ABSORPTION SPECTRA FROM TDDFT: DO HYBRID FUNCTIONALS ACCOUNT FOR EXCITONIC EFFECTS?

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MOTIVATION

- Accurate calculation of optical absorption and electron energy loss spectra of **extended systems**
- Still a challenging task in solid state theory
- **Hybrid functionals** yield truly impressive band gaps
- Do hybrid functionals improve the description of the optical absorption spectra and related properties?
- Time-dependent HSE approach

OVERVIEW

- **Limitations of ab initio methods**
- **Introduction of hybrid functionals**
- **Assessment of hybrid functionals**
- **Theoretical approaches for calculating excitation spectra:**
  - MBPT (GW and the Bethe-Salpeter euqation)
  - TD-DFT
  - TD-HSE
- **TD-HSE results for Si, GaAs, C, SiC, and LiF**
  - Absorption spectra
  - Static dielectric constants

AB INITIO MODELING

- **Density functional theory (DFT)**
  - Ground state properties with good precision
  - KS-DFT is highly efficient (up to 1000 atoms possible)
- **Limitations stemming from (semi)-local density functionals LDA & GGA:**
  - Thermochemistry: up to 1 eV error
  - Structural properties: 2-3% error
  - Elastic constants: 10%
  - Strongly correlated systems (transition metal oxides)
  - Van der Waals bonding missing
  - Band gap problem
  - Description of electronic excitations

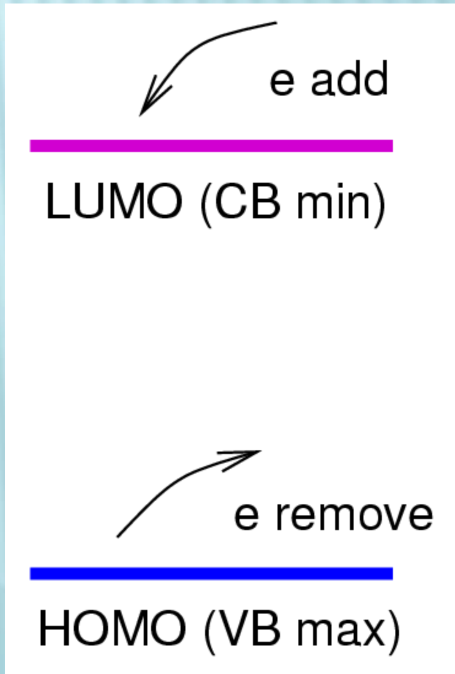
THE BAND GAP PROBLEM

- **When the Kohn-Sham (KS) eigenvalue differences are interpreted as excitation energies**
- **The band gap is a well defined ground state property**

→ **wrong using local and semi-local DFT**

- **Fundamental gap**

$$\begin{aligned} E_g &= (E[N+1]-E[N])-(E[N]-E[N-1]) \\ &= \quad -A \qquad\quad +I \\ &= \quad E_{\mathrm{CBMIN}}[N] \;\; -E_{\mathrm{VBMAX}}[N] \ldots \text{in LDA/GGA} \end{aligned}$$



→ **Large errors in LDA/GGA/HF**

- **Lack of Integer-discontinuity in the LDA/GGA/HF**

ALTERNATIVES

- **Quantum Monte Carlo**
- **Post-Hatree-Fock methods (MP2, CI, CC)**
- **Many-body perturbation theory**
  - *GW* approximation
  - Bethe-Salpeter Equation (BSE)
- **Time-dependent density functional theory**
- **Hybrid density functionals**
  - Have been verz successful in quantum chemistry for small molecules
  - E.g., polarizability and magnetic properties (NMR, etc.)

HYBRID FUNCTIONALS

- **Characterized by the admixture of a certain amount of nonlocal Fock exchange energy to a part of (semi)local density functional exchange energy.**
- **Two groups:**
  - PBE-based
    - **PBE0[1] (parameter-free)**
    - **HSE03[2] (one-parameter)**
  - B3-based[3]
    - **B3LYP**
    - **B3PW91**

    three-parameter

1. M. Ernzerhof and G. E. Scuseria, J. Chem. Phys. **110**, 5029 (1999).
2. J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003).
3. A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

PERDEW-BURKE-ERNZERHOF HYBRID: PBE0[1,2]

- Fraction of ¼ non-local Fock exchange rationalized by the adiabatic connection theorem[3].
- Remainder of ¾ is PBE exchange.
- PBE correlation is straightforwardly added.

$$\boxed{E_{xc}^{\mathrm{PBE0}} = \frac{1}{4}E_{x}^{\mathrm{HF}} + \frac{3}{4}E_{x}^{\mathrm{PBE}} + E_{c}^{\mathrm{PBE}}}$$

1. M. Ernzerhof and G. E. Scuseria, J. Chem. Phys. **110**, 5029 (1999).
2. C. Adamo and V. Barone, J. Chem. Phys. **110**, 6158 (1999).
3. J. P. Perdew, M. Ernzerhof, and K. Burke, J. Chem. Phys. **105**, 9982 (1996).

HEYD-SCUSERIA-ERNZERHOF HYBRID: HSE[1,2]

$$\mathrm{E}_{xc}^{\mathrm{HSE}} = \frac{1}{4}\mathrm{E}_{x}^{\mathrm{HF,SR}}(\mu) + \frac{3}{4}\mathrm{E}_{x}^{\mathrm{PBE,SR}}(\mu) + \mathrm{E}_{x}^{\mathrm{PBE,LR}}(\mu) + \mathrm{E}_{c}^{\mathrm{PBE}}$$

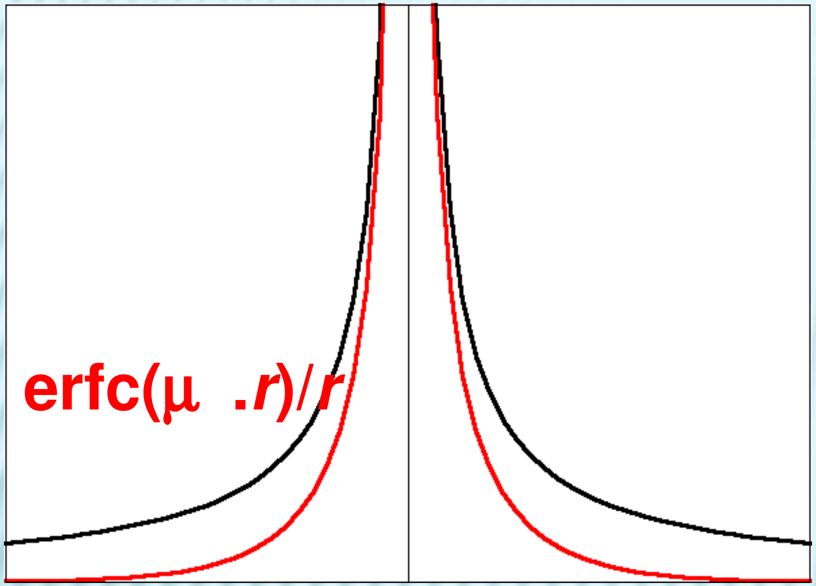
Screened Coulomb –kernel (μ= range separation)

$$\frac{1}{r} = S_{\mu}(r) + L_{\mu}(r) = \frac{\mathrm{erfc}(\mu r)}{r} + \frac{\mathrm{erf}(\mu r)}{r}$$

where $r = |r - r'|$

١. J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003).
٢. A. V. Krukau, O.A. Vydrov, A. F Izmaylov, and G.E. Scuseria, J. Chem. Phys. **125**, 224106 (2006).

COULOMB INTERACTION



$$\iint d^3 d^3 r' \frac{\phi_a^*(\mathbf{r})\phi_b(\mathbf{r})\phi_b^*(\mathbf{r}')\phi_a(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$\iint d^3 d^3 r' \frac{\phi_a^*(\mathbf{r})\phi_b(\mathbf{r})\mathrm{erfc}(\mu|\mathbf{r}-\mathbf{r}'|)\phi_b^*(\mathbf{r}')\phi_a(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Screened Coulomb kernel accelerates the convergence of two-electron integrals!

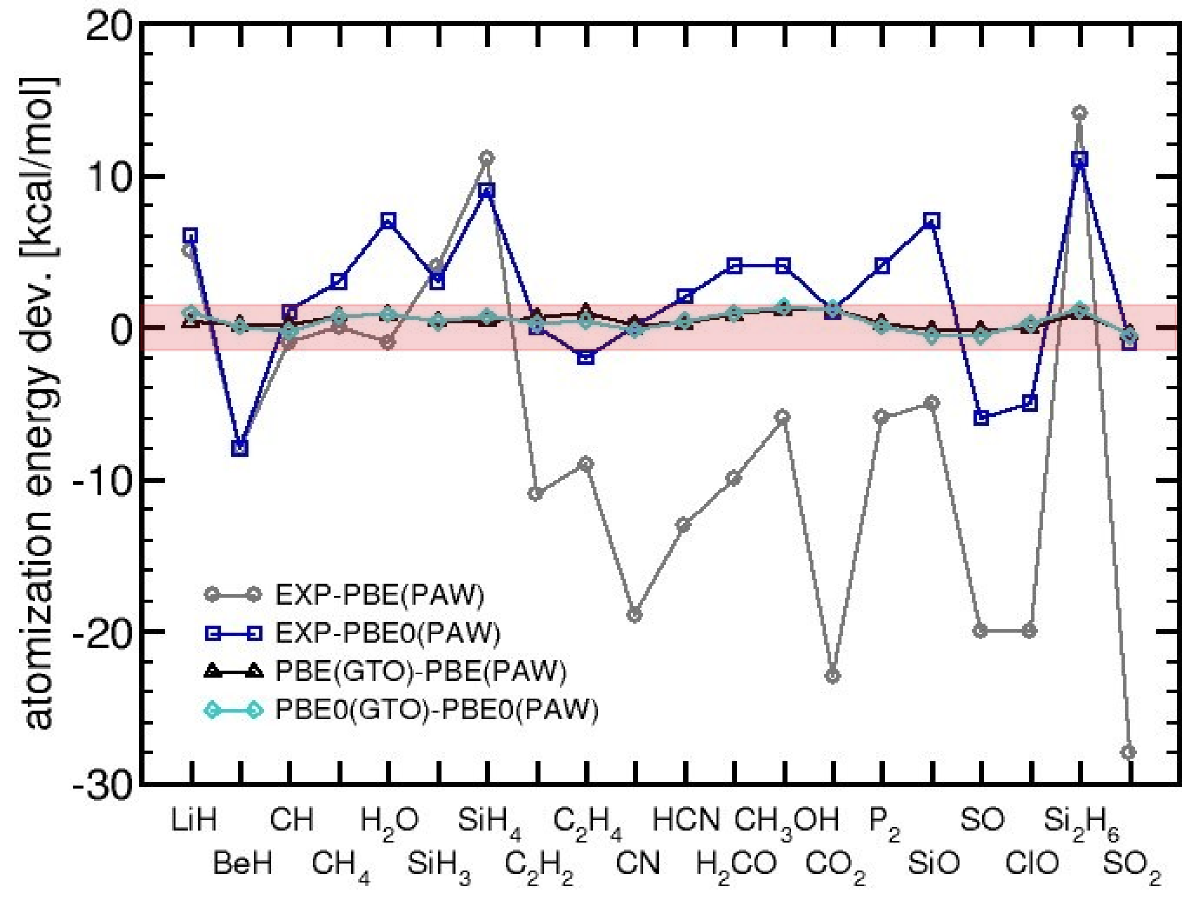
„BECKE 3-PARAMETER“ HYBRIDS: B3LYP[1]

$$E_{xc}^{\mathrm{B3LYP}} = 0.80\, E_{x}^{\mathrm{LDA}} + 0.20\, E_{x}^{\mathrm{HF}} + 0.72\, \Delta E_{x}^{\mathrm{B88}}$$
$$+ 0.81\, E_{c}^{\mathrm{LYP}} + 0.19\, E_{c}^{\mathrm{LDA}}$$

