



Site de Grenoble
Polygone Scientifique

GDR CORREL meeting, July 07-10 2015
Location : Aix-Marseille university, France



The GW and Bethe-Salpeter Green's function formalisms
(an introduction)

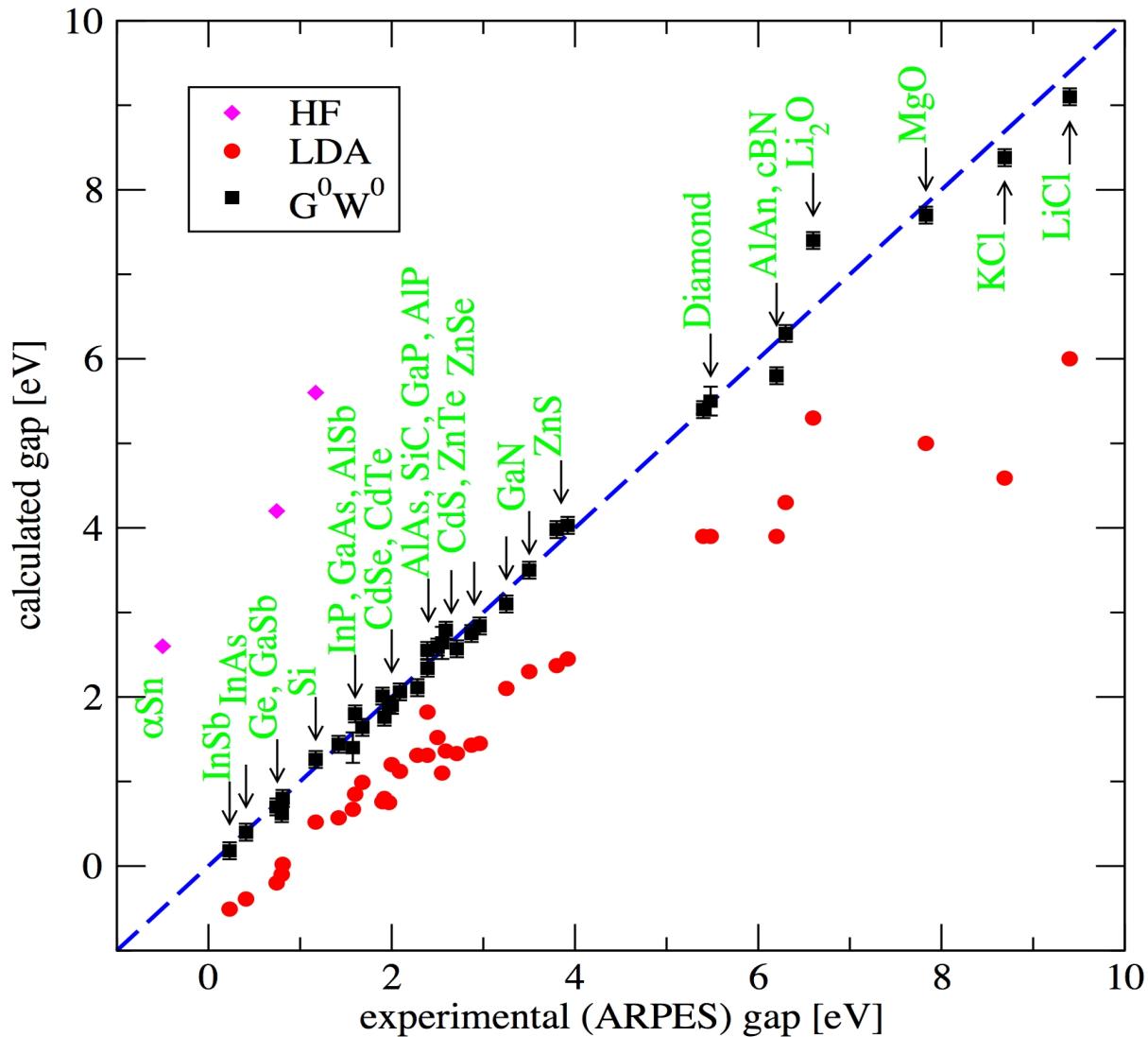
X. Blase

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To start with: the gap of semiconductors and insulators

Compiling data from the literature (courtesy V. Olévano) :



Silicon gap: 1.17 eV (Exp)

≈0.6 eV (DFT-LDA Kohn-Sham)

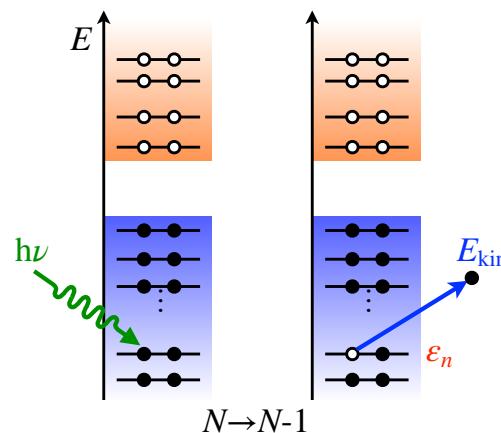
≈6 eV (HF)

Outline

The GW formalism:

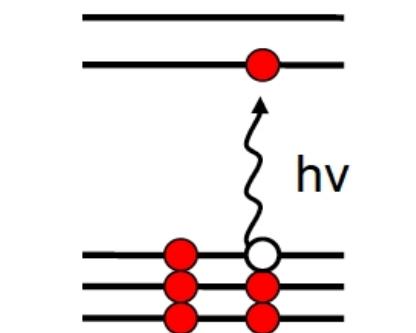
- 1) The time-ordered Green's function
- 2) Lehman representation and relation to photoemission
- 3) The Green's function equation of motion
- 4) Hedin's set of self-consistent equations
- 5) The GW approximation
- 6) Exemples

Photoemission



The Bethe-Salpeter equation:

- 1) The Bethe-Salpeter equation (BSE)
- 2) Charge-transfer excitations
- 3) Benchmark on standard organic set



Optical absorption

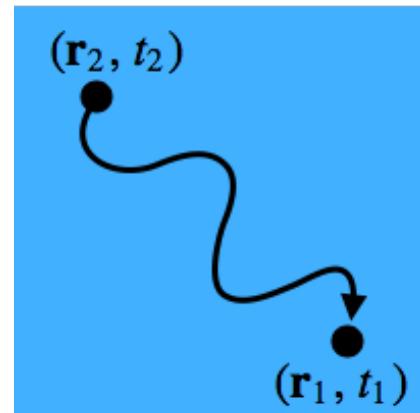
The one-particle time-ordered Green's function

$$i\hbar G^T(\mathbf{r}t, \mathbf{r}'t') = \frac{\langle \psi_H^0 | \hat{\psi}_H(\mathbf{r}t) \hat{\psi}_H^\dagger(\mathbf{r}'t') | \psi_H^0 \rangle}{\langle \psi_H^0 | \psi_H^0 \rangle} \quad t \geq t',$$
$$= -\frac{\langle \psi_H^0 | \hat{\psi}_H^\dagger(\mathbf{r}'t') \hat{\psi}_H(\mathbf{r}t) | \psi_H^0 \rangle}{\langle \psi_H^0 | \psi_H^0 \rangle} \quad t < t'$$

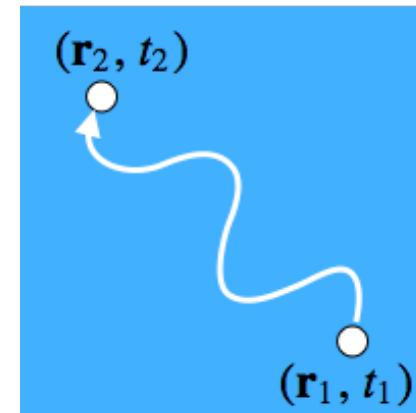
$|\psi_H^0\rangle$ is the N-electron ground-state (H stands for Heisenberg representation)

$\hat{\psi}_H(\mathbf{r}t)$ and $\hat{\psi}_H^\dagger(\mathbf{r}'t')$ are destruction/creation field operators

Electron propagation
from $(\mathbf{r}_2 t_2)$ to $(\mathbf{r}_1 t_1)$



Hole propagation
from $(\mathbf{r}_1 t_1)$ to $(\mathbf{r}_2 t_2)$



Lehman representation

Writing the electron propagator in the Schrödinger representation

$$i\hbar G^e(\mathbf{r}t, \mathbf{r}'t') = \theta(t - t') \langle \psi_S^0(t) | \hat{\psi}_S(\mathbf{r}) e^{-i\hat{H}(t-t')/\hbar} \hat{\psi}_S^\dagger(\mathbf{r}') | \psi_S^0(t') \rangle$$

and introducing the closure relation for the (N+1)-electron system:

$$e^{-i\hat{H}(t-t')/\hbar} = \sum_n e^{-iE_n^{N+1}(t-t')/\hbar} |\psi_H^{n,N+1}\rangle \langle \psi_H^{n,N+1}|$$

one obtains:

$$i\hbar G^e(\mathbf{r}t, \mathbf{r}'t') = \theta(t - t') \sum_n f_n^{N+1}(\mathbf{r}) \bar{f}_n^{N+1}(\mathbf{r}') e^{-i\varepsilon_n^{N+1}(t-t')/\hbar}$$

$$f_n^{N+1}(\mathbf{r}) = \langle \psi_H^0 | \hat{\psi}_S(\mathbf{r}) | \psi_H^{n,N+1} \rangle \quad \text{Lehman (addition) amplitudes}$$

$$\varepsilon_n^{N+1} = (E_n^{N+1} - E_0^N) \quad \text{Electron-addition energies}$$

This resembles an independent-electron formulation but replacing the one-body orbitals by Lehman amplitudes and the « electronic energies » by total energy differences between the N-electron and (N+1)-electron systems.

Lehman representation (II)

Proceeding similarly for the hole-propagator, one obtain:

$$i\hbar G(\mathbf{r}t, \mathbf{r}'t') = \theta(t - t') \sum_n f_n^{N+1}(\mathbf{r}) \overline{f}_n^{N+1}(\mathbf{r}') e^{-i\varepsilon_n^{N+1}(t-t')/\hbar} \\ - \theta(t' - t) \sum_n f_n^{N-1}(\mathbf{r}) \overline{f}_n^{N-1}(\mathbf{r}') e^{-i\varepsilon_n^{N-1}(t-t')/\hbar}$$

where we have introduced the “removal” Lehman amplitude and energies:

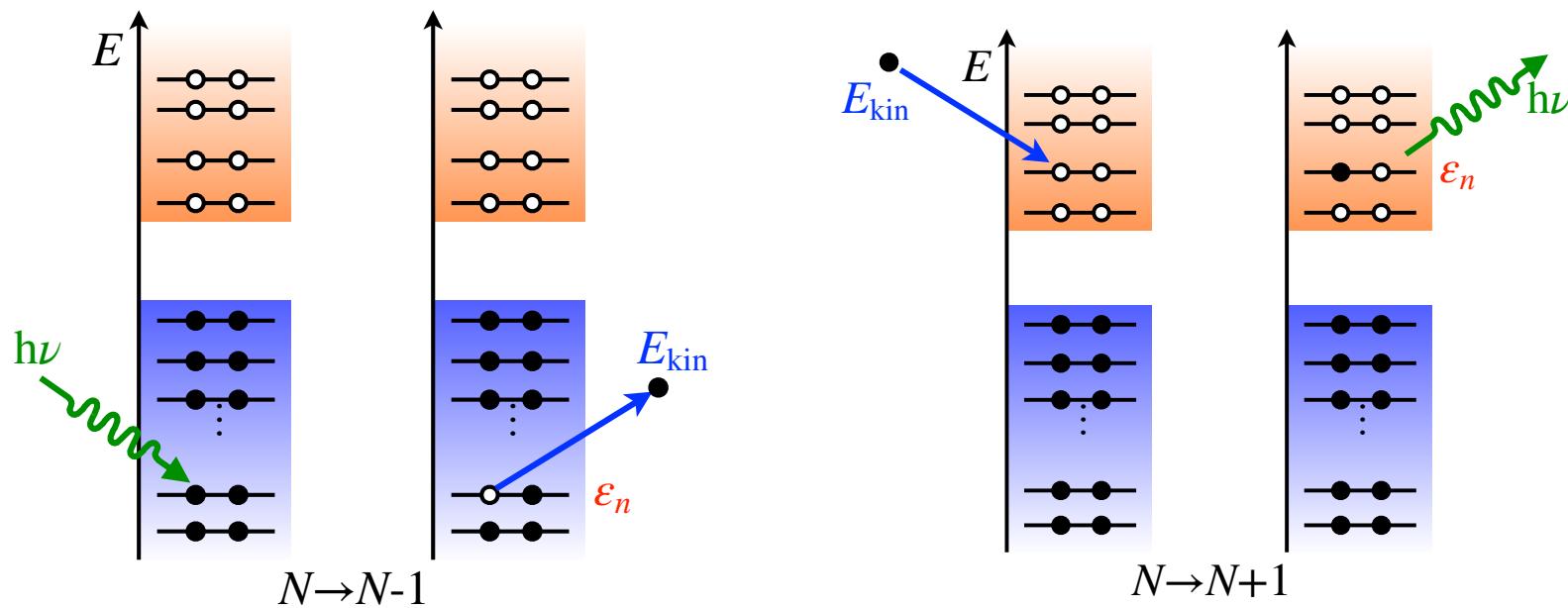
$$f_n^{N-1}(\mathbf{r}) = \langle \psi_H^{n,N-1} | \hat{\psi}_S(\mathbf{r}) | \psi_H^0 \rangle \quad \text{Lehman (removal) amplitude}$$

$$\varepsilon_n^{N-1} = (E_0^N - E_n^{N-1}) \quad \text{Electron-removal energy}$$

