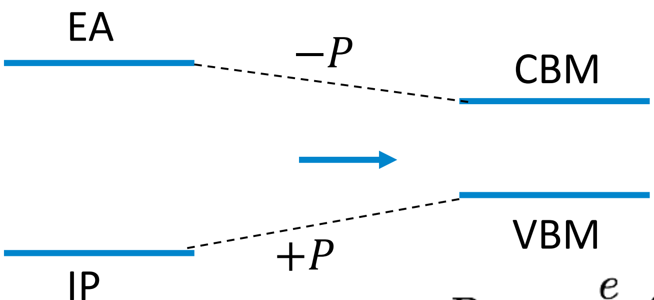


OT – Screened - RSH

Sahar Sharifzadeh

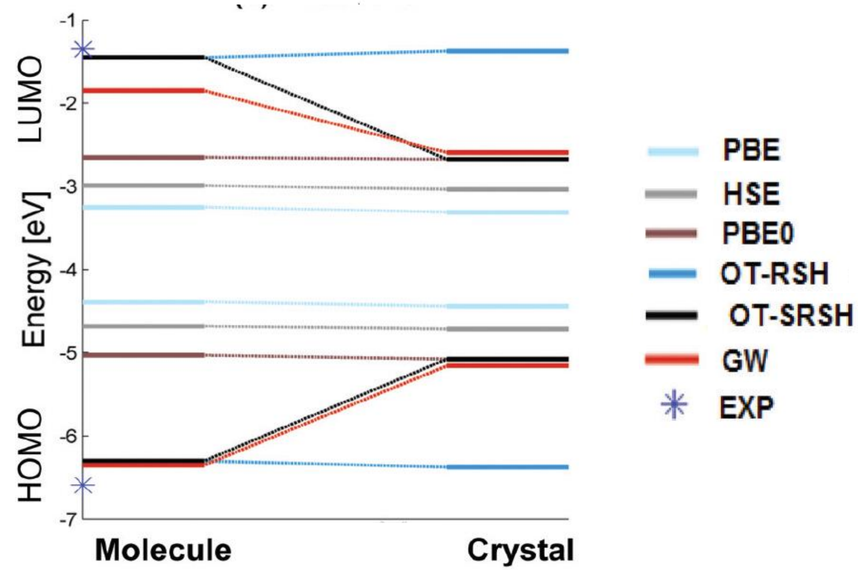






$$P = -\frac{e}{2R}\left(1 - \frac{1}{\epsilon}\right)$$

S. Sharifzadeh, A. Biller, L. Kronik, and J. B. Neaton, PRB 85, 125307 (2012)



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

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

$$\alpha + \beta = \frac{1}{\varepsilon} \longrightarrow E_{xc}^{SRSH} = (1-\alpha)E_{lx}^{SR} + \alpha E_{xx}^{SR} + \left(1-\frac{1}{\varepsilon}\right)E_{lx}^{LR} + \frac{1}{\varepsilon}E_{xx}^{LR} + E_{lc}$$

Molecular tuning!

TD – OT - Screened- RSH


Manish Jain

$$E_{xc}^{SRSH} = (1-\alpha)E_{lx}^{SR} + \alpha E_{xx}^{SR} + (1-\frac{1}{\varepsilon})E_{lx}^{LR} + \frac{1}{\varepsilon}E_{xx}^{LR} + E_{lc}$$

$$\langle ai| \left[\frac{1}{|r-r'|} + (1-\alpha) f_x^{SR} + (1-\frac{1}{\varepsilon}) f_x^{LR} + f_c \right] |bj\rangle$$
$$-\langle ab| \left[\alpha \frac{\mathrm{erfc}(\gamma(|\mathrm{r}-\mathrm{r}'|)}{|r-r'|} + \frac{1}{\varepsilon} \frac{\mathrm{erf}(\gamma(|\mathrm{r}-\mathrm{r}'|)}{|r-r'|} \right] |ij\rangle$$