- **Favorite hybrid functional in quantum chemistry.**
- **A three parameter functional – fitted to atomization energies, ionizaton potentials, proton affinities of the G2 test set of molecules.**
- **Does not fulfill the uniform electron gas limit (failure of the LYP-correlation energy functional).**

1. P. J. Stephens, F.J. Devlin, C.F. Chabalowski, and M.J. Frisch, J. Phys. Chem. **98**, 11623 (1994).

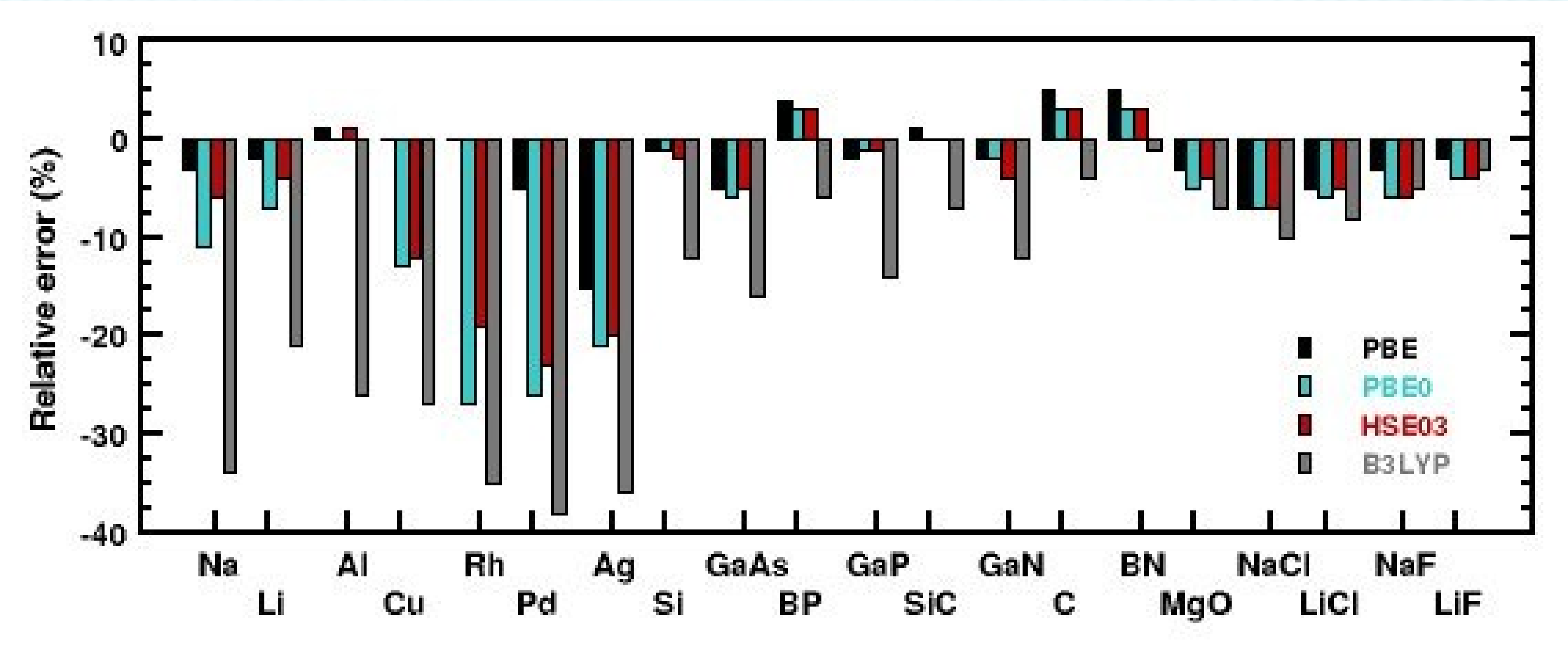
ASSESSMENT OF HYBRIDS: ATOMIZATION ENERGIES OF MOLECULES[1,2]



- Agreement between PAW and GTO calc. for both, PBE and PBE0 is excellent: difference < 1.5 kcal/mol.
- Compared to EXPT.:
  PBE: MAE =8.6 kcal/mol
  PBE0: MAE=3.7 kcal/mol

1. M.Ernzerhof and J.P. Perdew, J. Chem. Phys. **110**, 5029 (1999).
2. J. Paier *et al.*, J. Chem. Phys. **122**, 234102 (2005).

ASSESSMENTS HYBRIDS: ATOMIZATION ENERGIES OF SOLIDS[1,2]

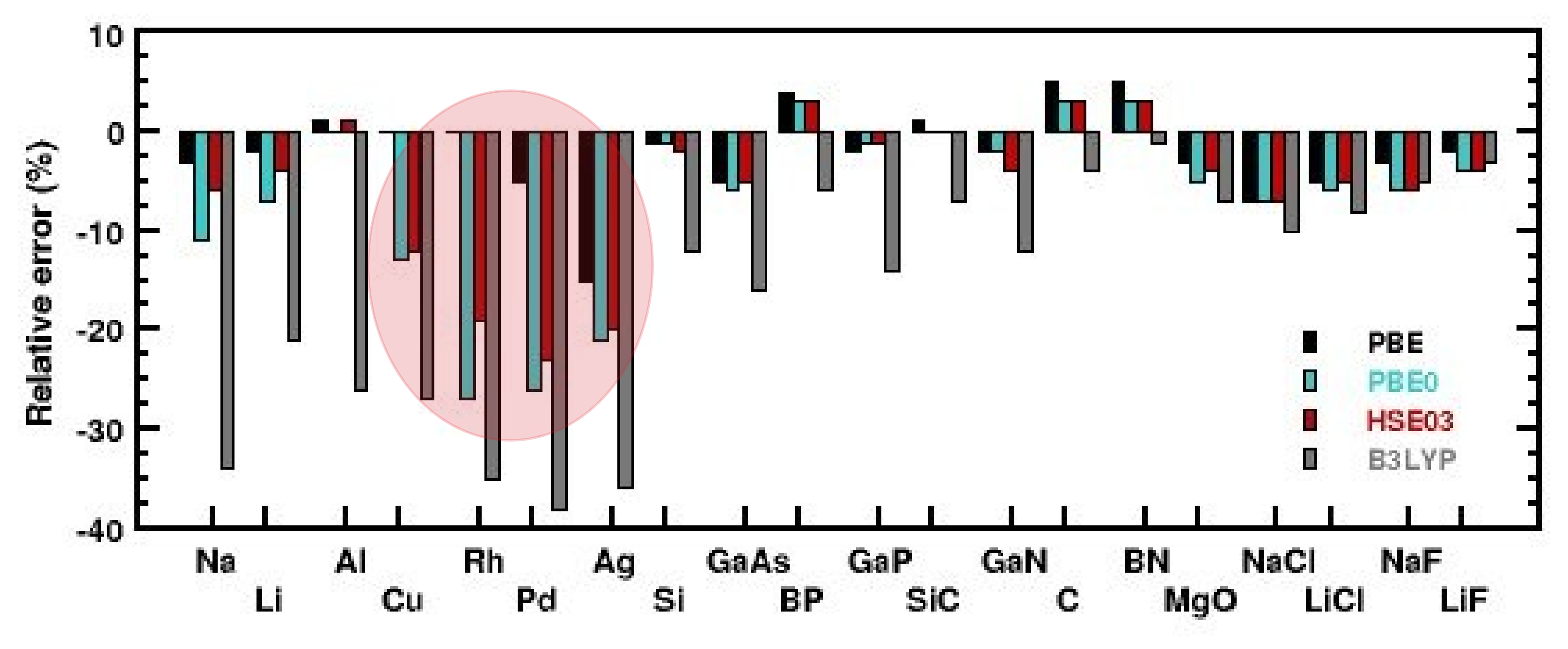


- PBE outperforms HF/DFT hybrid functionals!
- MARE of 3.4% (PBE) compared to 7.4% (PBE0), 6.3% (HSE), and 17.6% (B3LYP).

1. J. Paier *et al.*, J. Chem. Phys. **124**, 154709 (2006).
2. J. Paier, M. Marsman, and G. Kresse J. Chem. Phys. **127**, 24103 (2007).

ATOMIZATION ENERGIES OF SOLIDS

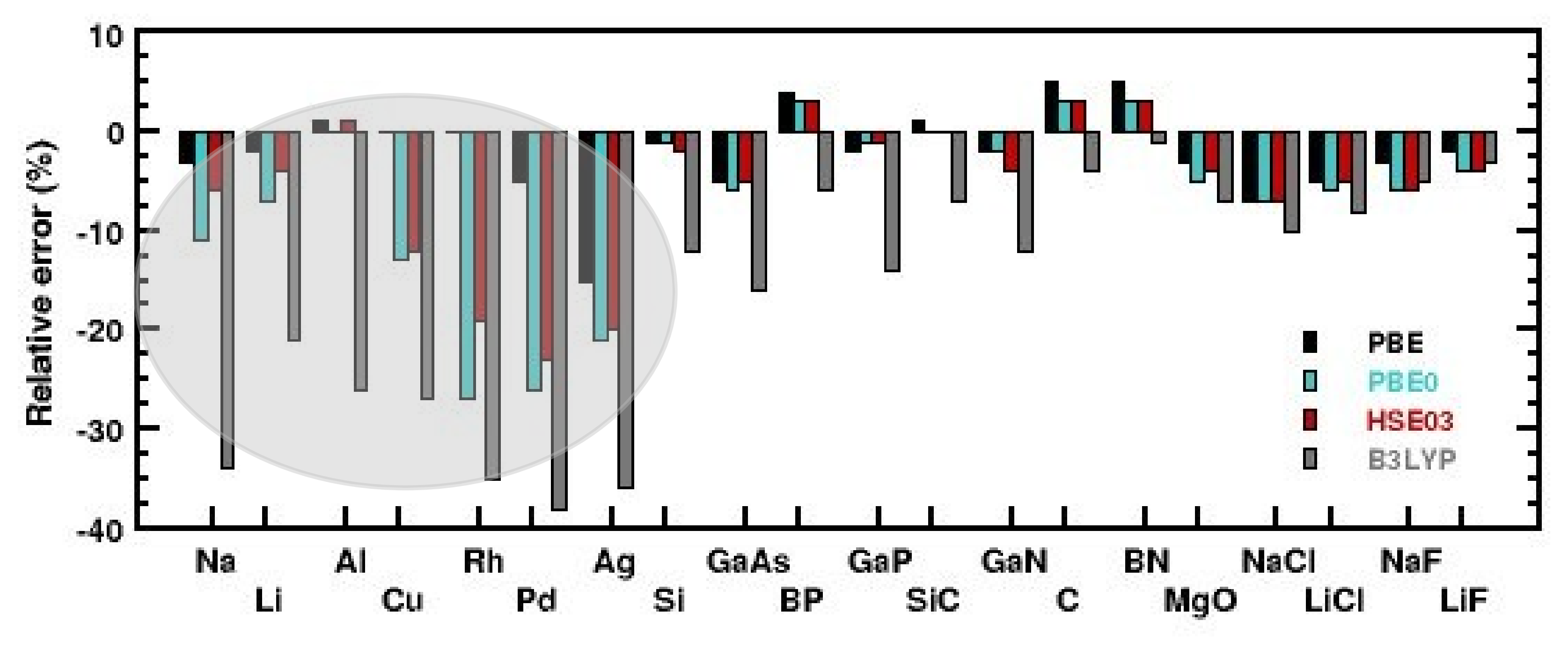
Increasing band gaps



HF exchange causes an overestimation of the exchange splitting in d elements → increase in spin-polarization energy → underestimation of the atomization energy