NOTE: you will see a lot of times (t^+) => a trick to select electron or hole channels !

e.g. $t'=t^+$ makes $(t'-t)$ positive => selects the hole-channel (occupied states)

Photoemission and addition/removal energies



Energy conservation:

$$\begin{aligned} \text{before} &\rightarrow h\nu + E_{N,0} \\ \text{after} &\rightarrow E_{\text{kin}} + E_{N+1,n} \end{aligned}$$

The binding energy is:

$$\begin{aligned} h\nu - E_{\text{kin}} &= E_{N,0} - E_{N-1,n} = " \varepsilon_n " \\ \text{e.g. IP} &= -(E_{N,0} - E_{N-1,0}) \end{aligned}$$

Energy conservation:

$$\begin{aligned} \text{before} &\rightarrow E_{\text{kin}} + E_{N,0} \\ \text{after} &\rightarrow h\nu + E_{N+1,n} \end{aligned}$$

The binding energy is:

$$\begin{aligned} E_{\text{kin}} - h\nu &= E_{N+1,n} - E_{N,0} = " \varepsilon_n " \\ \text{e.g. AE} &= -(E_{N+1,n} - E_{N,0}) \end{aligned}$$

« Electronic energy levels » are really differences of energy between the N -electron ground-state and ground/excited states of the $(N-1)$ and $(N+1)$ -electrons system.

Green's function in the frequency domain

G depends on $(t-t')$. Fourier transform of G : $g(\omega) = \int d\tau e^{i\omega\tau} g(\tau)$

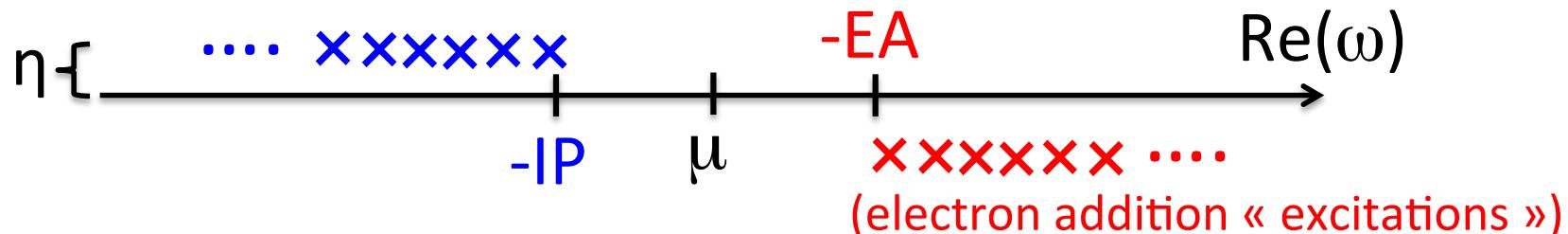


$$\theta(\pm\tau) = \mp \lim_{\eta \rightarrow 0^+} \frac{1}{2i\pi} \int_{-\infty}^{+\infty} d\omega \frac{e^{-i\omega\tau}}{\omega \pm i\eta}$$

$$G(\mathbf{r}, \mathbf{r}'; \omega) = \sum_n \frac{f_n(\mathbf{r}) f_n^*(\mathbf{r}')}{\hbar\omega - \varepsilon_n + i\eta\hbar \operatorname{sgn}(\varepsilon_n - \mu)}$$

The poles of G are the addition/removal energies as measured experimentally.
The spectral weights are associated with the Lehman amplitudes.

(hole addition « excitations »)



How can we calculate G ? Green's function hierarchy

Considering the commutation relations and the equation-of-motion of field operators (Heisenberg representation) :

$$i\hbar \frac{\partial \hat{\psi}_H(\mathbf{r}t)}{\partial t} = \left\{ \hat{\psi}_H(\mathbf{r}t), \hat{H} \right\}, \quad \text{with: } \hat{\psi}_H(\mathbf{r}t) = e^{i\hat{H}t/\hbar} \hat{\psi}_S(\mathbf{r}) e^{-i\hat{H}t/\hbar}$$

and the definition of the Hamiltonian with field operators:

$$\hat{H} = \int d\mathbf{r} \hat{\psi}^\dagger(\mathbf{r}) \underbrace{\left\{ \frac{-\nabla^2}{2} + V^{ext}(\mathbf{r}) \right\}}_{h_0} \hat{\psi}(\mathbf{r}) + \iint d\mathbf{r} d\mathbf{r}' \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}^\dagger(\mathbf{r}') v(\mathbf{r}-\mathbf{r}') \hat{\psi}(\mathbf{r}') \hat{\psi}(\mathbf{r})$$

one ends-up with the equation of motion for the 1-body Green's function, with $\mathbf{1}=(\mathbf{r}_1, t_1)$,
that involves .. a two-body Green's function:

$$i\hbar \frac{\partial G(1, 2)}{\partial t_1} - \hat{h}_0(\mathbf{r}_1) G(1, 2) + i\hbar \int d3 v(1^+ 3) G_2(13; 23^+) = \delta(12)$$

Green's function hierarchy to linear response

Instead of "shaking" the system by adding a (N+1) particle (electron or hole), let's shake-it by an external local potential $\phi(\mathbf{r},t)$. One can show (go to interaction representation) that:

$$G_2(13; 23^+) = G(12) \overbrace{G(33^+)}^{n(3)} - \frac{\partial G(12)}{\partial \phi(3)}$$

which also involves the two-body Green's function. This equation makes a connection with response theory, namely the way the N-electron system respond to an external perturbation. As a result ($\hbar=1$ in the following):

$$\boxed{i \frac{\partial G(12)}{\partial t_1} - \left(\hat{h}_0(\mathbf{r}_1) + V(1) \right) G(12) - i \int d3v(1^+3) \frac{\partial G(12)}{\partial \phi(3)} = \delta(12)}$$

with: $V = V^H + \phi$

This equation only involves the one-body Green's function !

(References: Martin and Schwinger, Phys. Rev. 1959 ; Hedin; Phys. Rev. 1965)

The self-energy and Dyson equation

To obtain an operator-acting-on-G, let's use $G^{-1}G=I$ to show :

$$-\int d3 v(1^+3) \frac{\partial G(12)}{\partial \phi(3)} = \int d3 \left(\overbrace{\iint d45 v(1^+4) \frac{\partial G^{-1}(15)}{\partial \phi(4)} G(53)}^{i\Sigma(13)} \right) G(32)$$

Σ is the self-energy operator ! One then obtain the equation of motion for G:

$$i \frac{\partial G(12)}{\partial t_1} - \left\{ \hat{h}_0(1) + V^H(1) + \phi(1) \right\} G(12) - \int d3 \Sigma(13) G(32) = \delta(12)$$

$G(12)$ verifies an « inhomogeneous » Schrödinger equation with the right-hand-side source term equal to a time-space delta-function => G is a « mathematical » Green's function (George Green, British mathematical physicist 1793 – 1841)

The self-energy Σ accounts for exchange and correlation. It is a non-local, time-dependent and in general non-hermitian operator.

The Dyson equation

Starting with:

$$i \frac{\partial G(12)}{\partial t_1} - \left\{ \hat{h}_0(\mathbf{r}_1) + V^H(\mathbf{r}_1) + \phi(1) \right\} G(12) - \int d3 \Sigma(13)G(32) = \delta(12)$$

and defining the Hartree G_0 Green's function that verifies:

$$i\hbar \frac{\partial G_0(1,2)}{\partial t_1} - \left(\hat{h}_0(\mathbf{r}_1) + \overbrace{V^H(\mathbf{r}_1) + \phi(1)}^{V(1)} \right) G_0(1,2) = \delta(12).$$

one obtains the Dyson equation relating the unknown G to G_0 and Σ :

$$G(12) = G_0(12) + \iint d34 G_0(13)\Sigma(34)G(42)$$

or
$$G^{-1} = G_0^{-1} - \Sigma$$

G_0 is easy to get => if we are given a self-energy, G is known straightforwardly.

A second central ingredient: the screened Coulomb potential

The external potential ϕ induces a charge density variation $\delta n(1) = \int d2 \chi(1, 2)\phi(2)$

This variation of charges generates as well a potential:

$$\delta V^H(2) = \int d1 \delta n(1)v(12)$$

If the perturbation is created by a $Q=+1$ point charge located in (1), then the total potential variation seen in (2) is:

$$\begin{aligned} W(12) &= v(12) + \int d3d4 v(13)\chi(34)v(42) \\ &= v(12) + \int d3d4 v(13)\chi_0(34)W(42) \end{aligned}$$

$$\chi(12) = \chi_0(12) + \int d3d4 \chi_0(13)v(34)\chi(42)$$

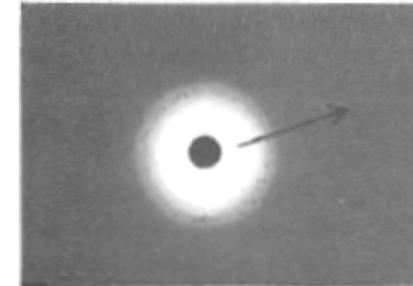
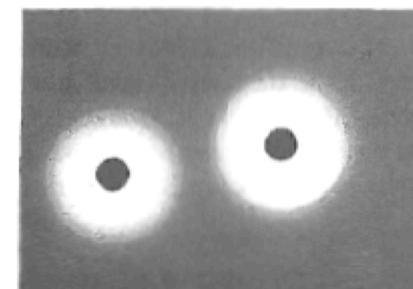


Fig. 0.11 Quasi Electron Propagates Through System



Two Quasi Electrons Interact only Weakly Because of Shielding

From R.D. Mattuck, « A guide to Feynman Diagrams in the Many-Body problem »

$\chi_0 = \partial n(1)/\partial(\phi(2) + V^H(2))$ is the independent-electron polarizability.

Short-range and long-range screening in solids

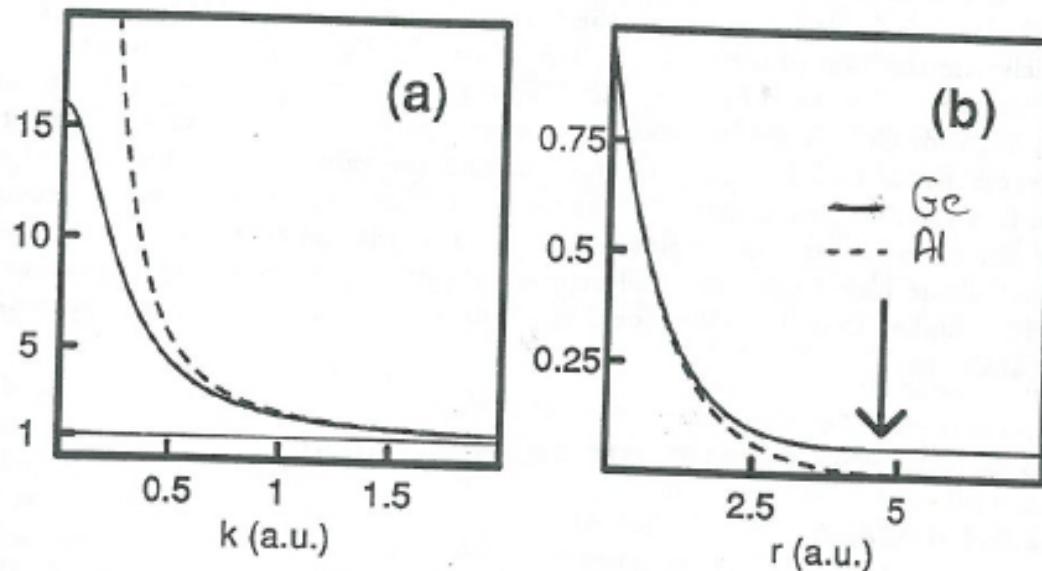


Figure 2.1. (a): Diagonal dielectric functions $\epsilon(k)$ for Al (dashed) and Ge (solid) (b): Ratio $\phi(r)/\phi_0(r)$ between the screened and unscreened potentials of a point charge, from the dielectric functions shown in (a).