LR decay: $1/\varepsilon|r-r'|$

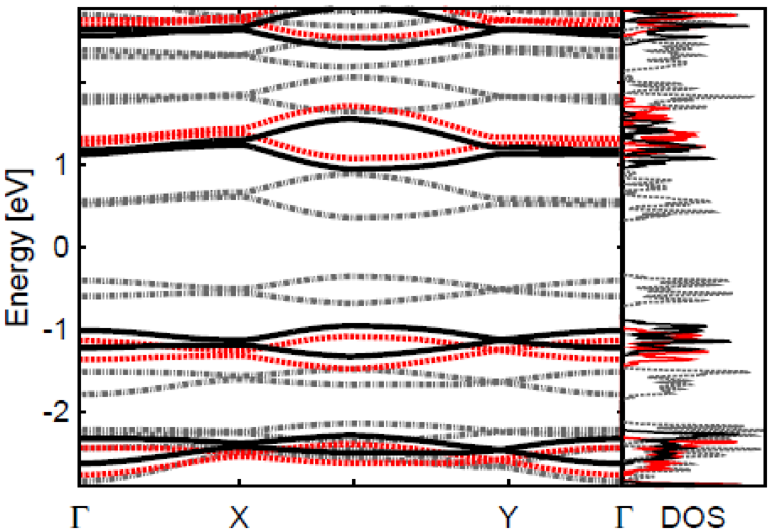
$$f_x^{SR}[n(r)] = \frac{\delta v_x^{SR}[n(r)]}{\delta n(r')} =$$
$$\frac{1}{(9\pi n^2)^{1/3}} \left[\frac{\gamma^2}{(3\pi^2 n)^{2/3}} \left(1 - \exp\left(-\frac{(3\pi^2 n)^{2/3}}{\gamma^2} \right) \right) - 1 \right]$$
$$\times \delta(r-r')$$

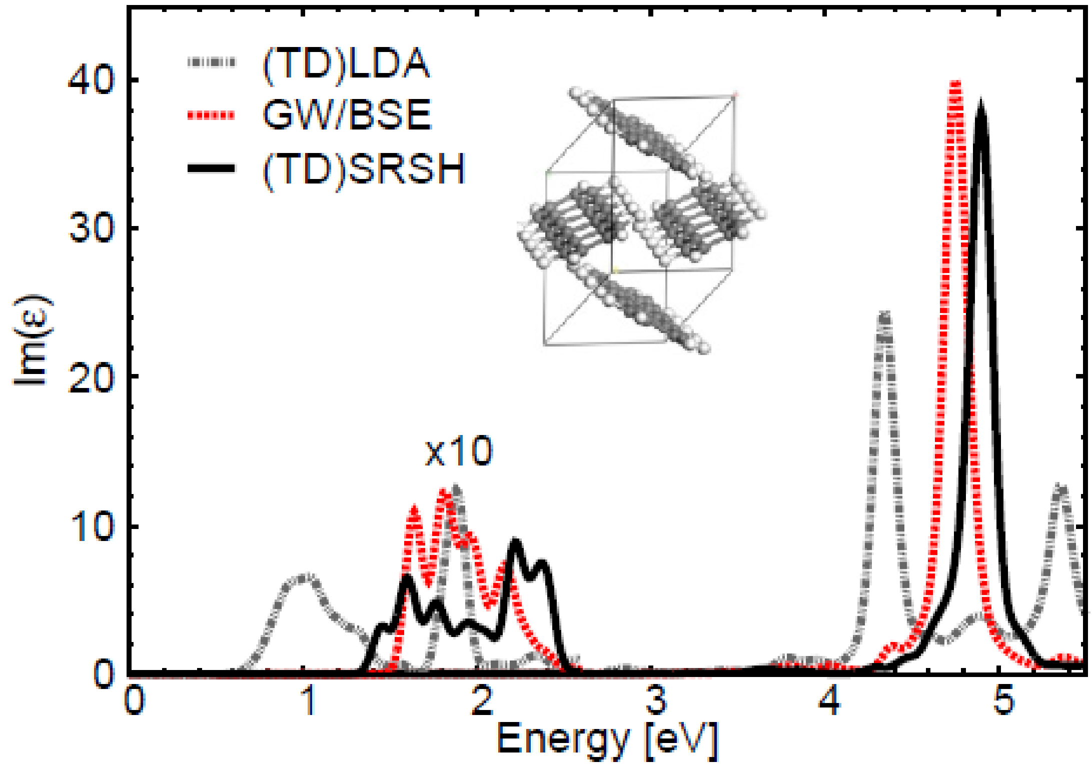
BerkeleyGW
www.berkeleygw.org

SRA, M. Jain, S. Sharifzadeh, J. B. Neaton and L. Kronik Phys. Rev. B 92, 081204(R) (2015)