ATOMIZATION ENERGIES OF SOLIDS

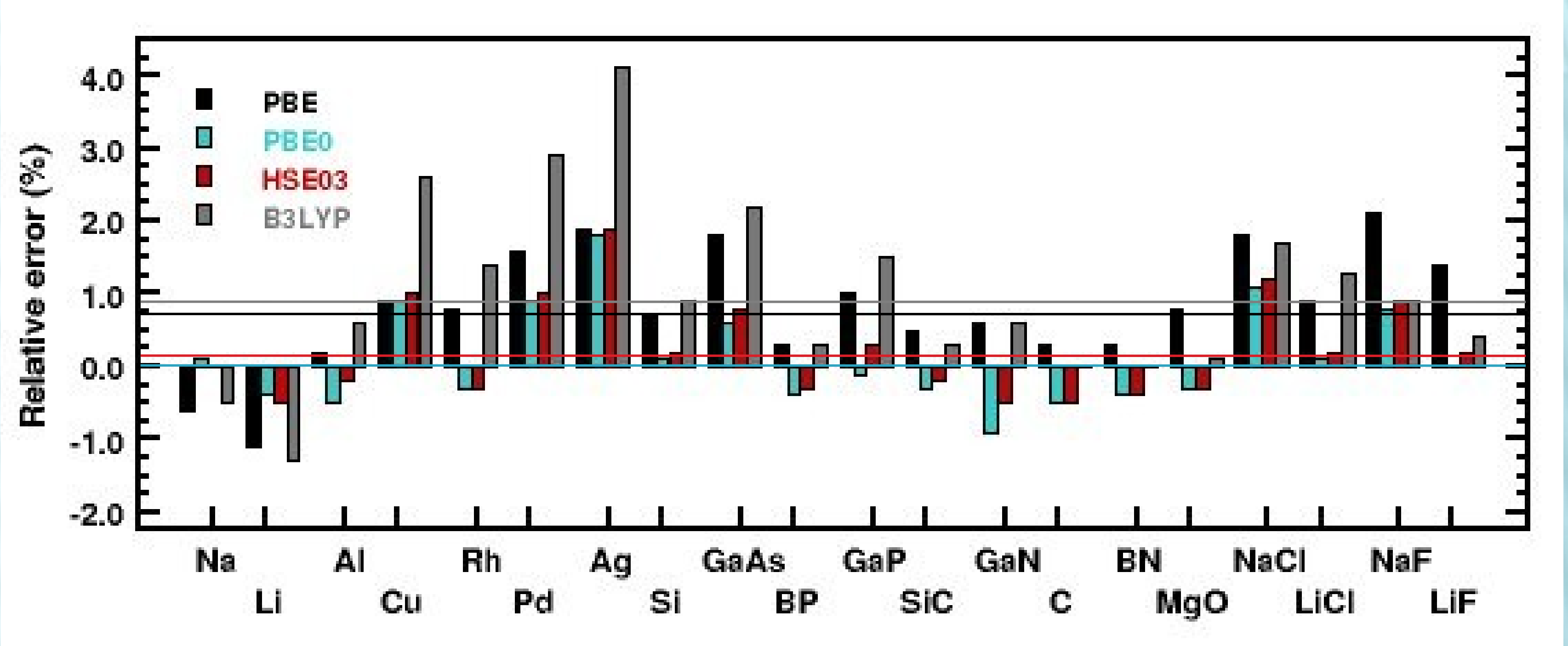
Increasing itinerant character



B3LYP performs badly for all metals

- → 2/3 are related to the LYP correlation energy
- → 1/3 due to the choice of the three parameters

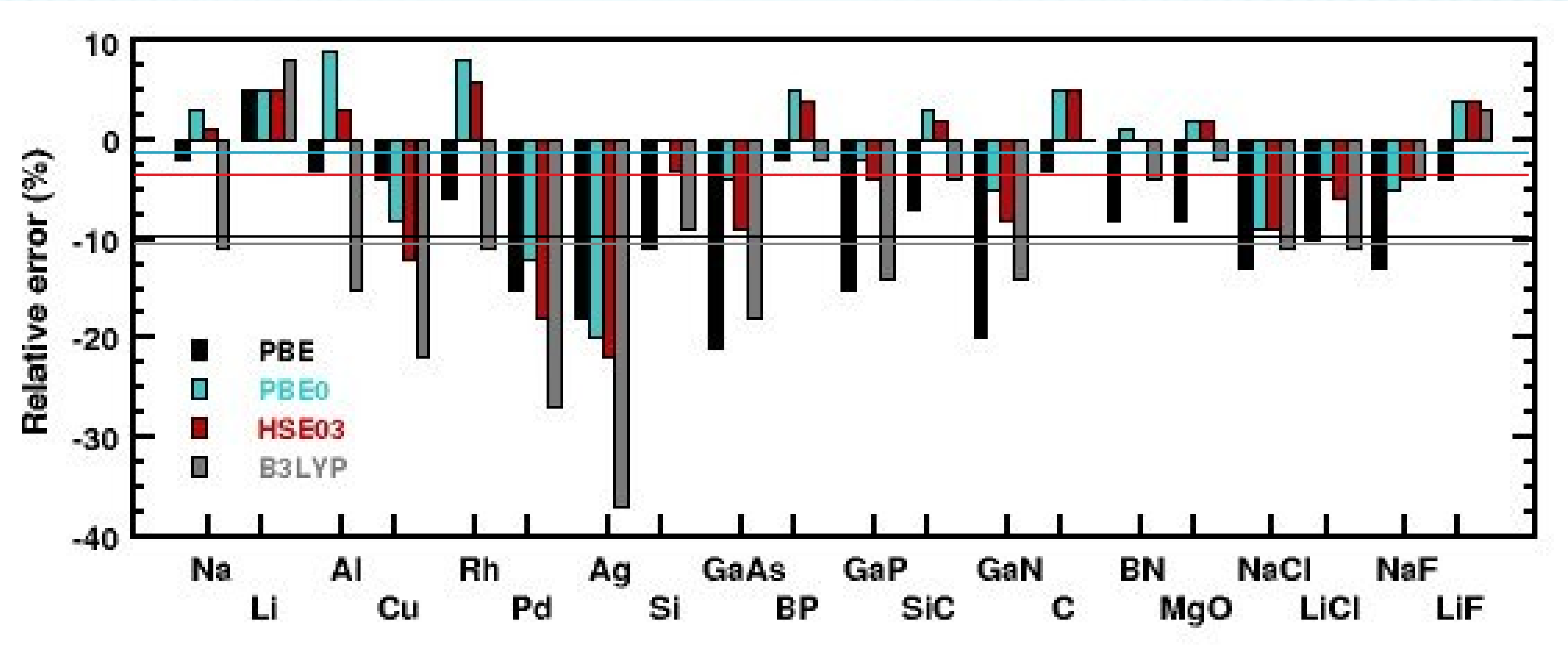
ASSESSMENTS HYBRIDS: LATTICE CONSTANTS[1]



- Overall agreement between PBE and experiment is satisfactory
- PBE0 and HSE significantly improve upon PBE
- B3LYP performs equally well as PBE, except for d metals

1. M. Marsman *et al.*, J. Phys.: Condens. Matter **20**, 64201 (2008).

ASSESSMENTS HYBRIDS: BULK MODULI[1]



- Very sensitive to the calculated equilibrium volume
- Underestimation of bulk moduli due to overestimation of the lattice constants.
- Best description by PBE0 closely followed by HSE

1. M. Marsman *et al.*, J. Phys.: Condens. Matter **20**, 64201 (2008).

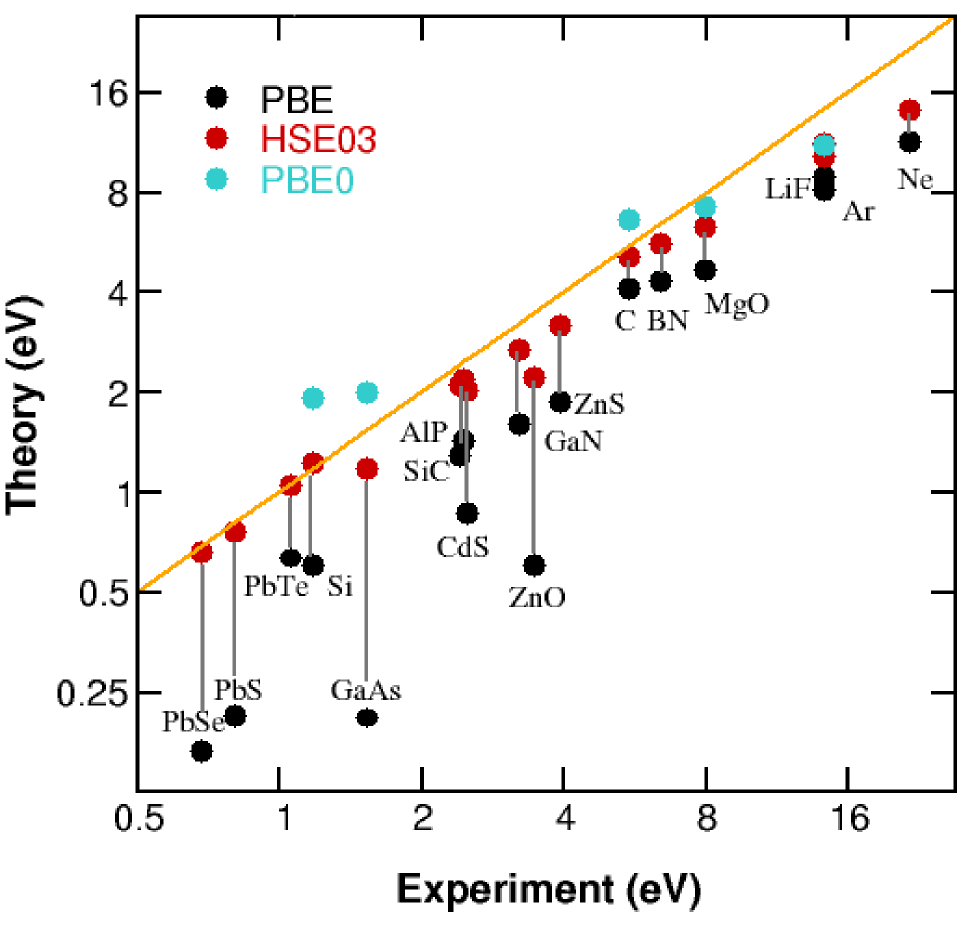
ASSESSMENTS HYBRIDS: TMOs[1]

		LDA	HSE	B3LYP	EXPT.
MnO	a_o	4.31	4.44	4.50	4.45
	M_s	4.14	4.52	4.73	4.58
	E_g	0.4	2.8	3.92	3.9
FeO	a_o	4.17	4.33	4.37	4.33
	M_s	3.26	3.63		3.32/4.2
	E_g	0	2.2	3.7	2.4
CoO	a_o	4.10	4.26	4.32	4.25
	M_s	2.23	2.67	2.69	3.35/4.0
	E_g	0	3.4	3.63	2.5
NiO	a_o	4.06	4.18	4.23	4.17
	M_s	1.06	1.65	1.67	1.64
	E_g	0.4	4.2	4.10	4.0

- Hybrids substantially improve upon LDA
- HSE latt. const. and local spin mag. moments are excellent
- CoO: much too small M_s due to neglect of SOC (no contribution from the orbital moment)

1. M. Marsman *et al.*, J. Phys.: Condens. Matter **20**, 64201 (2008).

ASSESSMENTS HYBRIDS: BAND GAPS[1,2]



- Usual underestimation by PBE
- PBE0 and HSE yield improved band gaps
- HSE performs best for small- to medium-gap systems
- In large-gap systems (week dielectric screening) 25% of HF exchange is not enough!