In a metal, the screened Coulomb potential decays exponentially with a Yukawa-like decay law: $W(\mathbf{r}, \mathbf{r}') \approx e^{-k_f |\mathbf{r} - \mathbf{r}'|} / |\mathbf{r} - \mathbf{r}'|$

In a semiconductor, the screened Coulomb potential converges to the bare Coulomb potential renormalized by the macroscopic dielectric constant (13-14 in Si).

$$W(\mathbf{r}, \mathbf{r}') = \int d\mathbf{r}'' \epsilon^{-1}(\mathbf{r}, \mathbf{r}'') v(\mathbf{r}'', \mathbf{r}') \Rightarrow \frac{1}{\epsilon_M |\mathbf{r} - \mathbf{r}'|} \text{ (long range)}$$

Courtesy: Raffaele Resta,
Lecture Notes, Methods of
Electronic Structure Theory,
SISSA, Trieste.

Finally: $\Sigma(12) = -i \iint d345 v(1^+3) \frac{\partial G^{-1}(14)}{\partial V(5)} \frac{\partial V(5)}{\partial \phi(3)} G(42)$

Gathering everything: $\epsilon^{-1}(35)$

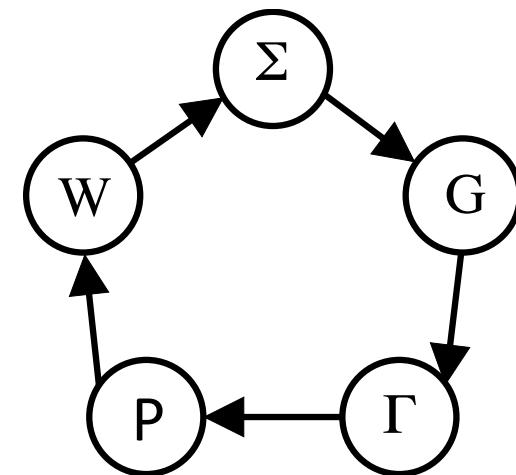
$$G(12) = G_0(12) + \iint d3d4 G_0(13)\Sigma(34)G(42)$$

$$W(12) = v(12) + \iint d3d4 v(13)P(34)W(42)$$

$$P(12) = -i \iint d3d4 G(23)G(42)\Gamma(34; 1)$$

$$\Sigma(12) = i \iint d34 W(1^+3)G(14)\Gamma(42; 3)$$

$$\Gamma(12; 3) = \delta(12)\delta(13) + \text{higher order in } W$$

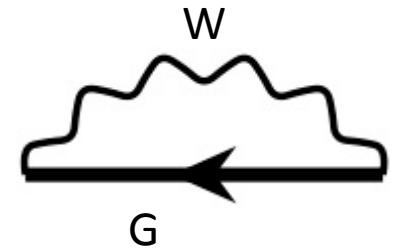


where we have introduced the 3-body vertex function:

$$\Gamma(12; 3) = -\frac{\partial G^{-1}(12)}{\partial V(3)} = -\frac{\partial G_0^{-1}(12)}{\partial V(3)} + \frac{\partial \Sigma(12)}{\partial V(3)} = \delta(12)\delta(13) + \frac{\partial \Sigma(12)}{\partial V(3)}$$

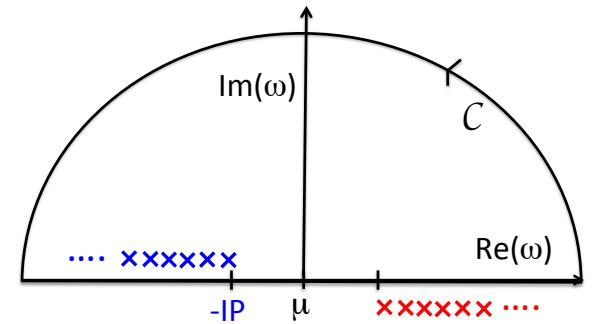
The GW self-energy : the self-energy to lower order in W

$$\Sigma(\mathbf{r}, \mathbf{r}'; E) = \frac{i}{2\pi} \int_{-\infty}^{+\infty} d\omega e^{i\omega 0^+} G(\mathbf{r}, \mathbf{r}'; \omega) W(\mathbf{r}, \mathbf{r}'; \omega - E)$$

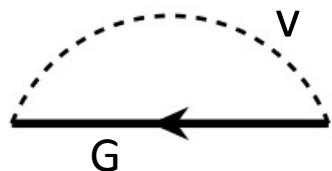


Exercice: the exchange operator in Green's function language

$$G_{HF}^T(\mathbf{r}; \mathbf{r}' : \omega) = \sum_n \frac{\phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}')}{\hbar\omega - \varepsilon_n + i\eta \text{sgn}(\varepsilon_n - \mu)}$$



$$\frac{i}{2\pi} \int_{-\infty}^{\infty} d\omega e^{i\omega 0^+} G_{HF}^T(\mathbf{r}, \mathbf{r}'; \omega) v(\mathbf{r}, \mathbf{r}') = \frac{i}{2\pi} 2i\pi \sum_n^{\text{occupied}} \phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}') v(\mathbf{r}, \mathbf{r}')$$



$$= - \sum_n^{\text{occupied}} \frac{\phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Practicals (and « pragmatics »): the traditional G_0W_0 scheme

One should start with Hartree eigenstates ... in practice, we take the « best » mean field Green's function we have: Kohn-Sham DFT one !

$$\chi_0^{KS}(\mathbf{r}, \mathbf{r}'; \omega) = \sum_{ij} (f_i - f_j) \frac{\phi_i^{KS}(\mathbf{r}) [\phi_j^{KS}(\mathbf{r})]^* [\phi_i^{KS}(\mathbf{r}')]^* \phi_j^{KS}(\mathbf{r}')}{\hbar\omega - (\varepsilon_i^{KS} - \varepsilon_j^{KS}) + i\eta \operatorname{sgn}(\varepsilon_i^{KS} - \varepsilon_j^{KS})}$$

$$\Rightarrow W = v + v\chi_0 W$$

$$G_{KS}^T(\mathbf{r}, \mathbf{r}'; \omega) = \sum_n \frac{\phi_n^{KS}(\mathbf{r}) [\phi_n^{KS}(\mathbf{r}')]^*}{\hbar\omega - \varepsilon_n^{KS} + i\eta \operatorname{sgn}(\mu - \varepsilon_n^{KS})}$$

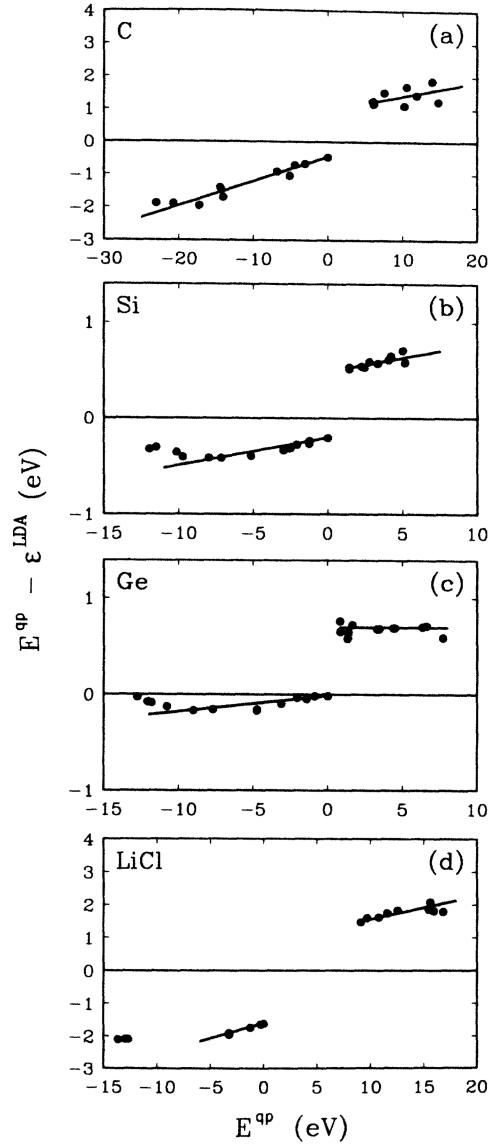
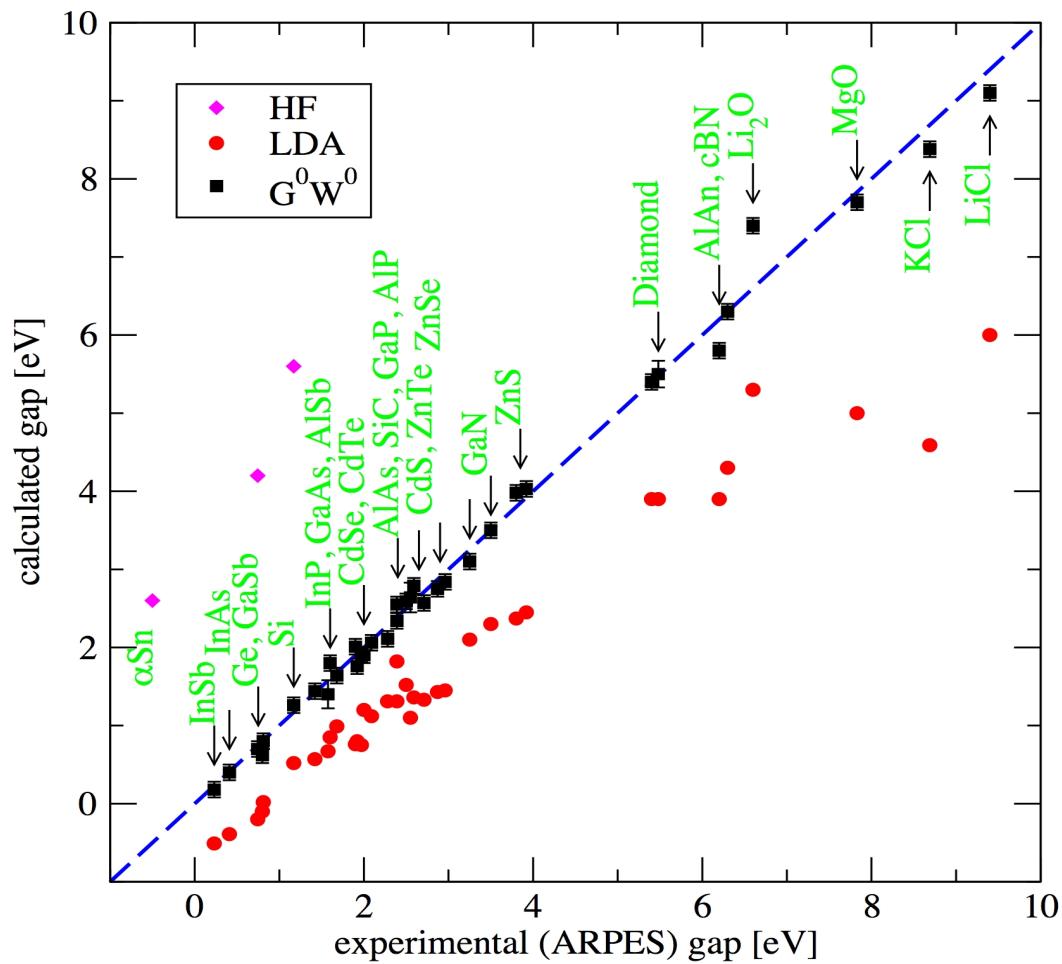
Finally, in the spirit of first-order perturbation theory:

$$\varepsilon_n^{GW} = \varepsilon_n^{KS} + \langle \phi_n^{KS} | \Sigma(\varepsilon_n^{GW}) - V^{XC} | \phi_n^{KS} \rangle$$

Pioneers: L. Hedin 1965 (free electron gas): Strinati/Mattausch/Hanke 1980 (tight-binding) ; Hybertsen/Louie 1986 and Godby/Schlüter/Sham 1988 (*ab initio* calculations).