Optical Spectra- Molecular Crystals

Crystal	Band Gap (eV)				Optical Gap (eV)				Exciton B.E (eV)		
	LDA	SRSH	GW	EXP	TD-LDA	TD-SRSH	BSE	EXP	SRSH	GW-BSE	Expt.
Pentacene	0.7	2.0	2.2	2.2	0.7	1.5	1.7	1.8	0.5	0.5	0.4

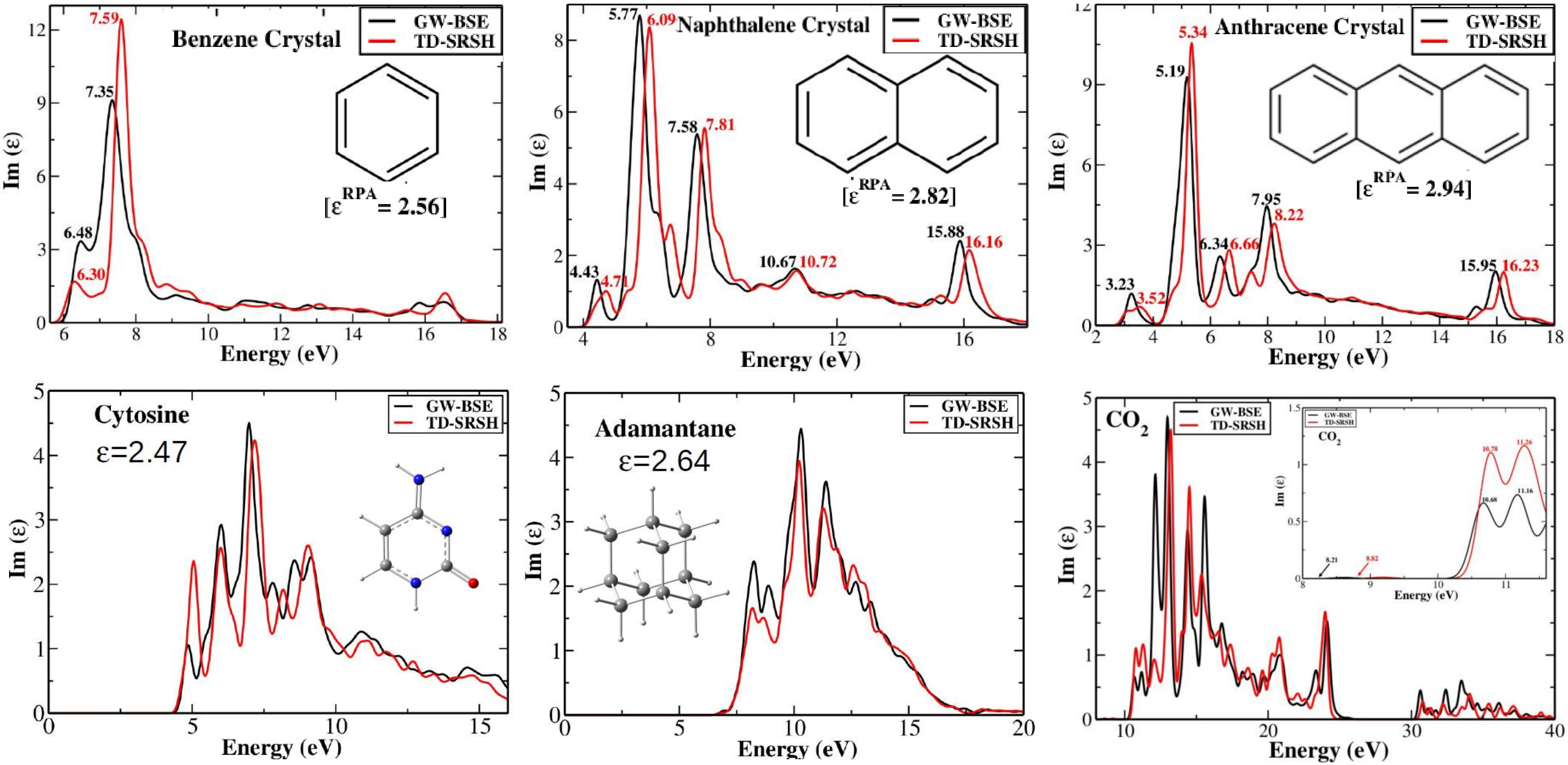




SRA, M. Jain, S. Sharifzadeh, J. B. Neaton and L. Kronik PRB 92, 081204(R) (2015)