١. J. Paier *et al.*, J. Chem. Phys. **124**, 154709 (2006).
٢. M. Marsman *et al.*, J. Phys.: Condens. Matter **20**, 64201 (2008).

ASSESSMENTS HYBRIDS: CONCLUSIONS

- **HSE:**
  - Lattice constans & bulk moduli are clearly improved for insulators and semiconductors.
  - Band gaps are excellent for wide range of semiconductors, except for very large gap systems.
  - Transition metals are problematic, at least in terms of bulk moduli.
  - Atomization energies not improved compared to PBE.
- **B3LYP:**
  - The structural properties are slightly worse than PBE.
  - Atomization energies extremely poor for metals (HEG limit not fulfilled!)

MANY-BODY PERTURBATION TECHNIQUES[1]

- **Hedin‘s equations:**

$$\Sigma(1,2)=i\int G(1,3)\Gamma(3,2;4)W(4,1)d(3,4)$$

$$W(1,2)=v(1,2)+\int v(1,3)P(3,4)W(4,2)d(3,4)$$

$$\chi(1,2)=-i\int G(1,3)G(4,1)\Gamma(3,4;2)d(3,4)$$

$$\Gamma(1,2;3)=\delta(1,2)\delta(1,3)+\int\frac{\delta\Sigma(1,2)}{\delta G(3)}G(4,5)G(7,5)\Gamma(6,7;3)d(4,5;6,7)$$

- **Dyson equation: Links G and Σ**

$$\underset{\big\downarrow}{G}(1,2)=G_0(1,2)+\int \underset{\big\downarrow}{G_0}(1,3)\Sigma(4,3)G(4,2)d(3,4)$$

Interacting Green‘s function

motion of free electrons in the electro-static Hartree potential

1. G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002).

MANY-BODY PERTURBATION TECHNIQUES[1]

- Hedin‘s equations together with the Dyson‘s equation form a set that in principles must be solved self-consistently for G.
- Can be omitted in GW approximation: G_0W_0 and GW_0 calculations.
- GW approximation:

$$\Sigma(1,2)=iG(1,3)W(3,1)$$
$$W(1,2)=v(1,2)+\int v(1,3)P(3,4)W(4,2)d(3,4)$$
$$\chi(1,2)=-iG(1,2)G(2,1^+)$$
$$\Gamma(1,2;3)=\delta(1,2)\delta(1,3)$$

RPA for the polarization χ !

1. G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002).

THE *GW* APPROXIMATION[1]

- Vertex corrections are neglected
- Simple expression for the self-energy Σ , that allows to calculate the interacting Green's function G from an independent-particle system G_0.
- Extends the Hartree-Fock approximation by replacing the bare Coulomb v potential by the dynamically screened one W.

  $\Sigma_x = iGv \quad \longrightarrow \quad \Sigma_{GW} = iGW$
- Static approximation of the *GW* self-energy: COHSEX
  - Coulomb hole term (local): $\frac{1}{2}v(\varepsilon^{-1}-1)$
  - Screened exchange term: $W(\mathbf{r},\mathbf{r}') = \varepsilon^{-1}v$

1. G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002).

GW HISTORY AND CHALLENGES:

- *GW* is a rather "old" method but computationally very demanding
- Foundation of *GW*:
  L. Hedin, Phys. Rev. **139**, A796 (1965)
- First Pseudopotential *GW* using LDA wavefunctions
  + 1st order perturbation theory using *GW*
  $G=G_{\mathrm{LDA}}$ $W = \varepsilon_{\mathrm{LDA}} v$
  M. S. Hybertsen, S. G. Louie, Phys. Rev. B **34**, 5390 (1986), Sham and Schlüter
- Efficient implementations using pseudo-potentials
  Rojas, Godby, and Needs, Phys. Rev. Lett. **74**, 1827 (1995)
- Full potential (all electron) + self-consistency
  Faleev, van Schilfgaarde, Kotani, Phys. Rev. Lett. **93**, 126406 (2004)
- Excitons taken into account for construction of *W*
  Bruneval, Sottile, Olevano, Del Sole, and Reining, Phys. Rev. Lett. **94**, 186402-1 (2005)

ONE-ELECTRON THEORIES

- **Density functional theory**

$$\left(-\frac{\hbar^2}{2\mathrm{m}_e}\Delta+V^{\mathrm{ion}}(r)+V^{\mathrm{el}}(r)+V^{\mathrm{xc}}(r)\right)\varphi_n(r)=E_n\varphi_n(r)$$

- **Hartree Fock theory**

$$\left(-\frac{\hbar^2}{2\mathrm{m}_e}\Delta+V^{\mathrm{ion}}(r)+V^{\mathrm{el}}(r)\right)\varphi_n(r)+\int V^x(r,r')\varphi_n(r')d^3r'=E_n\varphi_n(r)$$

- ***GW***

$$\left(-\frac{\hbar^2}{2\mathrm{m}_e}\Delta+V^{\mathrm{ion}}(r)+V^{\mathrm{el}}(r)\right)\varphi_n(r)+\int \Sigma^{xc}(r,r',\omega)\varphi_n(r')d^3r'd\omega=E_n\varphi_n(r)$$

GW ESSENTIALS

- **Hartree-Fock: bare nonlocal Fock exchange**

$$V^{x}(r,r') = \sum_{\mathrm{occ}} \varphi_{m}(r)\,\varphi^{\text{¿}}_{m}(r') \times -\frac{e^{2}}{|r-r'|}$$

- ***GW*: replace bare 1/|r-r'| by dynamically screened Coulomb operator**

G

$$\Sigma^{xc}(r,r',E) = \int_{-\infty}^{\infty} d\omega \sum_{\mathrm{all}} \frac{\varphi_{m}(r)\,\varphi_{m}(r')}{\omega - E - E_{m} + i\delta\,\mathrm{sgn}[E_{m} - E_{Fermi}]} \times$$

$$\text{¿}$$

$$\text{¿} - e^{2} \int d r'' \frac{\varepsilon^{-1}(r,r'',\omega)}{|r''-r'|}$$

W

$$\text{¿}$$

THE *GW* APPROXIMATION APPLIED

- **G_0W_0 calculations:**
  - Start with KS-LDA/GGA wavefunctions and eigenvalues to construct G_0
  - Determine χ^0, ε^{-1} within RPA and W_0
  - Calculate $\Sigma_{GW}=\mathrm{i}\,G_0 W_0$
  - Determine the first-order change of energies, i.e., quasi-particle energies

$$\langle \varphi_n | -\frac{\hbar^{٢}}{٢\mathrm{m}_e}\Delta + V^{\mathrm{ion}} + V^{\mathrm{el}} + \Sigma^{xc}(E_n) | \varphi_n \rangle = E_n$$

- **GW_0 calculations: partial self-consistency in G:**

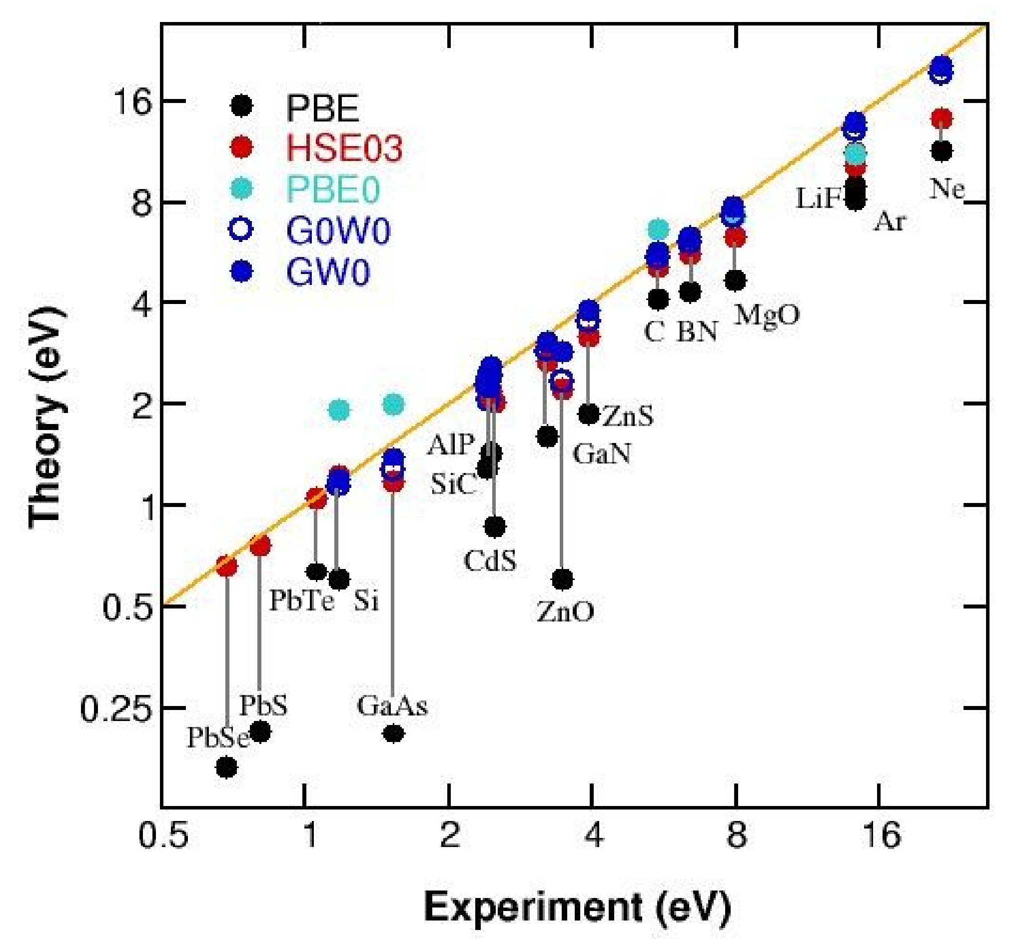
$$G(r,r')=\sum_m \frac{\varphi_m(r)\,\varphi_m(r')}{\omega - E - E_m + i\delta\,\mathrm{sgn}[E_m - E_{Fermi}]}$$

W_0 is kept fixed!