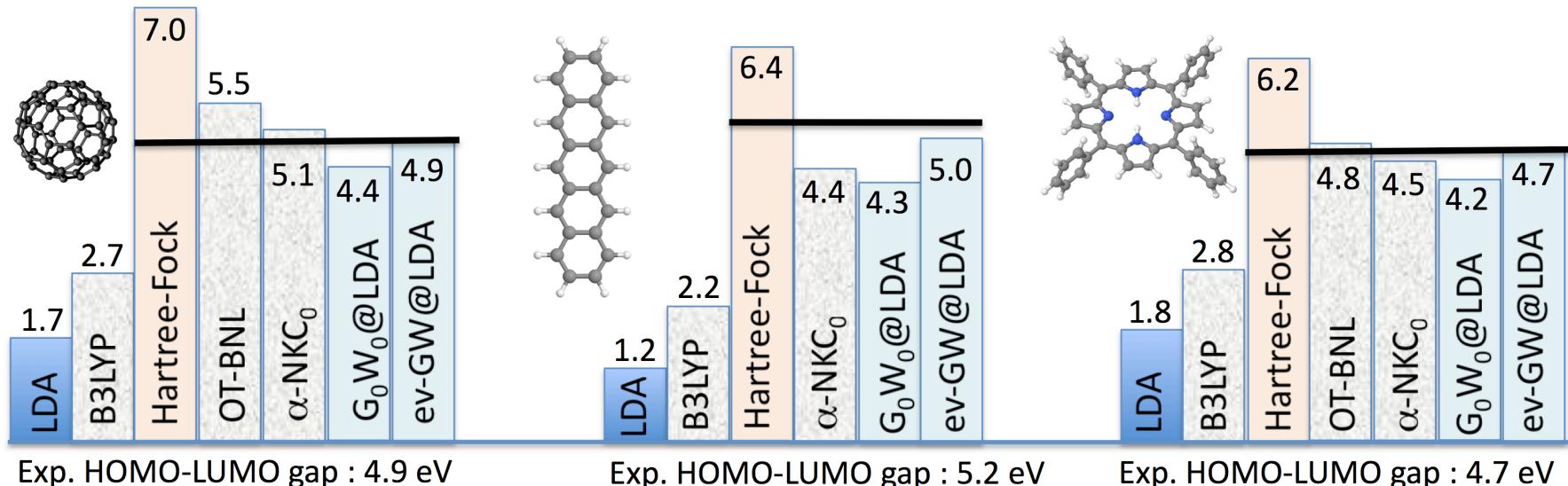
To start with: the gap of semiconductors and insulators

$E^{\text{GW}} - E^{\text{LDA}}$ (Hybertsen/Louie 1986)



Silicon gap: 1.17 eV (Exp) ≈ 0.6 eV (DFT-LDA KS) ≈ 6 eV (HF) ≈ 1.2 eV (G_0W_0 @LDA)

What about organic molecules (no long-range screening ...)



(Blase, Attaccalite, Olévano, 2011)

Self-consistent GW for small molecules

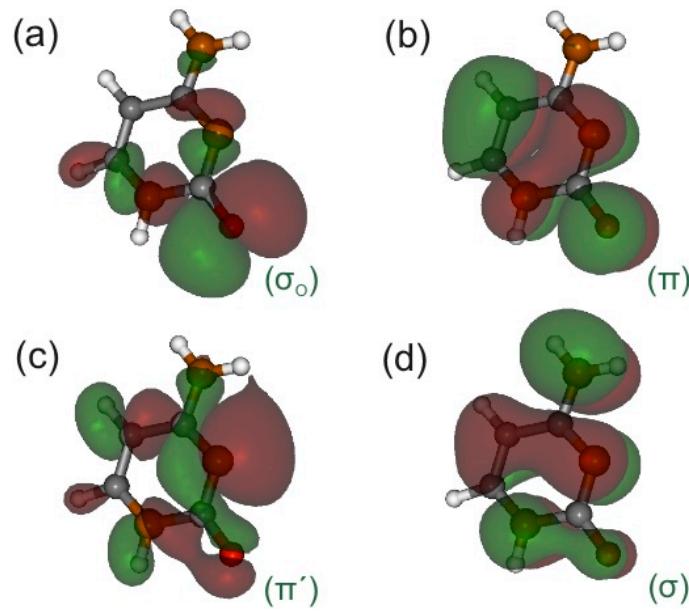
Stan *et al.* JCP 2009; Rostgaard *et al.*, PRB 2010; Strange *et al.* PRB 2011; Bruneval, JCP 2012; Caruso *et al.*, PRB 2013; Lischner *et al.*, PRB 2014; P. Koval *et al.*, PRB 2014; etc.

G_0W_0 with « best » starting point

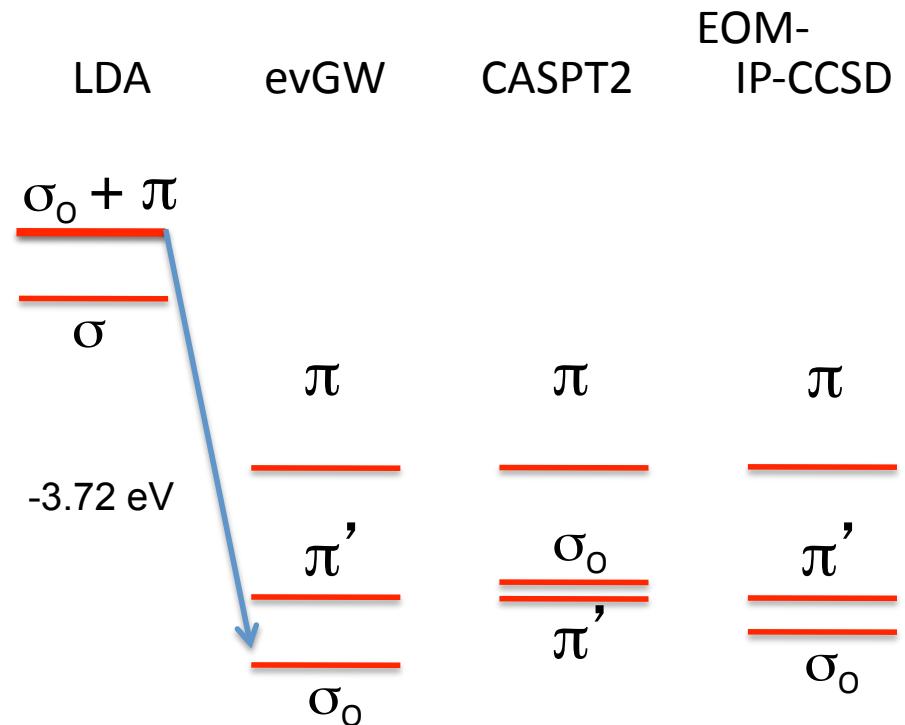
Hahn *et al.* PRB 2005; Blase *et al.* PRB 2011; Marom *et al.*, PRB 2011, 2012; Körzdörfer *et al.* PRB 2012; Bruneval *et al.*, PRB 2013; etc.

Simplest SCF scheme: partial self-consistency on eigenvalues only (evGW).

Beyond the scissor operator: level ordering and spacing below the gap



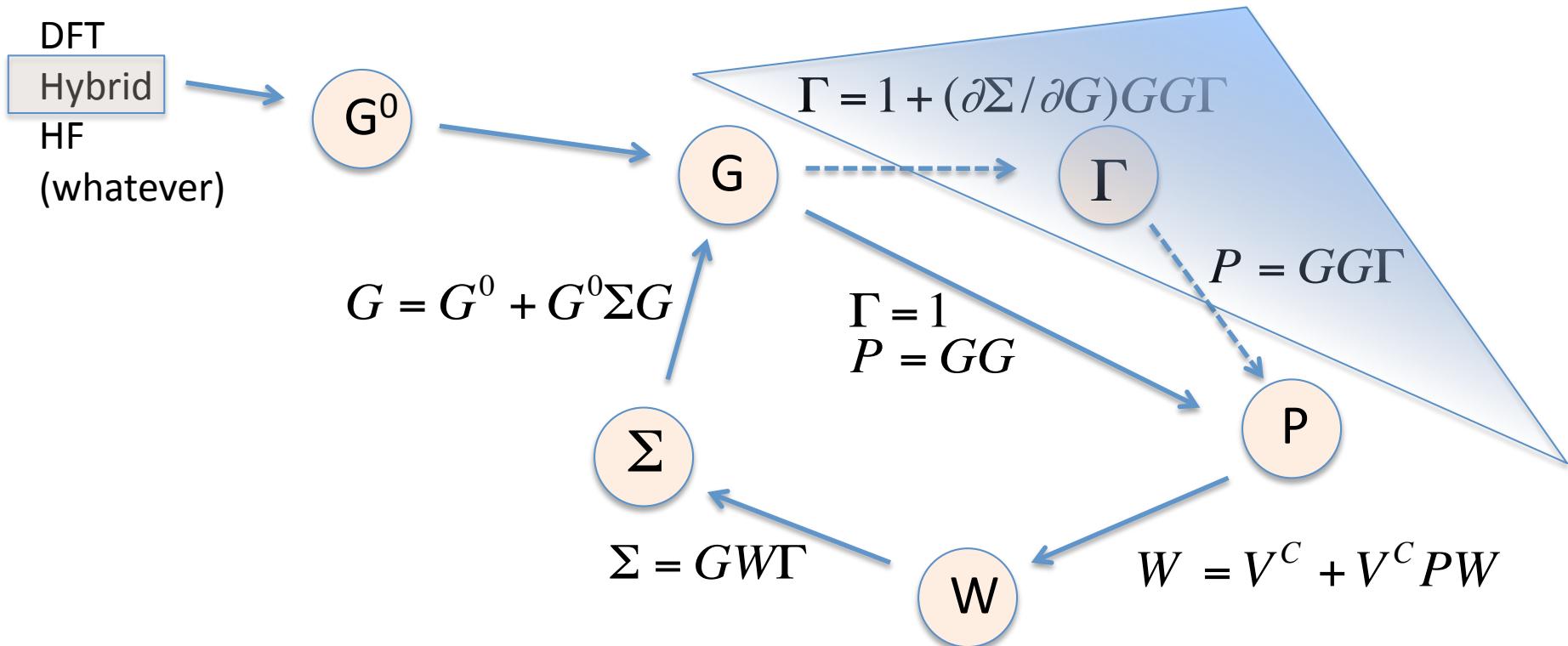
HOMO to (HOMO-3) in cytosine
(DNA nucleobases)



	LDA	evGW	CASPT2/CCSD(T)	EOM-IP-CCSD	Exp.
HOMO	6.167 (σ_0)	8.73 (π)	8.73/8.76 (π)	8.78 (π)	8.8-9.0
HOMO-1	6.172 (π)	9.52 (π')	9.42/ - (σ_0)	9.55 (π')	9.45-9.55
HOMO-2	6.81 (σ)	9.89 (σ_0)	9.49/ - (π')	9.65 (σ_0)	9.89

(Faber, Attaccalite, Olevano, Runge, Blase, 2011)

A difficult issue: self-consistency (cycling Hedin's set of equations)



Self-consistency: still an open question !

Which self-consistency ? “Quasiparticle-like G ” or not ?

Where does it converge ? Unicity of solution ? Dependence on starting point ?

Should we go to higher order (vertex corrections ?)

Do we improve all quantities (quasiparticle energies, satellites, total energy, etc.)

GW Self-Consistency

$$\mathbf{G}_0 \mathbf{W}_0 \rightarrow \mathbf{GW}_0, \mathbf{G}_0 \mathbf{W}, \mathbf{GW}$$

Quasiparticle Self-Consistency

- EV-scGW [Hibertsen, Louie, 1988]
- QPscGW [van Schilfgaarde, Kotani, Faleev, PRL 2006]
- scCOHSEX+ $\mathbf{G}_0 \mathbf{W}_0$ [Bruneval, Vast, Reining, PRB 2006]

Critical points:

- Conserving Approximations?
- Basis Sets and Convergence?
- GW scheme (e.g. imaginary axis, analytic continuation, Matsubara, Keldysh, etc.)?

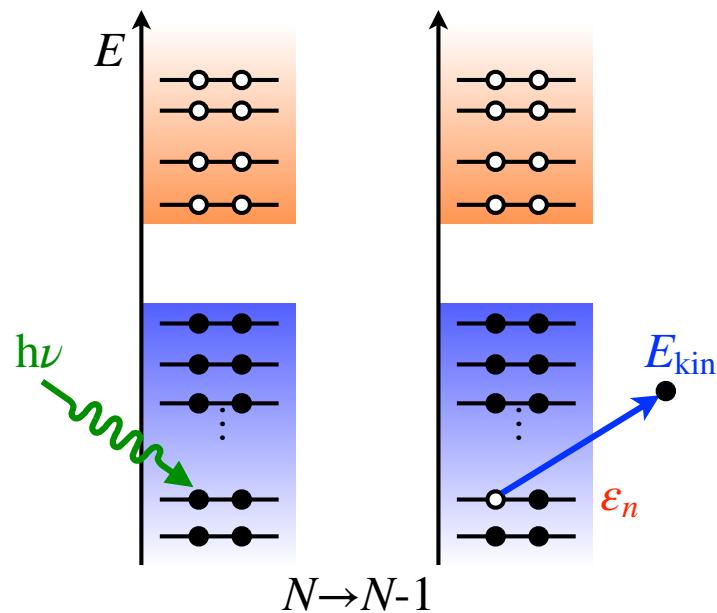
Full Self-Consistency

- Models (e.g. Jellium) [Holm von Barth, PRB 1998]: worst spectral QP, better Total Energies [Schindlmayr, Pollehn, Godby, PRB 1998]: not even Total Energies (Hubbard)
- Solids [Schone, Eguiluz, PRL 1998]: worst bandgaps (Si) and bandwidths (K)
- Real Atoms & Molecules [Stan, Dahlen, van Leeuwen, EPL 2006]: improvements by SC on both Total and QP [Rostgaard, Jacobsen, Thygesen, PRB 2010]: no net improvements, G0W0[HF] the best [Caruso, Rinke, Ren, Scheffler, Rubio, PRB 2012]: Improvements on Total Energies (but PBE better) [Marom et al. PRB 2012]: no clear improvements on QP