Optical Spectra- Molecular Crystals

Arun Manna



A. Manna, SRA, M. Jain, and L. Kronik, in preparation

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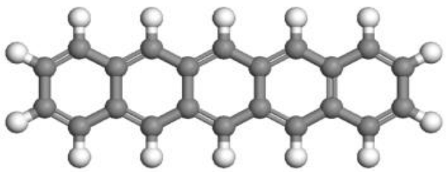

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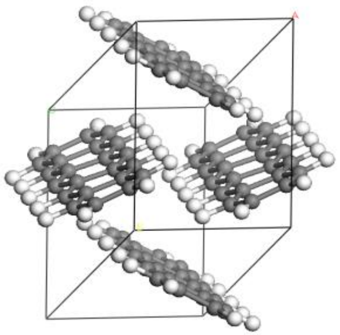

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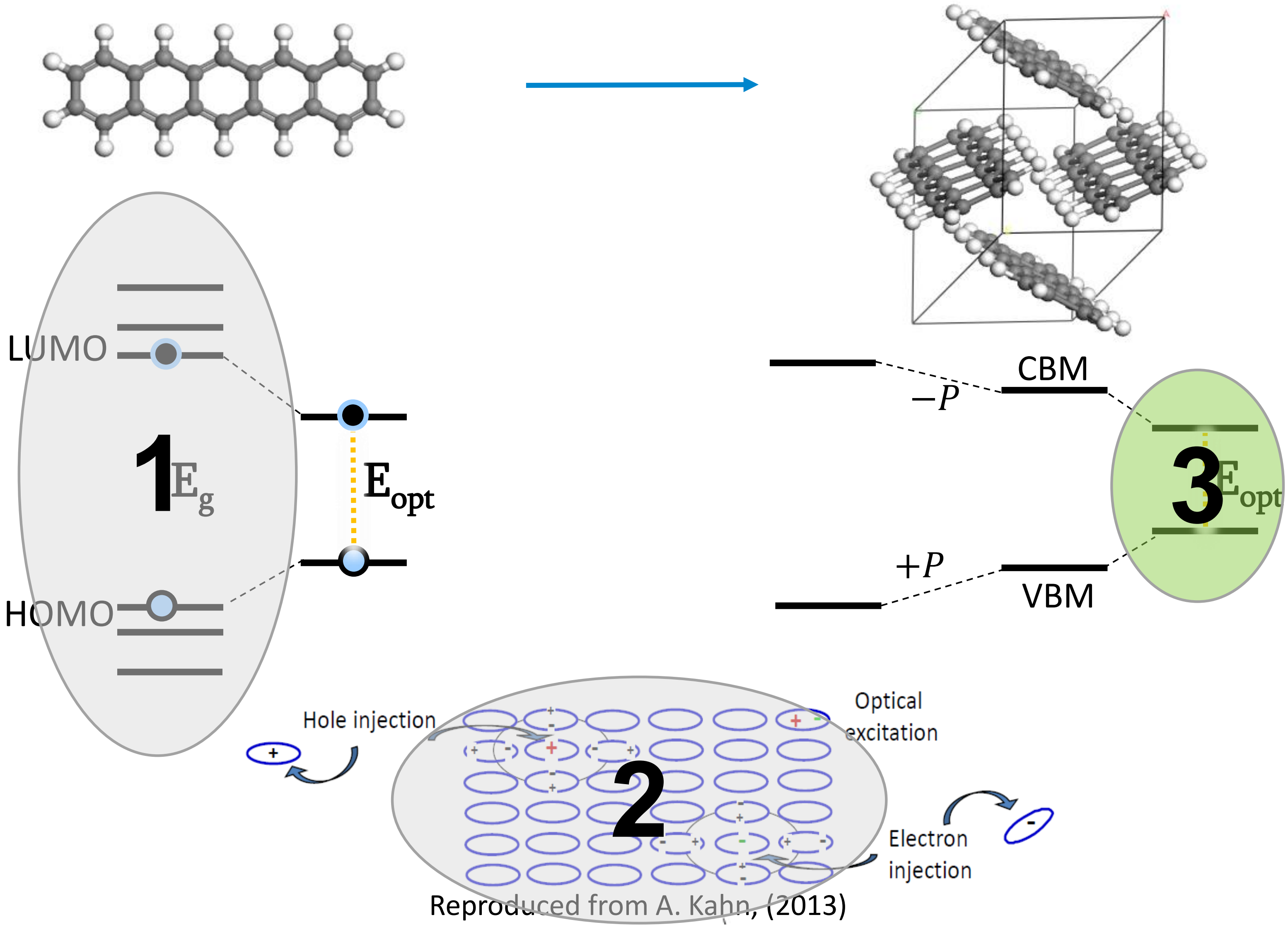
Excitations from TDDFT