- **Self-consistent GW calculations:**

Inclusion of electron-hole (e-h) attraction by to $\delta\Sigma/\delta G$

COMPARISON HSE AND *GW*: BAND GAPS[1,2]



- G_0W_0 gaps are larger than PBE ones, but consistently underestimated compared to EXPT.
- GW_0 further increases the gaps (roughly 7%)
- Throughout the series more accurate gaps than HSE
  - G_0W_0 MARE: 8.5%
  - GW_0 MARE: 4.5%
  - HSE MARE: 21%

1. M. Shishkin and G. Kresse, Phys. Rev. B 75, 235102 (2007).
2. M. Shishkin, M. Marsman, and G. Kresse, Phys. Rev. Lett. 99, 246403 (2007).

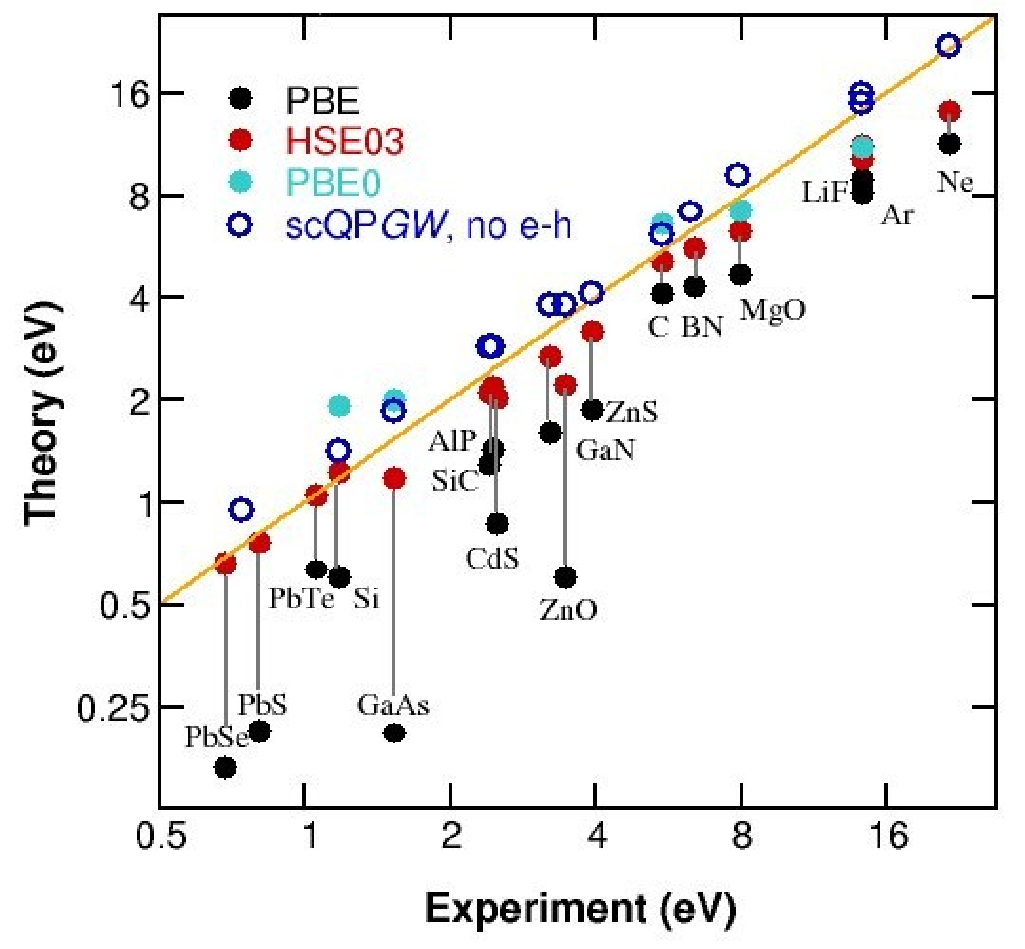
WHY IS THIS NOT GOOD ENOUGH?

- **Screening properties are calculated using density functional theory**
  - In some cases DFT is utterly wrong

ZnO: $\varepsilon_{\mathrm{DFT}} \approx 5.2$ $\varepsilon_{\mathrm{EXP}} \approx 3.5$

- **Wavefunctions are from density functional theory**
  - DFT always yields too weak localization due to Coulomb selfinteraction
    (electrons experience their own electrostatic potential)
  - Not able to predict localization versus dislocalization
  - Much too shallow d states in ZnO and GaAs with wrong hybridization between d states and conduction band electrons

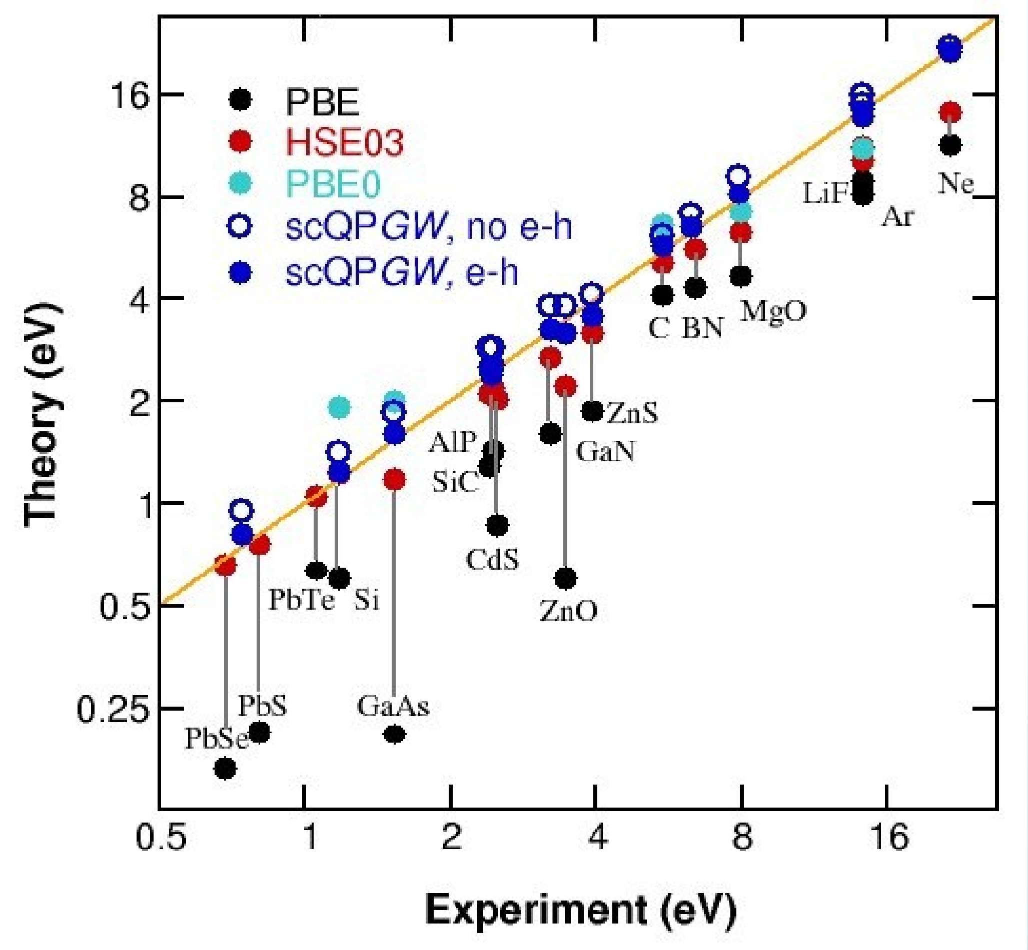
SELF-CONSISTENT QP*GW* BAND GAPS[1,2]



- scQP*GW*(no e-h): Significant overestimation
- Much worse than GW_0
- Static dielectric constants are now 20% too small
- Inclusion of vertex corrections (electron-hole interaction) in W required

١. M. Shishkin and G. Kresse, Phys. Rev. B 75, 235102 (2007).
٢. M. Shishkin, M. Marsman, and G. Kresse, Phys. Rev. Lett. 99, 246403 (2007).

SELF-CONSISTENT QP$GW^{\mathrm{TC\text{-}TC}}$ BAND GAPS[1,2]

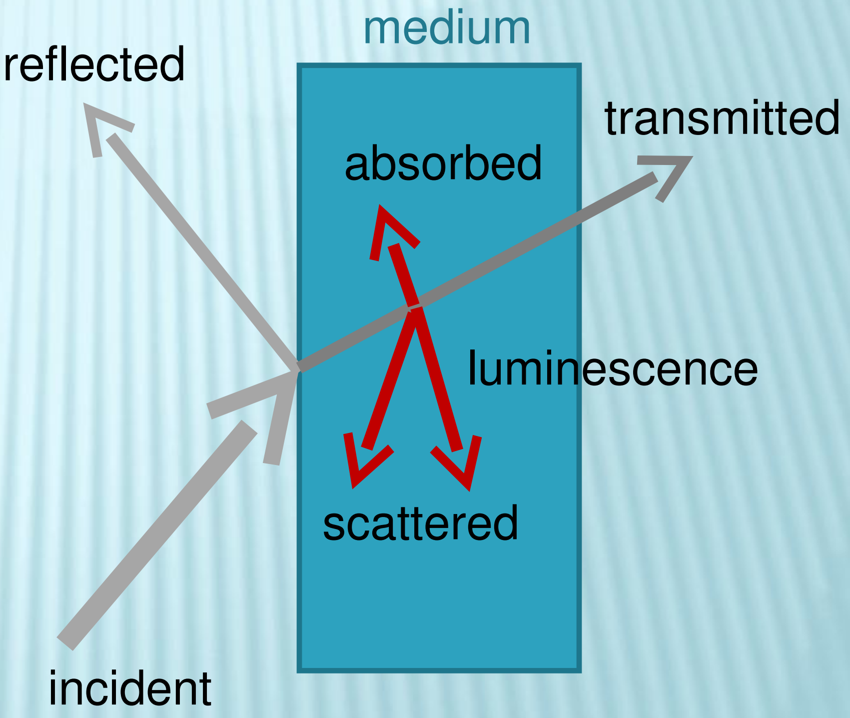


- scQP*GW*(with e-h): excellent results across all materials MARE: 3.5%
- Further slight improvement over GW_0
- Too expensive for large scale applications, but fundamentally important

1. M. Shishkin and G. Kresse, Phys. Rev. B 75, 235102 (2007).
2. M. Shishkin, M. Marsman, and G. Kresse, Phys. Rev. Lett. 99, 246403 (2007).