(courtesy V. Olévano, CECAM workshop, Green's function: next generation, 2015)

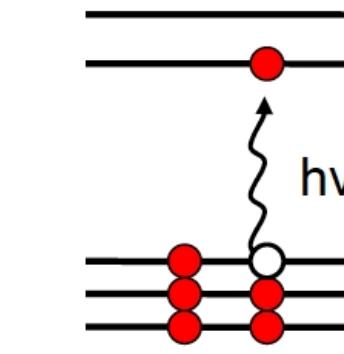
Optical properties and the Bethe-Salpeter equation (BSE) formalism

Photoemission \Leftrightarrow GW formalism

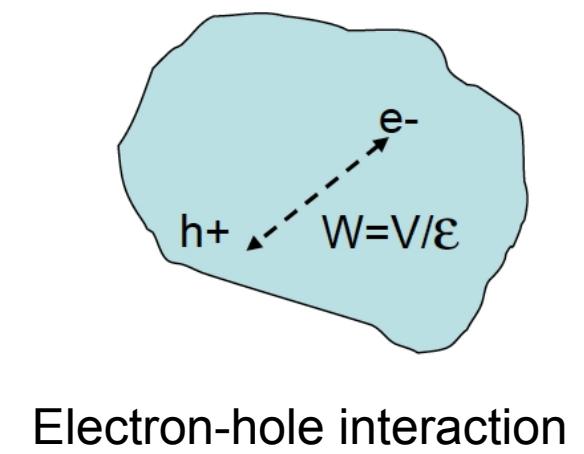


Propagation of an additional
electron OR a hole

Optical properties \Leftrightarrow Bethe-Salpeter equation



Optical absorption



Electron-hole interaction

Propagation of an electron-hole pair

Optical absorption in semiconductors

Optical spectrum in bulk silicon:

TDLDA: wrong onset and not enough « low energy » spectral weight

LR-TDDFT: adding a long-range kernel derived from GW/Bethe-Salpeter



Correct energy location and spectral weight !!



In silicon, the average electron-hole distance (effective bohr radius) is of the order of 50 Angström => local kernels cannot capture the long-range electron-hole interaction !!

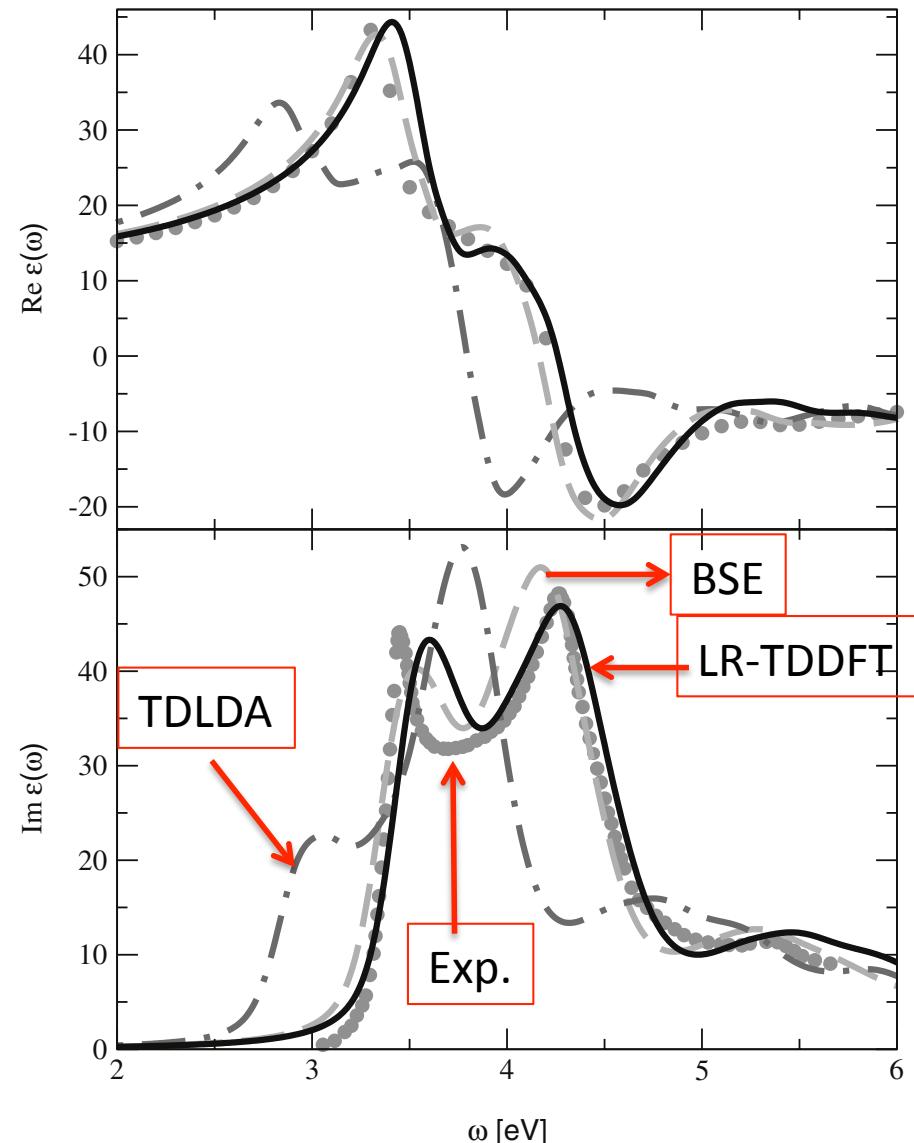


FIG. 1. Silicon, optical absorption (bottom), and refraction index (top panel) spectra. Dots: experiment. Dot-dashed curve: TDLDA result. Dashed curve: result obtained through the Bethe-Salpeter method. Continuous curve: TDDFT result using the long-range kernel derived in this work.

Optical properties and the Bethe-Salpeter formalism in a nutshell

TDDFT

$$\chi(1,2) = \frac{\partial n(1)}{\partial V^{ext}(2)}$$

Bethe-Salpeter

$$L(1234) = \frac{\partial G(1,2)}{\partial U^{ext}(3,4)}$$

Link: $n(1) = -i\hbar G(1, 1^+)$

Deriving the Dyson equation for G leads to a Dyson-like equation for L :

$$L(1234) = L^0(1234) + \int d(5678) L^0(1256)K(5678)L(7834)$$

$$L_0(1234) = G(12)G(34) \quad (\text{Propagation of non-interacting electron and hole})$$

$$K(5678) = v(57)\delta(56)\delta(78) + \boxed{\frac{\partial \Sigma(56)}{\partial G(78)}}$$

Need an expression
for the self-energy Σ

The Bethe-Salpeter formalism in a nutshell: standard approximations

- $\Sigma = iGW$ and $\frac{\partial GW}{\partial G} = W + G \frac{\partial W}{\partial G} \sim W + \text{higher order in } W$
- Neglect frequency dependence of W : $W(\mathbf{r}_1, \mathbf{r}_2; \omega=0)$ (adiabatic approximation)

Expressing the BSE Hamiltonian in the (occupied)x(virtual) product space, one obtains a BSE Hamiltonian formally similar than TD-DFT within Casida's formulation

$$\begin{pmatrix} R - \lambda I & C \\ -C^* & -R^* - \lambda I \end{pmatrix} \cdot \begin{pmatrix} [\phi_a(\mathbf{r}_e)\phi_i(\mathbf{r}_h)] \\ [\phi_i(\mathbf{r}_e)\phi_a(\mathbf{r}_h)] \end{pmatrix} = 0$$

The resonant term reads (for singlet excitations):

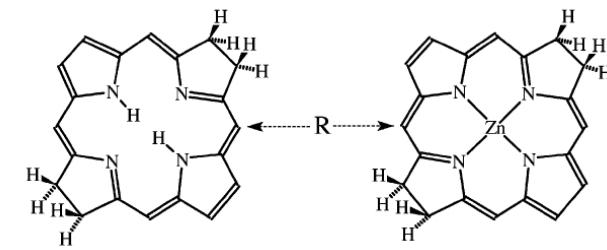
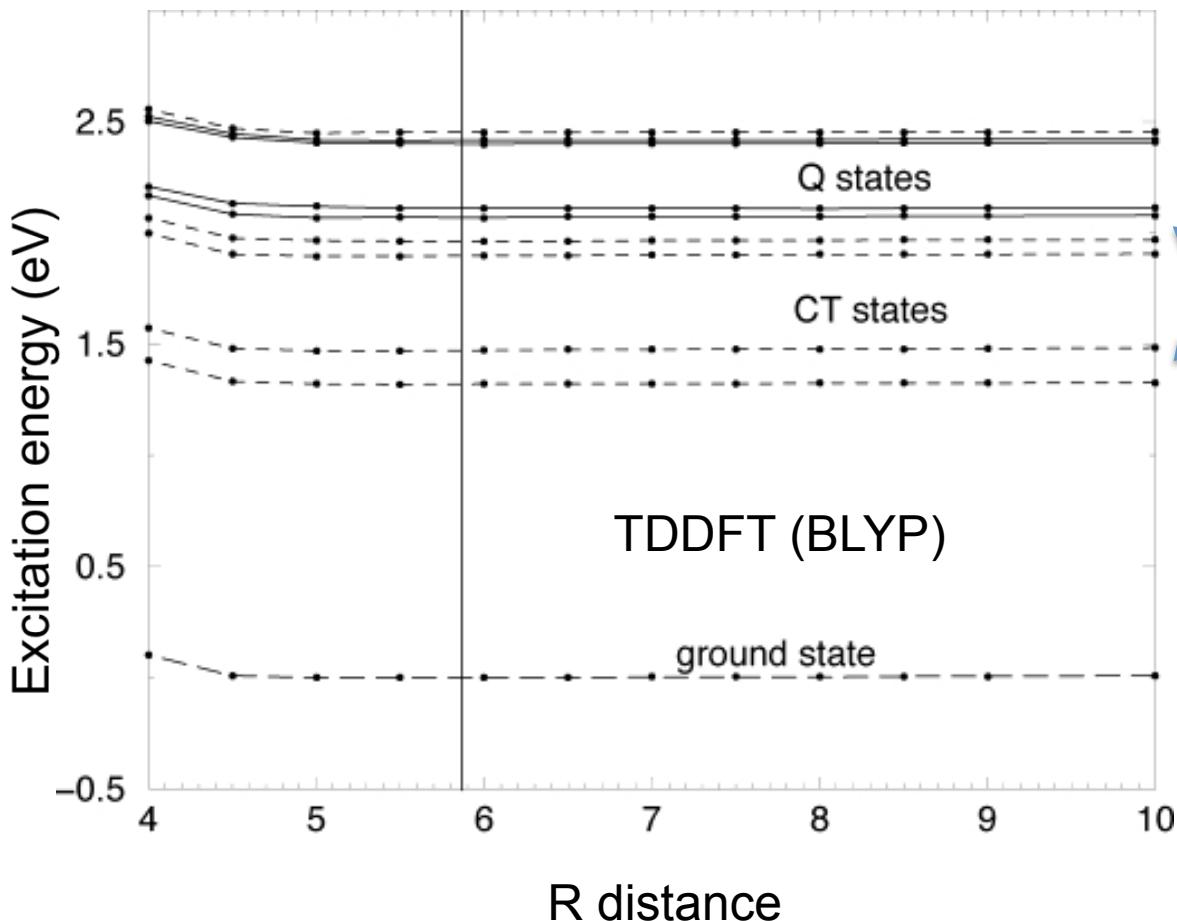
$$R_{ai,bj}^{\text{BSE}} = \delta_{a,b}\delta_{i,j} \left(\varepsilon_a^{\text{QP}} - \varepsilon_i^{\text{QP}} \right) - \langle \phi_a(\mathbf{r})\phi_i(\mathbf{r}')W(\mathbf{r}, \mathbf{r}')\phi_b(\mathbf{r})\phi_j(\mathbf{r}') \rangle + 2 \langle \phi_a(\mathbf{r})\phi_i(\mathbf{r})v(|\mathbf{r} - \mathbf{r}'|)\phi_b(\mathbf{r}')\phi_j(\mathbf{r}') \rangle .$$

GW occupied/
virtual energies

Failure of Time-Dependent Density Functional Theory for Long-Range Charge-Transfer Excited States: The Zincbacteriochlorin–Bacteriochlorin and Bacteriochlorophyll–Spheroidene Complexes

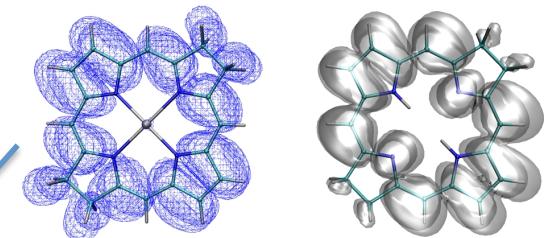
Andreas Dreuw*,† and Martin Head-Gordon‡