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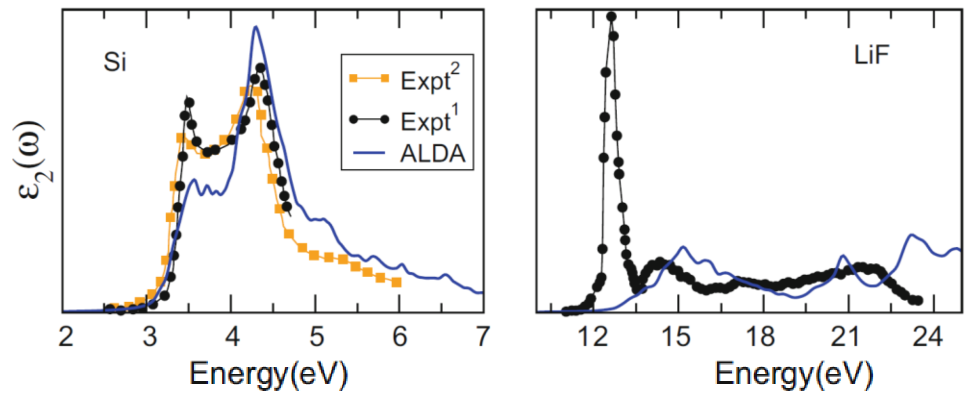
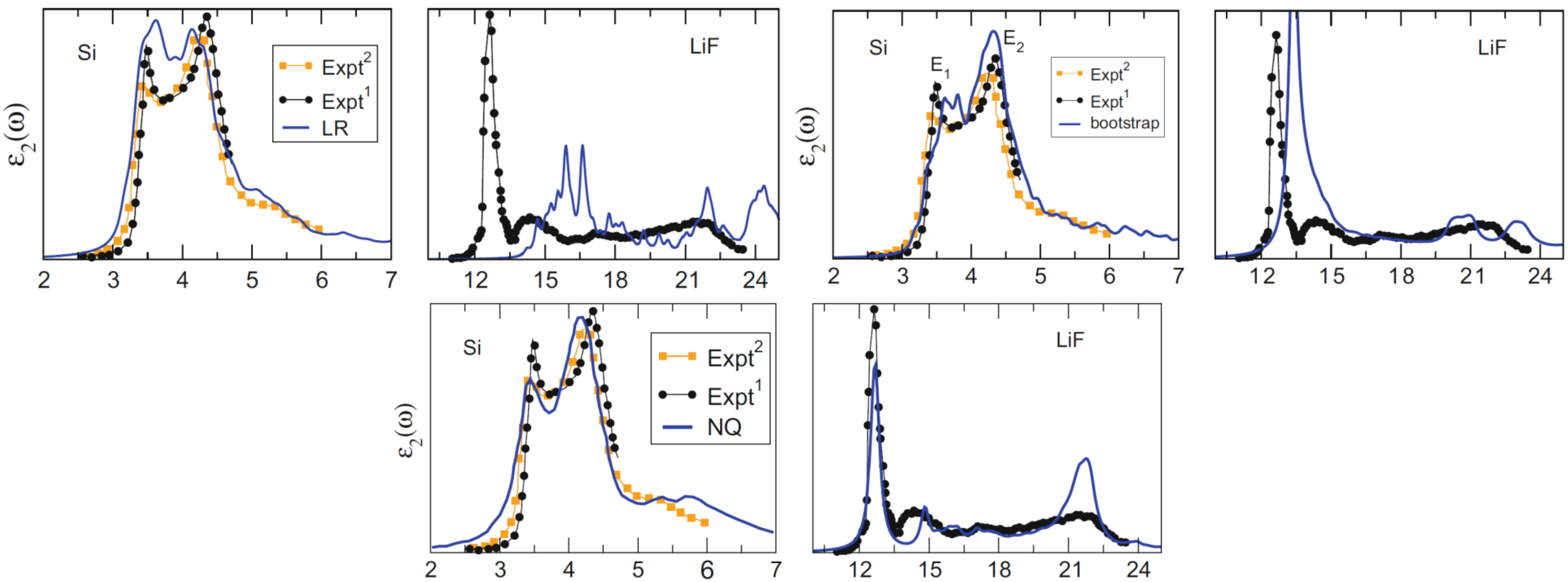
Solid state – other systems