OPTICAL PROPERTIES OF SOLIDS

- **Linear Response Theory[1,2]:**
  - Field strength of the incident radiation is weak
  - The induced polarization is linearly dependent on the electric field
  - Linear response functions $\chi(\omega)$ and $\varepsilon(\omega)$ describe the linear responses of a medium to an external field



1. S. L. Adler, Phys. Rev. **126**, 413 (1962).
2. N. Wiser, Phys. Rev. **129**, 62 (1963).

DIELECTRIC MATRIX

- **Random phase approximation (RPA)[1]:**
  - electrons and holes move independently in a self-consistent potential: $V_{tot}(r,t)=V_{ext}(r,t)+V_{ind}(r,t)$
  - Exchange and correlation effects on the response are neglected
  - Polarizability χ_0 directly yields the dielectric matrix ε :

$$V_{tot}(r)=\int dr'\,\varepsilon^{-1}(r,r')\,V_{ext}(r')$$

with

$$\varepsilon_{RPA}=1-v\chi_0$$

- **Dielectric response within DFT[2]:**

$$V_{tot}=V_{ext}+V_{ind}+V_{XC} \Rightarrow \varepsilon_{LDA}=1-v\chi_0(1-f_{XC}\chi_0)^{-1}$$

1. H. Ehrenreich and M. H. Cohen, Phys. Rev. **115**, 786 (1959).
2. S. Baroni and R. Resta, Phys. Rev. B **33**, 7017 (1986).

DIELECTRIC MATRIX

- **Irreducible polarizability matrix:**

$$\chi^0_{G,G'}(q,\omega)=\frac{1}{\Omega}\sum_{n,n',k}2w_k\left(f_{n',k+q}-f_{n,k}\right)\times\frac{\langle\psi_{n',k+q}|e^{i(q+G)r}|\psi_{n,k}\rangle\langle\psi_{n,k}|e^{-i(q+G')r'}|\psi_{n',k+q}\rangle}{E_{n',k+q}-E_{n,k}-\omega-i\eta}$$

- **Microscopic dielectric matrix:**

$$\varepsilon_{G,G'}(q,\omega)=\delta_{G,G'}-\frac{4\pi e^2}{|G+q||G'+q|}\chi^0_{G,G'}(q,\omega)$$

- **Macroscopic dielectric matrix:**

$$\varepsilon_\infty(q,\omega)=\lim_{q\to 0}\frac{1}{\varepsilon^{-1}_{00}(q,\omega)}$$

A) Calculation of the irreducible polarizability in RPA
B) Calculation of the microscopic DM
C) Inversion of the microscopic DM

١. H. Ehrenreich and M. H. Cohen, Phys. Rev. **115**, 786 (1959).
٢. S. L. Adler, Phys. Rev. **126**, 413 (1962); N. Wiser, Phys. Rev. **129**, 62 (1963).

LOCAL FIELD EFFECTS (LFE)[1,2]

- The system is non-homogeneous on the microscopic scale (the total perturbing potential $V_{tot}(\mathbf{r},t)$ varies, since $V_{ind}(\mathbf{r},t)$ varies on the atomic scale)
- Thus: the microscopic DM is not diagonal in reciprocal space (depends explicitely on r and r‘, and not simply on |r-r‘|: $\varepsilon_{\mathrm{G,G'}}(q,\omega)=\delta_{\mathrm{G,G'}}-v(q+G')\chi^{0}_{\mathrm{G,G'}}(q,\omega)$
- Neglecting the LFE (G=G‘=0 component of χ only):

$$\varepsilon_{\infty}(q,\omega)=\lim_{q\to 0}\varepsilon_{G=0,\mathrm{G'}=0}(q,\omega)$$

No matrix inversion required!

1. S. L. Adler, Phys. Rev. **126**, 413 (1962).
2. N. Wiser, Phys. Rev. **129**, 62 (1963).

BEYOND THE RPA:

- **So far: Interaction between electrons (and holes) are lacking!**
- **Going beyond RPA allows for the inclusion of the electron-hole (e-h) interaction**
  - Many-body perturbation techniques , in particular GW in combination with the Bethe-Salpeter equation (BSE)
  - Time-dependent density functional theory (TD-DFT)
  - TD-HSE approach?

OPTICAL PROPERTIES IN MBPT: BSE[1]

- Green‘s function theory to study two-particle excited states (e-h pairs)
- Key quantity is the polarizability χ , where the vertex corrections Γ (e-h attraction) is included
- BSE for the polarizability χ : $^4\chi = {}^4\chi_0 + {}^4\chi_0 K \, {}^4\chi$

with $K(1,2;3,4) = \delta(1,2)\delta(3,4)\nu(1,3) - \delta(1,3)\delta(2,4)W(1,2)$

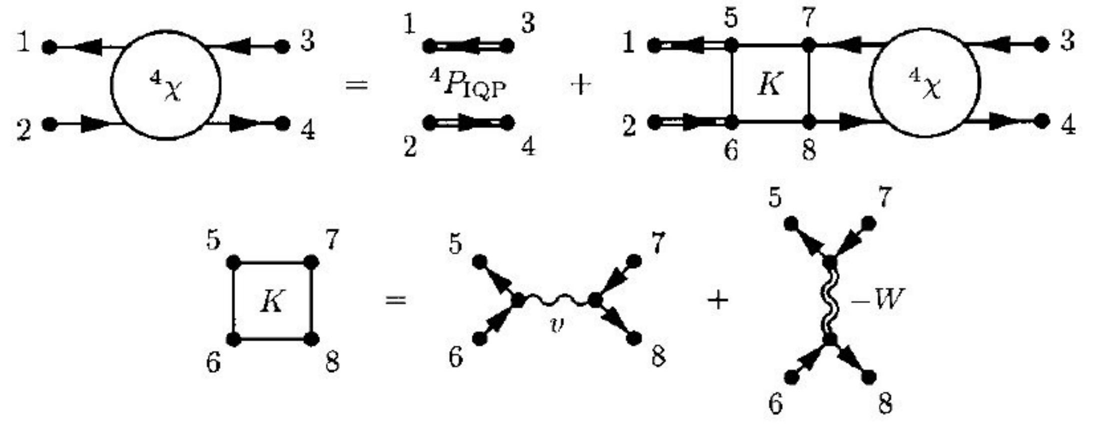
e-h exchange from the density variation of the Hartree term

e-h attraction from the variation of the self-energy

1. G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002).

THE BETHE-SALPETER EQUATION[1]

- **Four-point kernel**
- **Effective two-particle equation with an effective two-particle hamiltonian with an effective potential having**
  - local contributions that depend on the density
  - non-local contributions that are directly proportional to the density matrix ρ $(\mathbf{r},\mathbf{r}',t)$
- **BSE diagramm:**



1. G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002).

TIME-DEPENDENT DFT

- Evolution of the system under influence of a time-dependent external potential
- Runge-Gross Theorem[1]: one-one mapping between time-dependent densities and the external potentials
- Time-dependent Kohn-Sham equations[2]:

$$\left[-\frac{1}{2}\nabla^2+V_{eff}(r,t)\right]\psi_i(r,t)=i\frac{\partial}{\partial t}\psi_i(r,t)$$

$$\rho(r,t)=\sum_{i=1}^{N}|\psi_i(r,t)|^2$$

$$V_{eff}(r,t)=V_H(r,t)+V_{XC}(r,t)+V_{ext}(r,t)$$

All many-body effects are included in the time-dependent local exchange-correlation potental $V_{XC}(\mathbf{r},t)$

1. E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).
2. R. van Leeuwen, Phys. Rev. Lett. **82**, 3863 (1999).

EXCITATION ENERGIES IN TD-DFT[1]

- **Dyson-like equation** for the linear density response χ of an interacting many-electron system in terms of the non-interacting KS response χ_0
- **Only local potentials!**
  Allows to work with two-point functions.

$$\chi(r,t;r',t')=\frac{\delta\rho(r,t)}{\delta V_{ext}(r',t')}\Big|_{V_{ext}=\blacklozenge} \qquad \chi_0(r,t;r',t')=\frac{\delta\rho(r,t)}{\delta V_{eff}(r',t')}\Big|_{V_{eff}=0}$$

$$\chi(r,r'\omega)=\chi_0(r,r'\omega)+\int dr_1 dr_2 \chi_0(r,r_1,\omega)K(r_1,r_2,\omega)\chi_0(r_2,r',\omega)$$

$$K(r_1,r_2,\omega)=\frac{1}{|r_1-r_2|}+f_{XC}(r_1,r_2,\omega)$$

1. G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002).

ANALOGIES BETWEEN BSE & TD-DFT[1]

$$S = S_0 + S_0 K S$$

BSE: four-point quantities

- S = two-particle correlation function L
- $S_0 = L_0$ (indep. quasi-particle response)
- $K = \nu + F^{BSE}$
- $F^{BSE}_{(n_1 n_2)(n_3 n_4)} = -\int dr dr' \psi_{n_1}(r) \psi^{*}_{n_3}(r) \times W(r', r) \psi^{*}_{n_2}(r') \psi_{n_4}(r')$

TD-DFT: two-point quantities

- S = two-point polarizability χ $\quad \varepsilon^{-1} = 1 + \nu\chi$
- $S_0 = \chi_0$ (indep. particle response)
- $K = \nu + F^{TD\text{-}DFT}$
- $F^{TD-DFT}_{(n_1 n_2)(n_3 n_4)} = \int dr dr' \psi_{n_1}(r) \psi^{*}_{n_2}(r) \times f_{XC}(r, r') \psi^{*}_{n_3}(r') \psi_{n_4}(r')$

1. L Reining *et al.*, Phys. Rev. Lett. **88**, 66404 (2002).

HOW TO SOLVE THE DYSON EQUATION [1,2]

- Basis transformation from space to orbital space: $r \rightarrow \psi_{n,k}(r)$ *i.e.*, a **basis of pairs of occupied and empty states**
- Dyson equ. can be transformed to an effective two-particle Hamiltonian equation:

$$H^{2\mathrm{p}}_{(n_1 n_2)(n_3 n_4)} = (E_{n_2} - E_{n_1})\delta_{n_1 n_3}\delta_{n_2 n_4} + (f_{n_1} - f_{n_2}) K_{(n_1 n_2)(n_3 n_4)}$$

$$S_{(n_1 n_2)(n_3 n_4)} = \left[H^{2\mathrm{p}} - I\omega\right]^{-1}_{(n_1 n_2)(n_3 n_4)} (f_{n_4} - f_{n_3})$$

1. L. Reining *et al.*, Phys. Rev. Lett. **88**, 66404 (2002).
2. G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002).

OPTICAL SPECTRA FROM TD-DFT[1-4]

- **Including excitonic effects**
- **Without solving the BSE**
- **Response function:** $\chi=\chi_0(\chi_0-\chi_0 v\chi_0-\underbrace{\chi_0 f_{XC}\chi_0}_{T\text{-matrix}})^{-1}\chi_0$
- **For vertical transitions** vk **to** ck **(**$t=\{vck\}$**):**

$$T_{GG'}(\omega)=\underbrace{\frac{2}{N_k}\sum_t \frac{\Phi^*(t;G)\Phi(t;G')}{(E^{KS}_{ck}-E^{KS}_{vk}-\omega)^2}\left[\Delta E^{GW}_{ck}-\Delta E^{GW}_{vk}\right]}_{T_1}+\underbrace{\frac{2}{N_k^2}\sum_{tt'}\frac{\Phi^*(t;G)}{E^{KS}_{ck}-E^{KS}_{vk}-\omega}F^{BSE}_{tt'}\frac{\Phi(t';G')}{E^{KS}_{c'k'}-E^{KS}_{v'k'}-\omega}}_{T_2}$$

1. L. Reining *et al.*, Phys. Rev. Lett. **88**, 66404 (2002).
2. G. Adragna , R. Del Sole, and A. Marini, Phys. Rev. B **68**, 165108 (2003).
3. F. Sottile, V. Olevano, and L. Reining, Phys. Rev. Lett. **91**, 56402 (2003).
4. F. Bruneval *et al.*, Phys. Rev. Lett. **94**, 186402 (2005).