(UC Berkeley, Chemistry department, 2004)

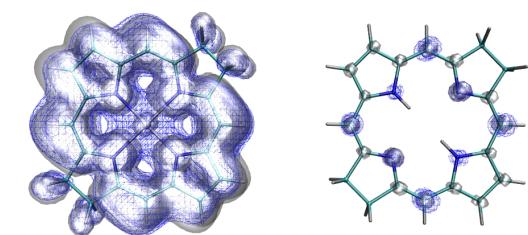


(charge-transfer excitation)

$ZnBC \rightarrow BC$ ($R = 6\text{\AA}$, $E_{BSE} = 3.18\text{eV}$)

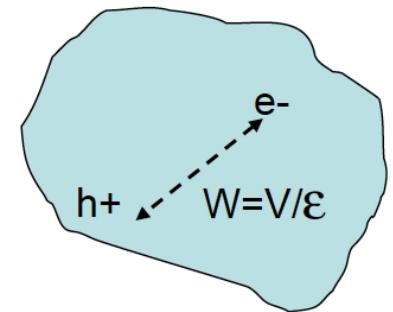


$ZnBC \text{ } Qy$ ($R = 6\text{\AA}$, $E_{BSE} = 2.34\text{eV}$)

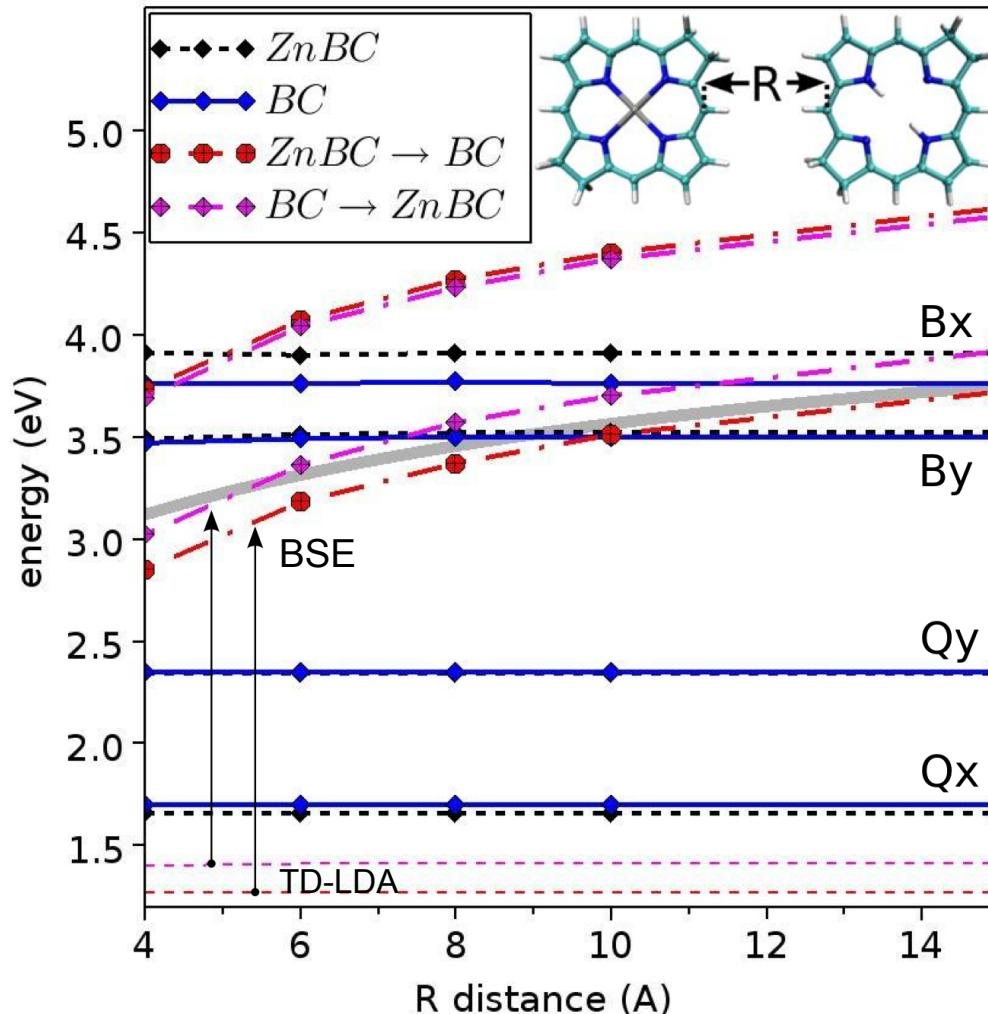


(intramolecular excitation)

The Bethe-Salpeter formalism: explicit screened nonlocal electron-hole interaction (on top of the GW “photoemission” band structure)



The bacteriochlorin-zincbacteriochlorin complex



Intramolecular excitations are at the « correct » energy location

	BSE	Exp
BC	Qx	1.70
ZnBC	Qx	1.67
ZnBC	Qy	2.36
BC	Qy	2.33

The correct « Mulliken » ($-1/R$) charge transfer (CT) excitonic binding energy is recovered !!

(Duchemin, Deutsch, Blase, PRL 2012)

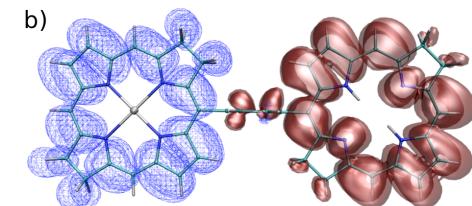
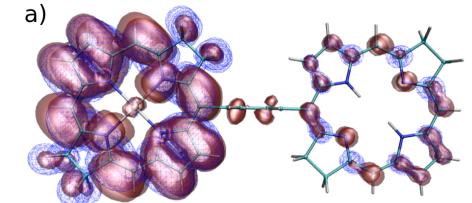
TDLDA, TD-HF, TD-SEX (=BSE) and charge-transfer excitations

TDDFT with charge density dependent kernel

$$K^{xc}(r, r') = v(r, r') + f^{xc}(r, r')$$

$$[K^{xc}]_{ij,kl} = \int d\mathbf{r} d\mathbf{r}' \underline{\phi_i^e(\mathbf{r})\phi_j^h(\mathbf{r})} K^{xc}(\mathbf{r}, \mathbf{r}') \phi_k^e(\mathbf{r}') \phi_l^h(\mathbf{r}'),$$

Goes to zero for charge-transfer excitations:
would need kernel divergency (V_{xc} discontinuity)



TD-Hartree-Fock and TD-Hartree-Screened-Exchange

$$H_{ij,kl}^{diag} = \delta_{i,k} \delta_{j,l} (\varepsilon_i^{QP} - \varepsilon_j^{QP})$$

$$H_{ij,kl}^{direct} = - \int d\mathbf{r} d\mathbf{r}' \underline{\phi_i^e(\mathbf{r})\phi_j^h(\mathbf{r}')} W(\mathbf{r}, \mathbf{r}') \phi_k^e(\mathbf{r}) \phi_l^h(\mathbf{r}') \quad \leftarrow \text{Comes from } \delta\Sigma^{\text{SEX}}$$

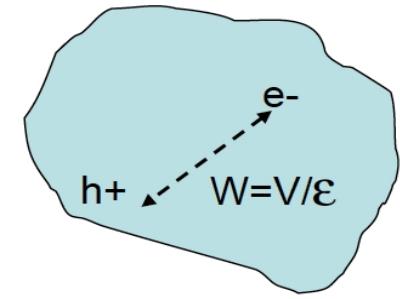
$$H_{ij,kl}^{exchange} = 2 \int d\mathbf{r} d\mathbf{r}' \underline{\phi_i^e(\mathbf{r})\phi_j^h(\mathbf{r}')} v(\mathbf{r}, \mathbf{r}') \phi_k^e(\mathbf{r}') \phi_l^h(\mathbf{r}). \quad \leftarrow \text{Comes from } \delta V^{\text{Hartree}}$$

$$\Sigma^{\text{SEX}}(r, r') = -\rho(r, r') W(r, r', \omega = 0) \quad \text{with: } \rho(r, r') = \sum_{v=occ} \phi_v(r) \phi_v^*(r') \quad \longrightarrow \text{Screened direct term}$$

$$\Sigma^X(r, r') = \frac{-\rho(r, r')}{|r - r'|} \quad \text{with: } \rho(r, r') = \sum_{v=occ} \phi_v(r) \phi_v^*(r') \quad \longrightarrow \text{Unscreened direct term}$$

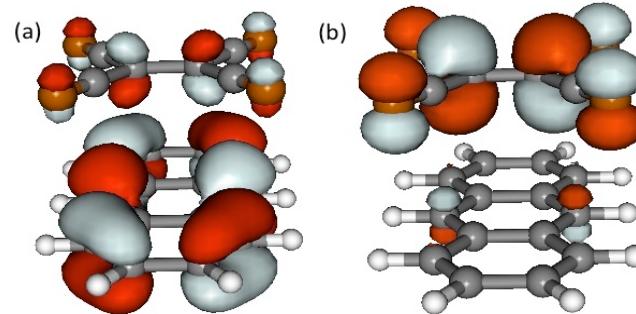
Charge transfer excitations: a standard TDDFT problem

Dreuw and Head-Gordon, JACS 2004
 => “Failure of TDDFT for charge transfer excitations”



The BSE « kernel » accounts for nonlocal electron-hole interaction:

$$\langle \phi_a(\mathbf{r})\phi_i(\mathbf{r}')W(\mathbf{r},\mathbf{r}')\phi_a(\mathbf{r})\phi_i(\mathbf{r}') \rangle = \iint d\mathbf{r}d\mathbf{r}'|\phi_a(\mathbf{r})|^2W(\mathbf{r},\mathbf{r}')|\phi_i(\mathbf{r}')|^2$$



Acceptor = TCNE (tetracyanoethylene)

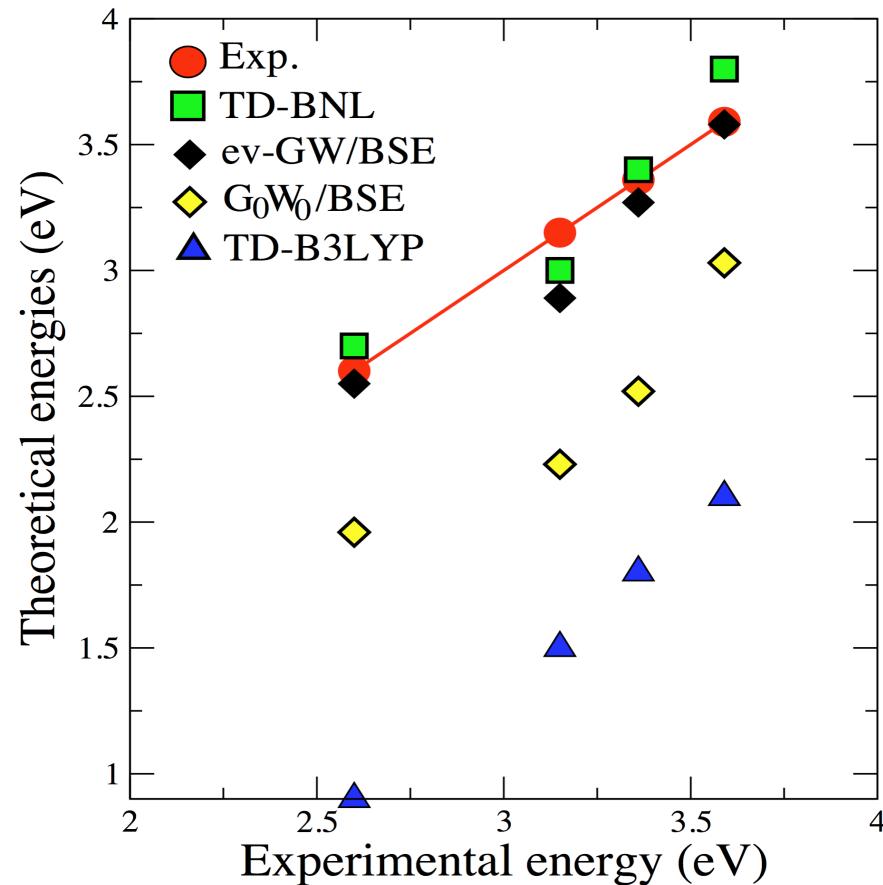
Donor = anthracene

█ TDDFT hybrid

BNL = Range-separated hybrid functional

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

(Stein, Kronik, Baer, JACS 2009)

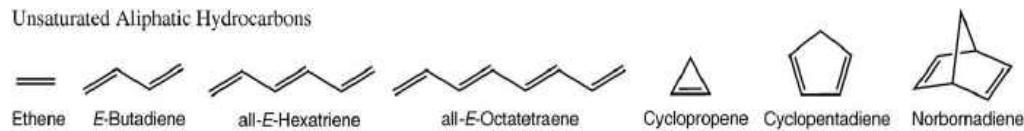


Benchmark vertical excitation energies on a « standard » molecular set (« Thiel's set »)

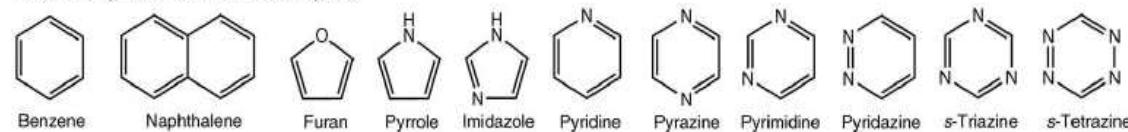
(Jacquemin, Duchemin, Blase, JCTC 2015)

This set contains 28 medium size molecules covering several classes of chromophores.
104 singlet transitions were studied at various levels of TDDFT and quantum chemistry
CC (CC2, CC3, EOM-CCSD) or complete active space CASPT2 perturbative techniques.