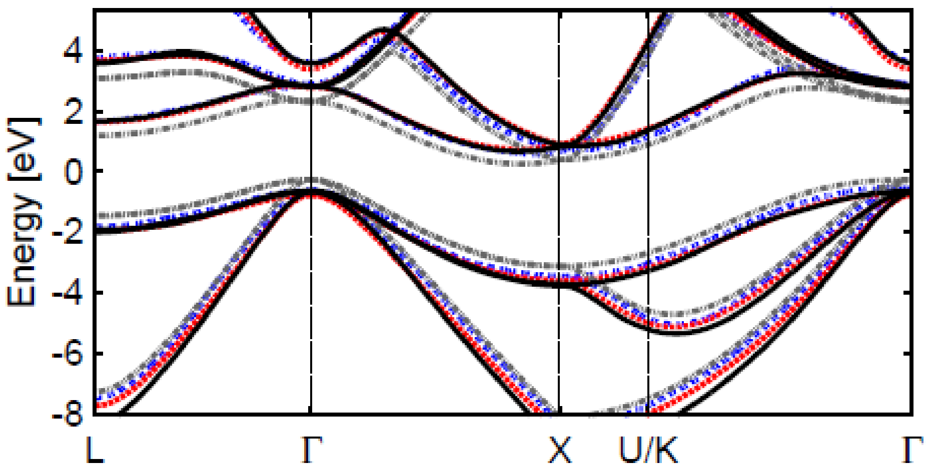


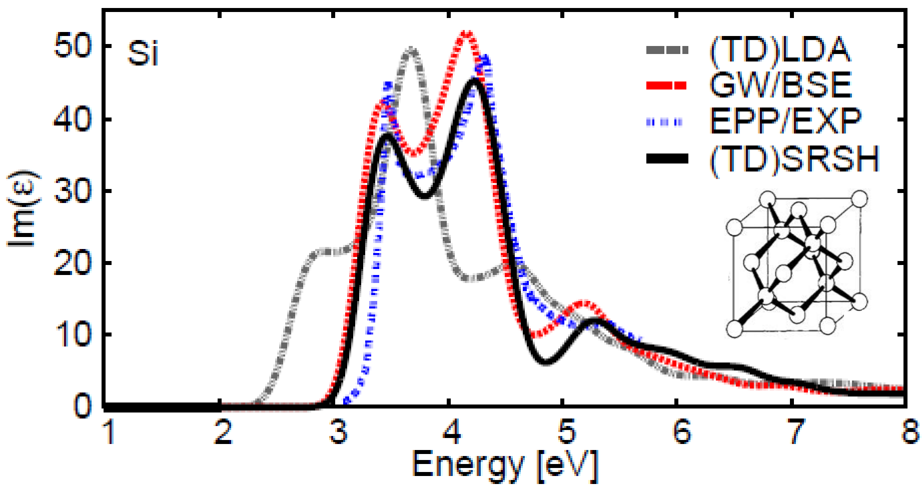
f_{xc} is missing a $1/q^2$ conribution



S. Sharma, J. K. Dewhurst, and E. K. U. Gross, Top. Curr. Chem. 347 **(2014)**

Solid state – other systems

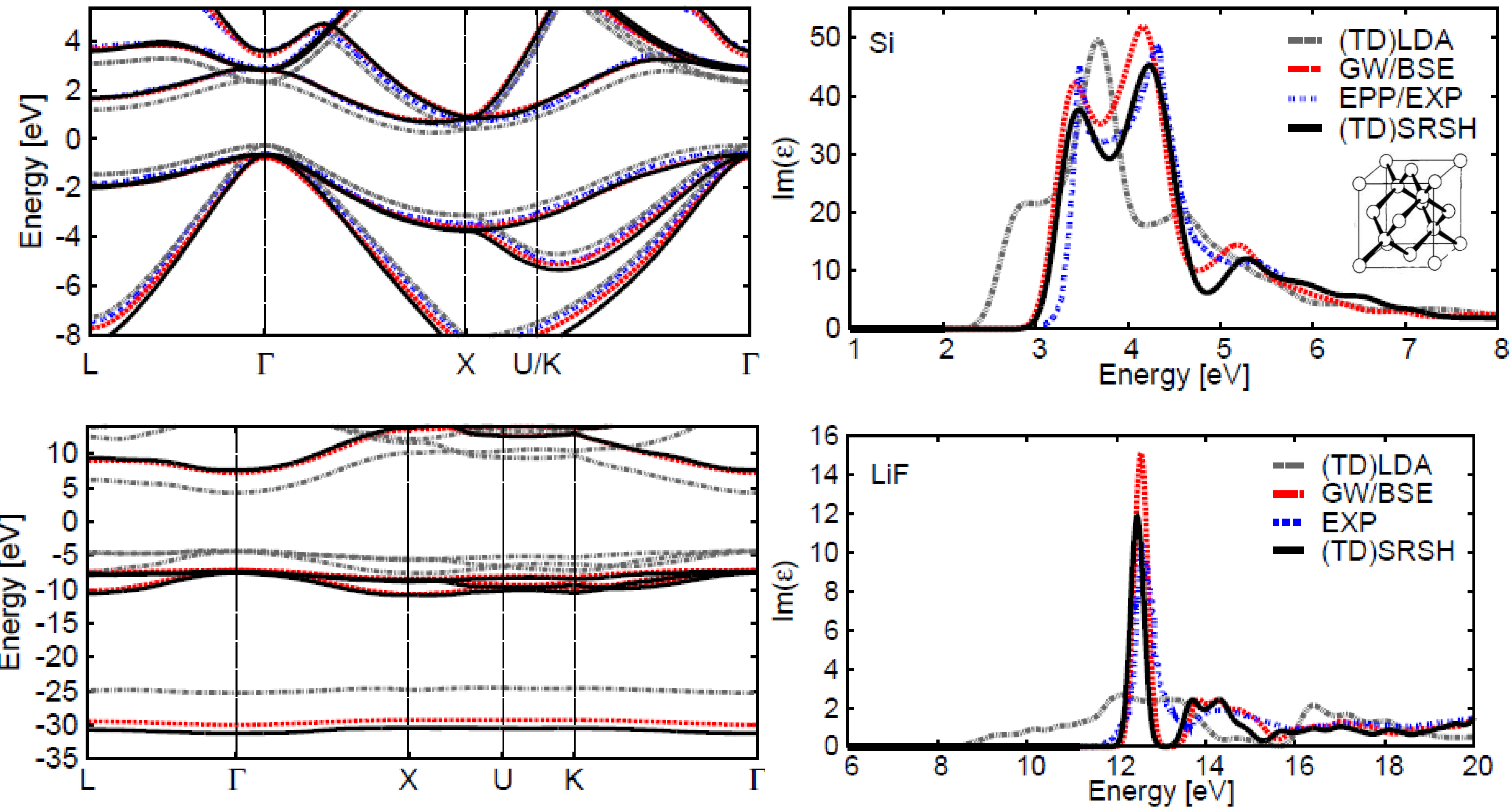




Parameter Setting

SRA, M. Jain, S. Sharifzadeh, J. B. Neaton and L. Kronik PRB 92, 081204(R) (2015)

Solid state – other systems



SRA, M. Jain, S. Sharifzadeh, J. B. Neaton and L. Kronik PRB 92, 081204(R) (2015)

Summary

1. Optimally-tuned range-separated hybrid functionals allow the prediction of accurate excitations within (TD)DFT
2. Solid-state generalization for molecular crystals, completely from first-principles, results with good optical spectra
3. Generalization to other type of solids, with one adjustable parameter, appears promising.

Leeor Kronik[1] | Arun Manna[1] | Manish Jain[2] | Sahar Sharifzadeh[3] | Jeffrey Neaton[4] | Roi Baer[5]

[1]Weizmann Institute of Science, Israel
[2]Indian Institute of Science, Bangalore, India
[3]Boston University, Boston , USA
[4]Lawrence Berkeley National Lab, Berkeley, USA
[5]Hebrew University of Jerusalem, Israel

ADAMS Fellowships מלגות אדאמס

Thank you!