OPTICAL SPECTRA FROM TD-DFT[1-4]

- *T*-matrix:

$$T_{GG'}(\omega)=\underbrace{\frac{2}{N_k}\sum_t \frac{\Phi^{\text{¿}}(t;G)\Phi(t;G')}{(E_{ck}^{KS}-E_{vk}^{KS}-\omega)^2}\left[\Delta E_{ck}^{GW}-\Delta E_{vk}^{GW}\right]}_{T_1}+\underbrace{\frac{2}{N_k^2}\sum_{tt'}\frac{\Phi^{\text{¿}}(t;G)}{E_{ck}^{KS}-E_{vk}^{KS}-\omega}F_{tt'}^{BSE}\frac{\Phi(t';G')}{E_{c'\mathrm{k'}}^{KS}-E_{v'\mathrm{k'}}^{KS}-\omega}}_{T_2}$$

- Contribution T_1 acts as an effective self-energy shift
- T_2 contains the e-h contribution by the screened Coulomb interaction $W(\mathbf{r},\mathbf{r}')$:

$$F_{tt'}^{BSE}=-\int drdr'\,\Phi(vk,v'k';r)W(r',r)\Phi^{\text{¿}}(ck,c'k';r')$$

- **Inclusion of whole *T* yields spectra identical to BSE results[3]**

1. L. Reining *et al.*, Phys. Rev. Lett. **88**, 66404 (2002).
2. G. Adragna , R. Del Sole, and A. Marini, Phys. Rev. B **68**, 165108 (2003).
3. F. Sottile, V. Olevano, and L. Reining, Phys. Rev. Lett. **91**, 56402 (2003).
4. F. Bruneval *et al.*, Phys. Rev. Lett. **94**, 186402 (2005).

THE TD-HSE APPROACH[1]

- **Effective XC kernel from the frequency-dependent non-local exchange term** $f_{x\text{-}nl}$
- **Similar T-matrix:** $T=\chi_0 f_{X-nl}\chi_0$
- **The $T(\mathbf{r}',\mathbf{r})$-matrix captures the following process:**
  - Change of the external potential at $\mathbf{r}$
  - Linear response of orbitals
  - Change of the non-local exchange potential
  - Linear response of orbitals and resultant charge density change at $\mathbf{r}'$
- **Hartree potential and the local XC potential are accounted for by:** $\chi_0(\nu+f_{XC-l})\chi_0$

$$f_{XC-l}=\delta(r-r')\frac{\delta^2 E_{XC-l}[n(r)]}{\delta n(r)\delta n(r')}$$

1. J. Paier, M. Marsman, and G. Kresse, Phys. Rev. B **78**, (in press).

THE TD-HSE APPROACH APPLIED[1]

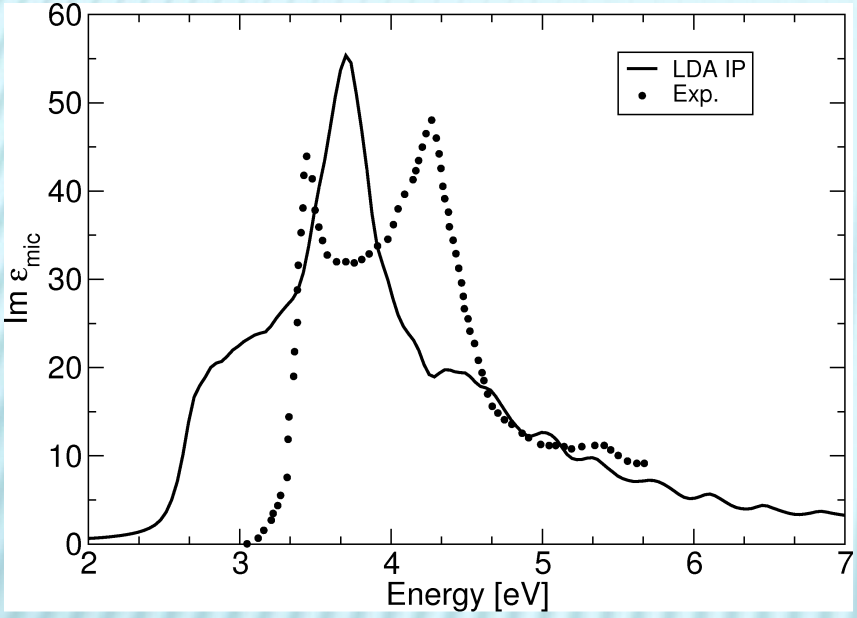
- Neglect frequency dependence of $f_{X\text{-}nl}$ and determine it only once at zero frequency
- Two-electron terms related to the coupling between resonant and antiresonant parts of the T-matrix are included
- Occupied and empty one-electron states are calculated using the HSE functional
- **Screened** Coulomb interaction $W(\mathbf{r},\mathbf{r}')$ as in BSE is replaced by ¼ of the non-local exchange term

THUS: excitonic effects can and should be approximately capured by hybrid functionals!

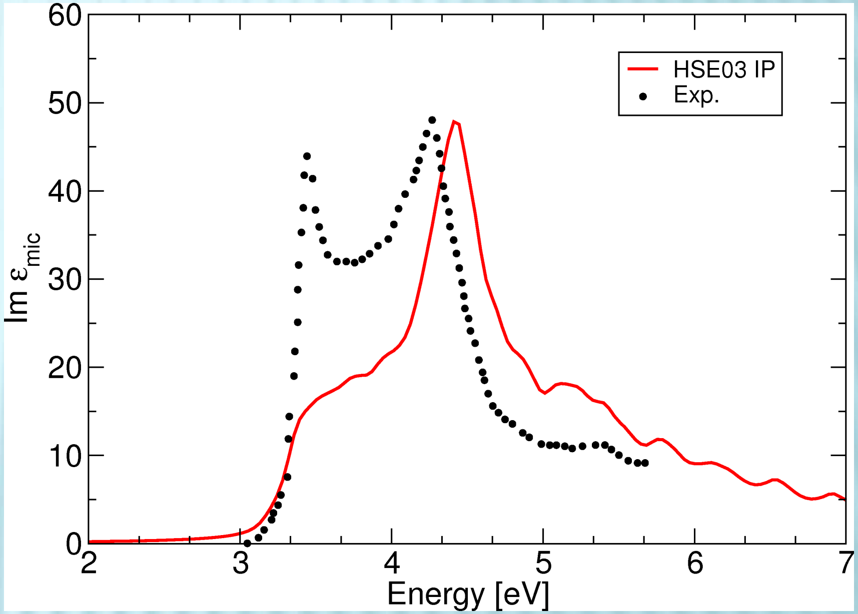
1. J. Paier, M. Marsman, and G. Kresse, Phys. Rev. B **78**, (in press).

OPTICAL ABSORPTION: BULK SILICON[1]

LDA: independent



HSE: independent



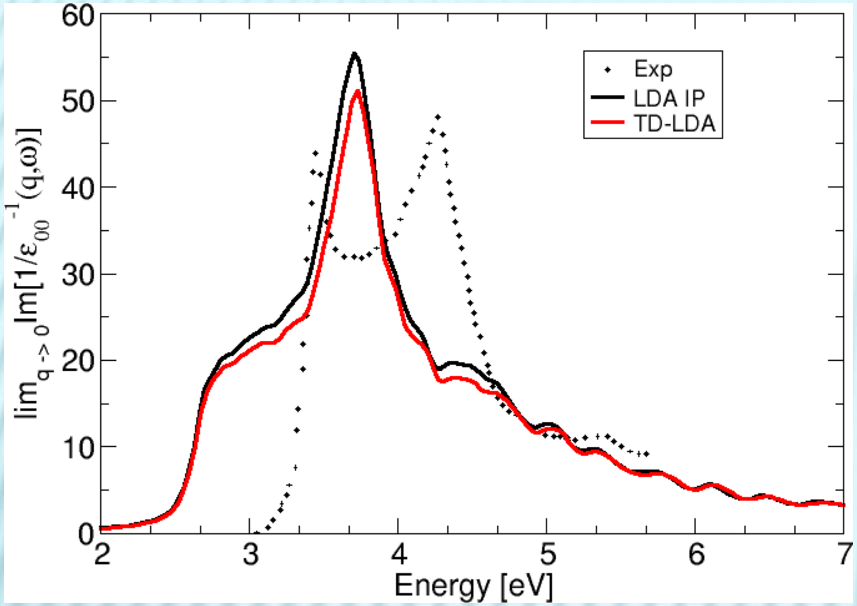
$$\varepsilon_{RPA}^{-1} = 1 + \nu\chi_0$$

Band gap opens in the case of HSE;
Similar to a scissors-corrected DFT approach!

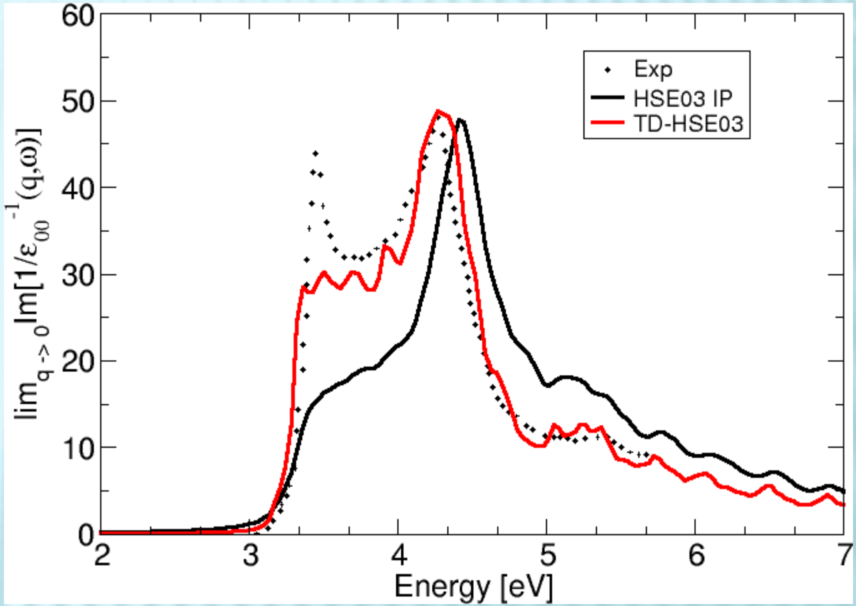
1. J. Paier, M. Marsman, and G. Kresse, Phys. Rev. B **78**, (in press).