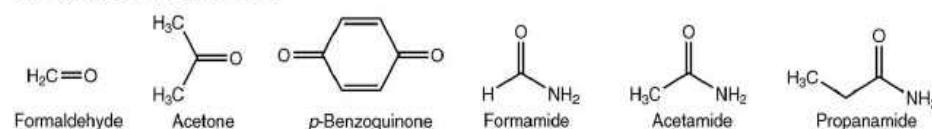
Unsaturated Aliphatic Hydrocarbons



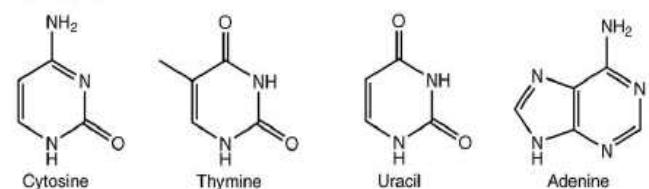
Aromatic Hydrocarbons and Heterocycles



Aldehydes, Ketones and Amides



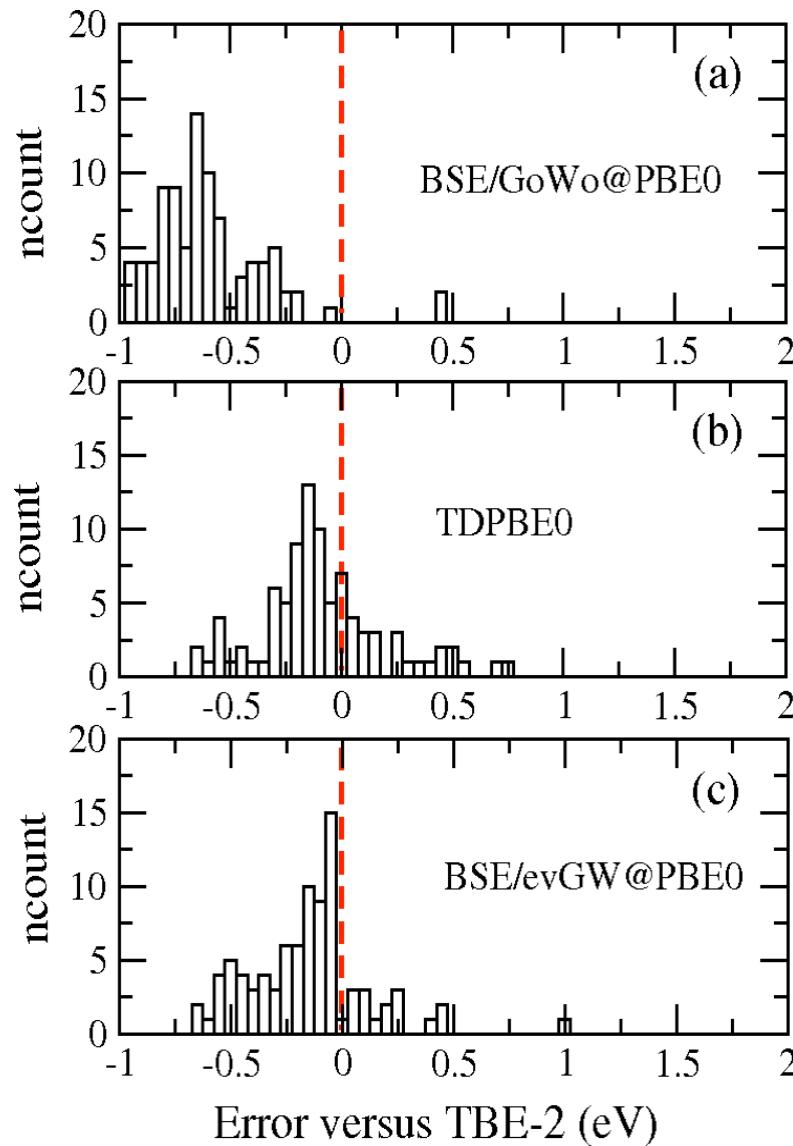
Nucleobases



Schreiber et al. JCP 128, 134110 (2008);
Silva-Junior et al., JCP 133, 174318 (2010);
Caricato et al., JCTC 2010, 6, 370;
Silva-Junior et al., Mol. Phys. 2010, 133;
Jacquemin et al. JCTC 2010, 6, 1532; etc.

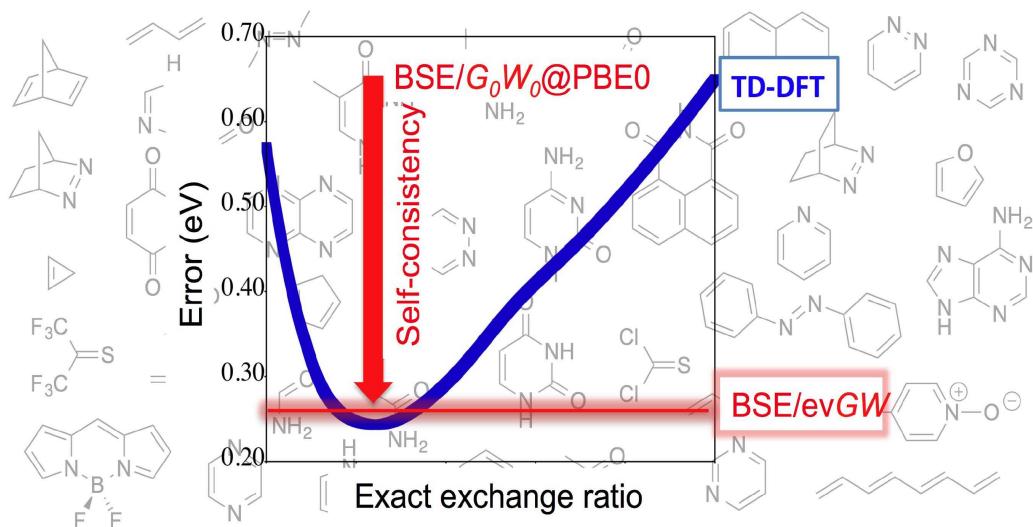
A “theoretical best estimate” (TBE) has been accumulated over the years. All approaches are compared on the same geometry and using the same basis (here aug-cc-pVTZ)

Overall statistics: importance of self-consistency and good agreement with the best TDDFT



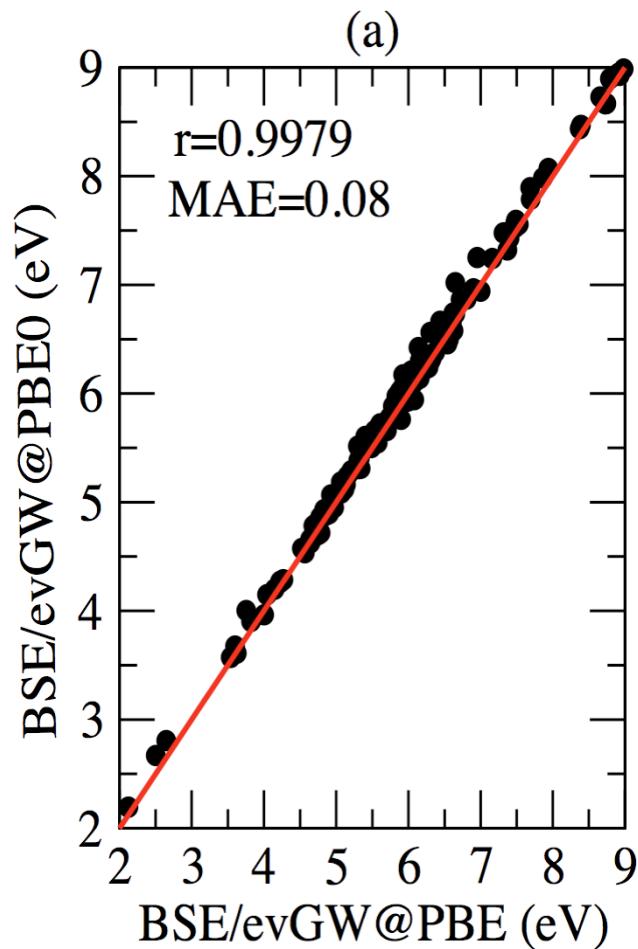
Even when starting with hybrid functional (PBE0), BSE on top of single-shot G_0W_0 calculations yield too low excitation energies (MSE=-0.65 eV)

BSE/evGW@PBE0 yields an error similar to the best TDDFT (MAE=0.25 eV)
 NOTE: TD-PBE: MAE=0.55 eV



(Note that this set does not contain charge-transfer excitations !!)

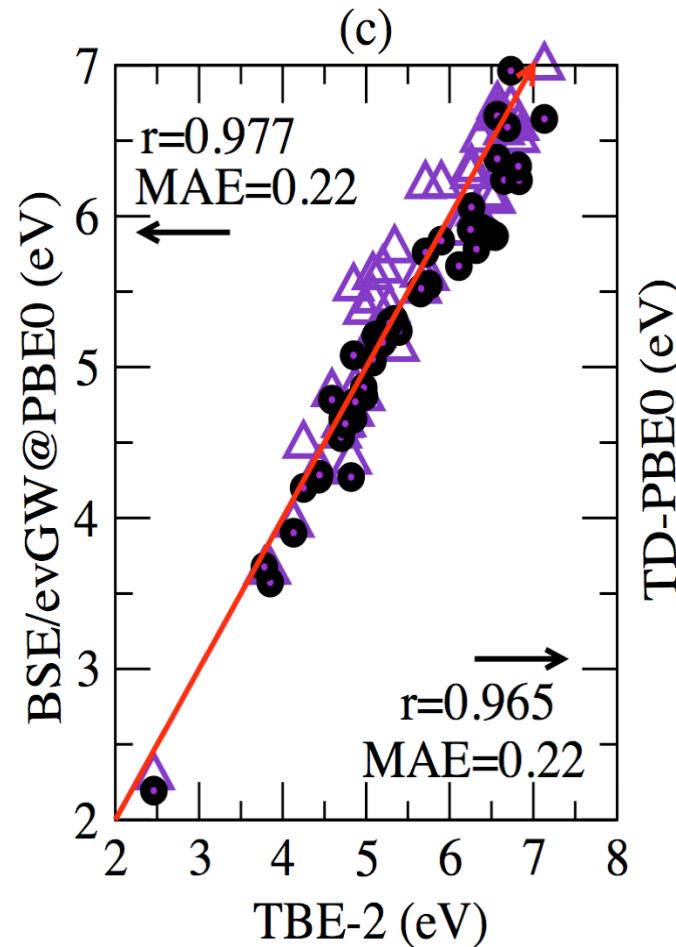
Overall statistics: weak starting point dependency for BSE/evGW scheme



Starting from PBE or PBE0 and updating ONLY the eigenvalues leads to very close results !!

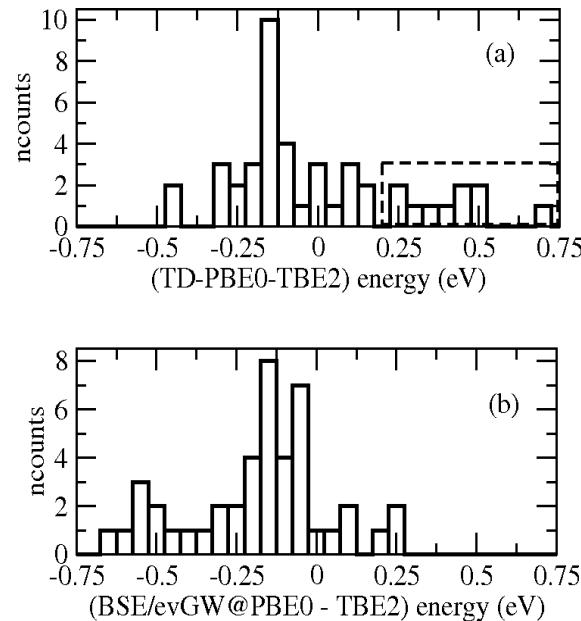
(Note: no transition metal atoms in the studied set !)