OPTICAL ABSORPTION: BULK SILICON[1]

TD-LDA:



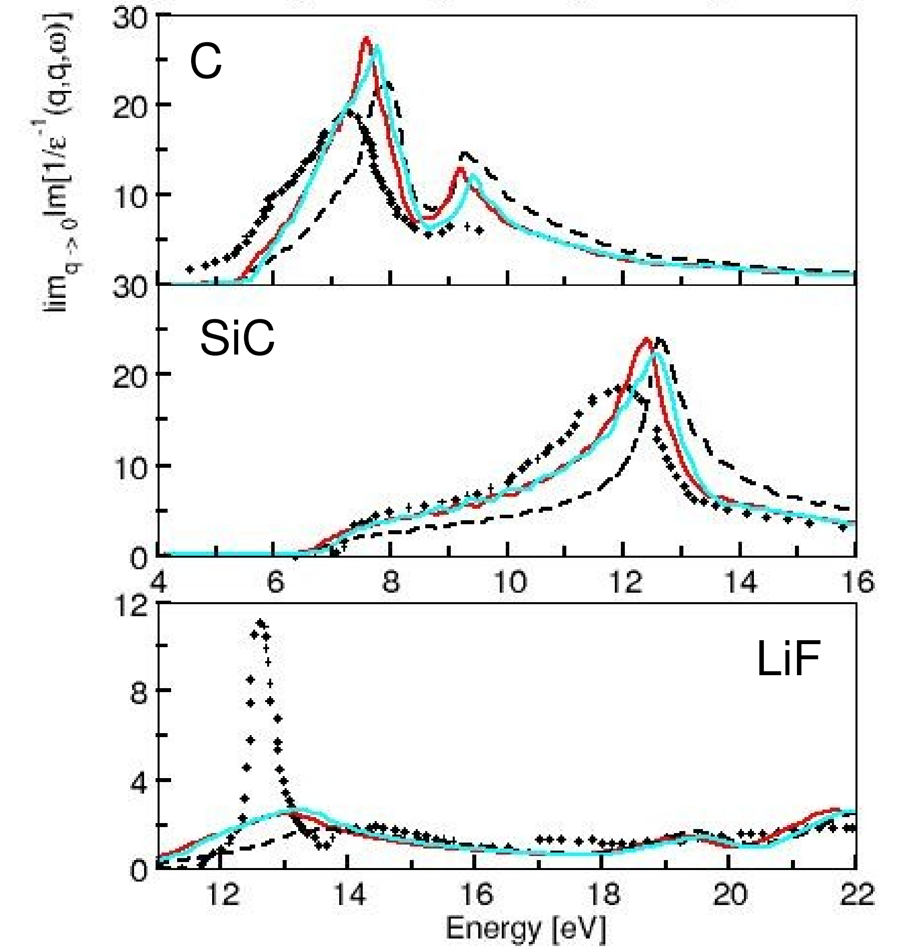
TD-HSE:

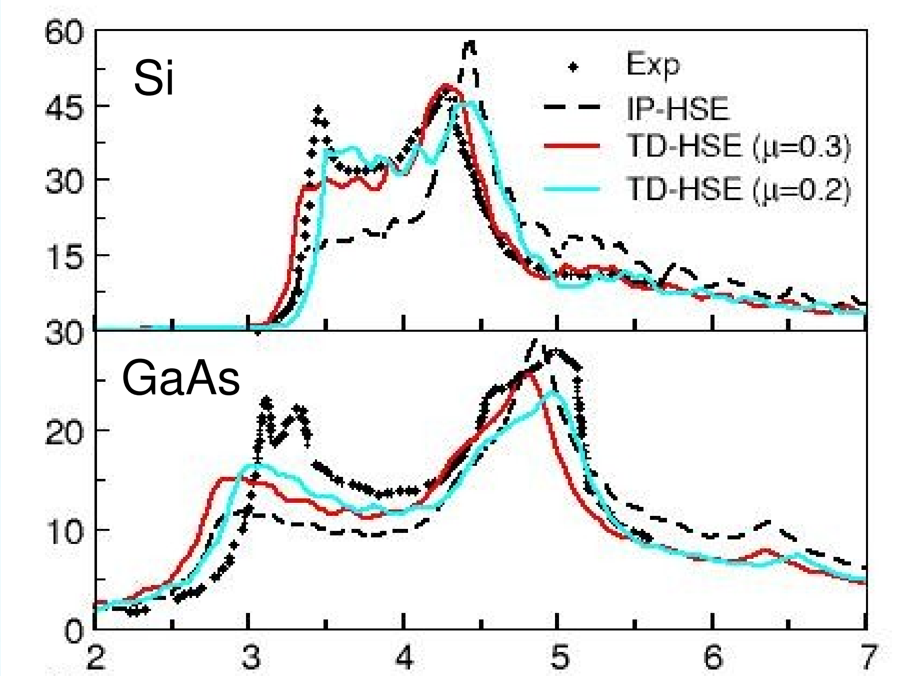


- Inclusion of the many-body effects via $f_{X\text{-}nl}$ causes a red-shift of the spectrum and a pronounced increase of the cross section at low energies.
- TD-HSE improves upon IP-HSE, but fails to describe the first exciton!

1. J. Paier, M. Marsman, and G. Kresse, Phys. Rev. B **78**, (in press).

OPTICAL ABSORPTION OF SEMICONDUTORS[1]

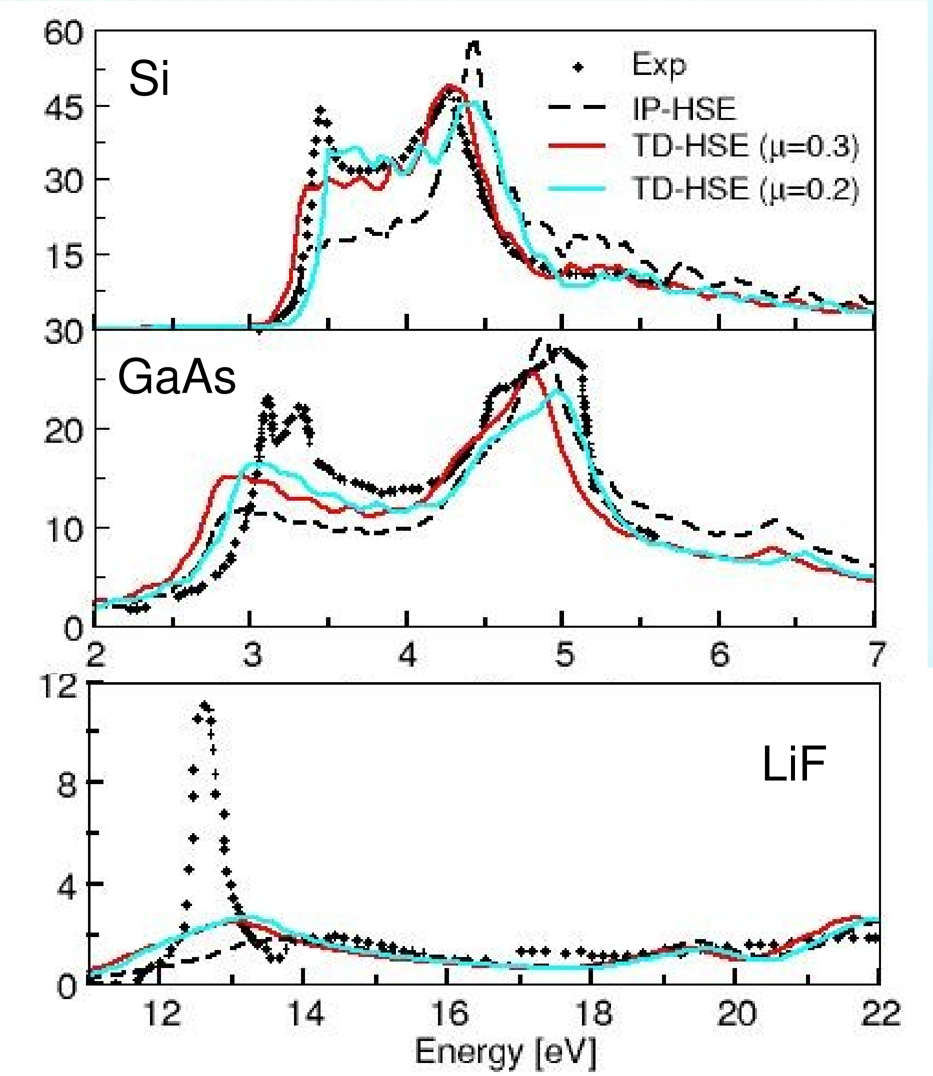




Limited interaction range of the HSE functional fails to account for all long-range excitonic effects?

١. J. Paier, M. Marsman, and G. Kresse, Phys. Rev. B **78**, (in press).

OPTICAL ABSORPTION OF SEMICONDUTORS[1]



- Reducing the range separation parameter μ means that exchange is enhanced for small $\mathbf{q}$
- This has the following effects on the spectra:
    - Slight opening of the gap resulting in a blue-shift of the absorption
    - Increase of the excitonic effects through $f_{X\text{-}nl}$
- Agreement with experiment is satisfactory!

1. J. Paier, M. Marsman, and G. Kresse, Phys. Rev. B **78**, (in press).

STATIC DIELECTRIC CONSTANTS[1]

	LDA	TD-LDA	HSE	TD-HSE	EXPT.
	ε_∞^{RPA}	ε_∞	ε_∞^{RPA}	ε_∞	
Si	14.1	13.35	10.94	11.31	11.9
GaAs	14.81	13.98	10.64	10.95	11.1
AlP	9.12	8.30	7.27	7.35	7.54
SiC	7.29	6.96	6.17	6.43	6.52
C	5.94	5.80	5.21	5.56	5.7
ZnO (*c*)	5.31	5.15	3.39	3.55	3.78
ZnO (*a*)	5.28	5.11	3.35	3.51	3.70
LiF	2.06	2.02	1.78	1.84	1.9

- LDA:overstimates the screening in RPA; REDUCTION due to inclusion of two-particle interaction (repulsive action of the Hartree kernel v).
- HSE:red-shift of the spectra and the increase of intensity at low frequencies causes an INCREASE of the static dielectric constant.

1. J. Paier, M. Marsman, and G. Kresse, Phys. Rev. B **78**, (in press).

CONCLUSIONS TD-HSE

- **Dielectric constants remain somewhat too small.**
- **Average deviation between theory and EXPT. decreases from 10% (LDA) to 3% (TD-HSE).**
- **Absorption spectra show reasonable agreement with experiment.**
- **Not as *universal* as GW/BSE ! Works best for medium-gap semiconductors .**
- **Hybrid functionals are an overall better compromise for semiconductors than purely local functionals.**

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  - Start grant bmF
  - SFB IR-ON
- **The VASP group**
  - Prof. G. Kresse
  - J. Paier
  - M. Marsman
  - J. Harl
  - M. Shishkin

ANNOUNCEMENT MORE 2008

Meeting on Optical Response of Extended systems

November 19-21 2008

Vienna, Austria

- **Scope:**
  - Bringing together experimentalists and theoreticians
  - Form a platform for leading experts to discuss and exchange their recent results and scientific concepts
- **Registration: www.physics.at**
- **deadline: October 19 2008**

- **Invited speakers:**
  - C. Ambrosch-Draxl
  - F. J. Garcia de Abajo
  - R. Gomez-Abal
  - M. Kociak
  - G. Kresse
  - A. Marini
  - L. Reining
  - A. Rubio
  - P. Schattschneider
  - W. Sigle
  - J. Verbeeck
  - W. Werner
  - P. Zeppenfeld