A closer look at the aromatic family



Same overall behavior for BSE and TD-PBE0 but a few transitions are too high in energy within TD-PBE0 (compensated by transitions too low within BSE).

A closer look to transitions with “multiple excitation” character



Aromatic family	CC3(%T ₁)	Error vs TBE-2		
		TD-PBE0	BSE	CC2
Pyridine	1 ¹ B ₂	85.9	0.68	0.23
Tetrazine	1 ¹ B _{2u}	84.6	0.52	-0.03
Triazine	1 ¹ A _{2'}	85.1	0.49	0.05
Pyridazine	2 ¹ A ₁	85.2	0.44	-0.04
Pyrimidine	1 ¹ B ₂	85.7	0.44	-0.03
Pyrazine	1 ¹ B _{2u}	86.2	0.40	-0.11
Benzene	1 ¹ B _{2u}	85.8	0.37	-0.04
Naphthalene	2 ¹ A _g	82.2	0.31	-0.06

Coupled-cluster techniques

$$|\Psi\rangle = e^T |HF\rangle$$

$$T = T_1 + T_2 + T_3 + \dots$$

$$T_1 = \sum_i^{\text{occ}} \sum_a^{\text{virt}} t_a^i \hat{a}_a^\dagger a_i$$

$$T_2 = \frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} t_{ab}^{ij} \hat{a}_a^\dagger \hat{a}_b^\dagger a_i a_j$$

$$CCSD: \quad T = T_1 + T_2$$

$$CCSDT: \quad T = T_1 + T_2 + T_3$$

CCSD(T): triples perturbative

CC3 = simplification on CCSD(T)

exCC3 = linear response CC3 for excited states

Conclusions and open questions

- It is not an easy task to solidly improve the GW approximation through self-consistency and it is still a matter of discussion on how to proceed and on what we gain for which physical observables ... but let's not throw out the baby with the bathwater: G_0W_0 with a reasonable starting point usually dramatically improve quasiparticle energies (within 0.1 eV accuracy ...) !
- Bethe-Salpeter can tackle charge-transfer and cyanine-like excitations and performs as well as the “best” TDDFT for standard (Frenkel) excitations.
- The problem of multiple-excitations is under discussion. The role of a dynamical W has been shown to be crucial in capturing such effects.

Refs: Ma, Y.; Rohlfing, M.; Molteni, C. Phys. Rev. B 2009, 80, 241405;
P. Romaniello et al. J. Chem. Phys. 2009, 130, 044108.
Elisa Rebolini PhD Thesis.

- Analytic forces in the excited states: everything to be done ! Standard scheme: vertical excitation within BSE and excited-state relaxation within TDDFT.

Ref: Ismail-Beigi, S.; Louie, S. G. Phys. Rev. Lett. 2003, 90, 076401.

Acknowledgements

Funding: ANR, H2020 + PRACE,GENCI



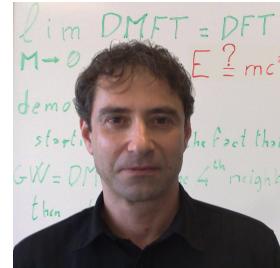
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Valério Olévano
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CEISAM, Nantes

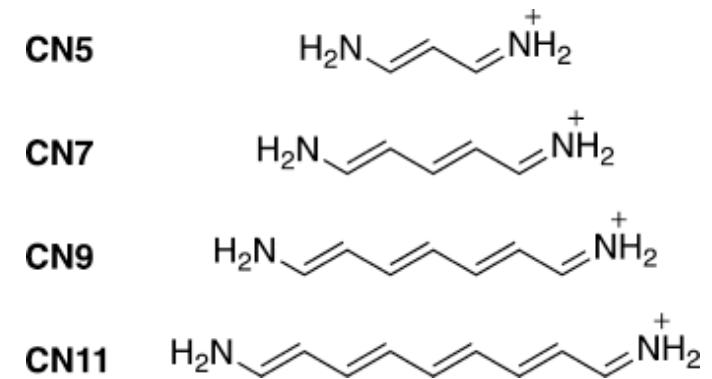
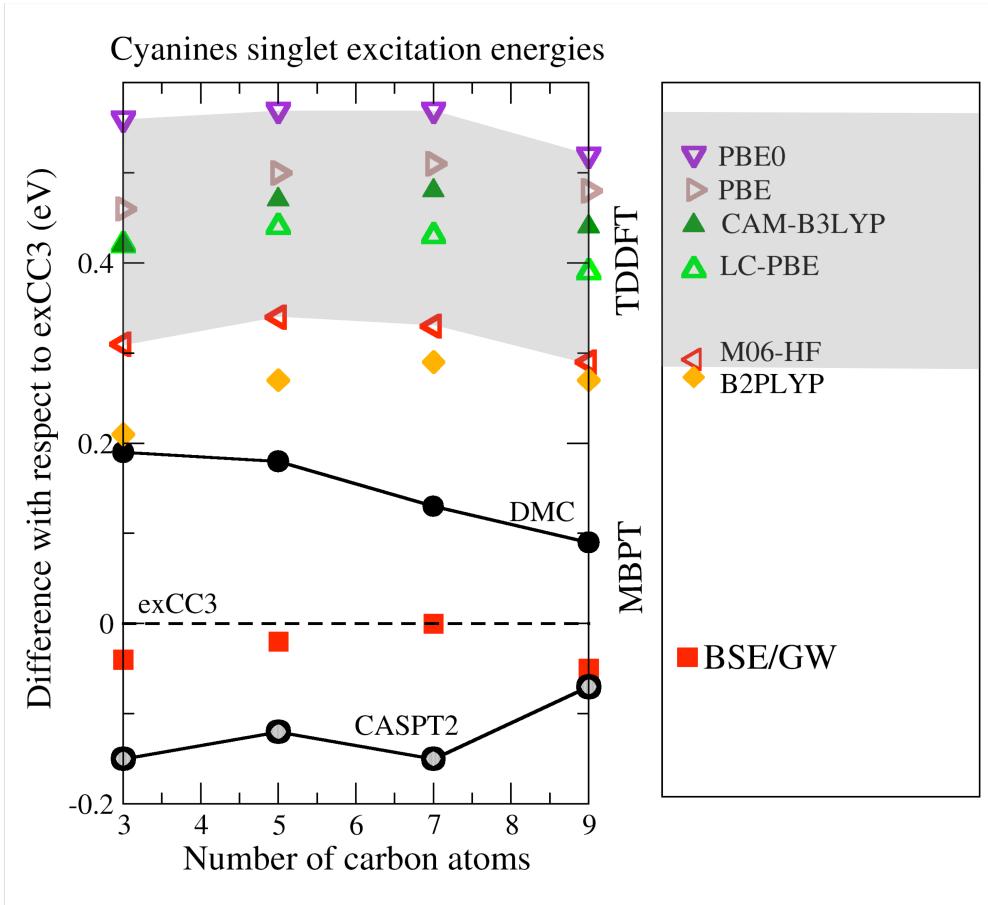
and

Paola Nava +

GDR CORÉV
méthodes corrélées pour la structure électronique

A puzzling (?) result: the « cyanines » family

Cyanines represent an important family of dyes.
 Lowest-lying excitations not charge-transfer states.
 No multi-determinental character of ground-states.
 Still TDDFT fails even with range-separated hybrids.



MAE with respect to exCC3 = 30 meV
 (exCC3 = approximation to EOM-CCSDT)

B2PLYP: double hybrid with « some »
 percentage of MP2 nonlocal correlations
 (Grimme and Neese, JCP 2007)

All electron aug-cc-pVTZ GW/BSE calculations with self-consistency at the COHSEX level
 (Boulanger, Jacquemin, Duchemin, Blase, JCTC 2014)

The GW method in codes

Most implementations rely on planewave basis as a signature of the GW solid-state community history. G_0W_0 becomes a nearly-standard post-processing of Kohn-Sham DFT band structure calculations.

Open-source PW codes: ABINIT (Louvain-la-Neuve), PWSCF (Trieste), BerkeleyGW, etc.

The GW method with “atomic” basis:
a few “private” codes (M. Rohlfing,
X. Blase, D. Foerster, etc.) + FHI-Aims +
.... Turbomole

Molecular Physics: An International Journal at the Interface Between Chemistry and Physics

Publication details, including instructions for authors and subscription information:
<http://www.tandfonline.com/loi/tmph20>

Coupled-cluster reference values for the GW27 and GW100 test sets for the assessment of GW methods

Katharina Krause^a, Michael E. Harding^b & Wim Klopper^{ab}

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One-Electron Energies from the Two-Component GW Method

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The GW-Method for Quantum Chemistry Applications: Theory and Implementation

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An auxiliary-basis Gaussian-based GW and Bethe-Salpeter code

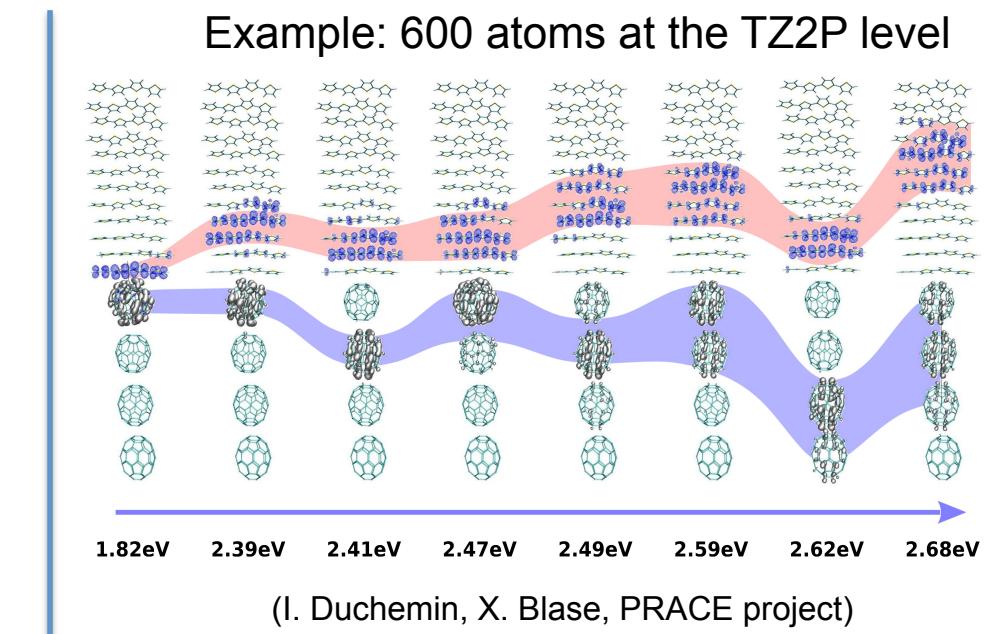
(Blase, Duchemin, CNRS/CEA Grenoble)



- Starting Kohn-Sham/Hartree-Fock eigenstates from Siesta or NWChem
 - => typically aug-cc-pVQZ basis calculations to converge GW within 0.1 eV
(**should we work on F12-GW ?? Remember lecture by W.Klopper**)
- Auxiliary basis with resolution of the identity techniques (Coulomb fitting)
 - => standard auxiliary basis from the Karlsruhe group
 - => O(N⁴) scaling (with the number of atoms)
- Full self-consistency: static COHSEX implemented so far
- Correlations: explicit energy integration through contour deformation

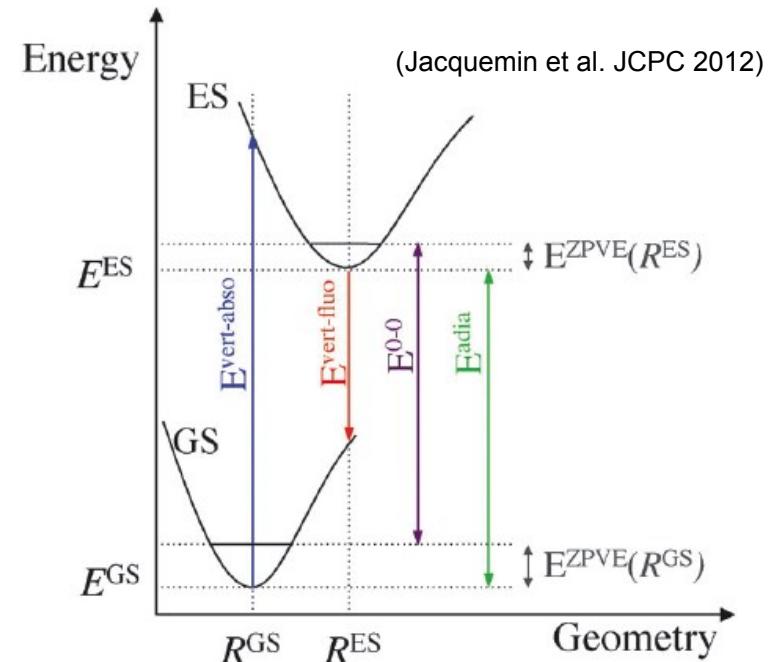
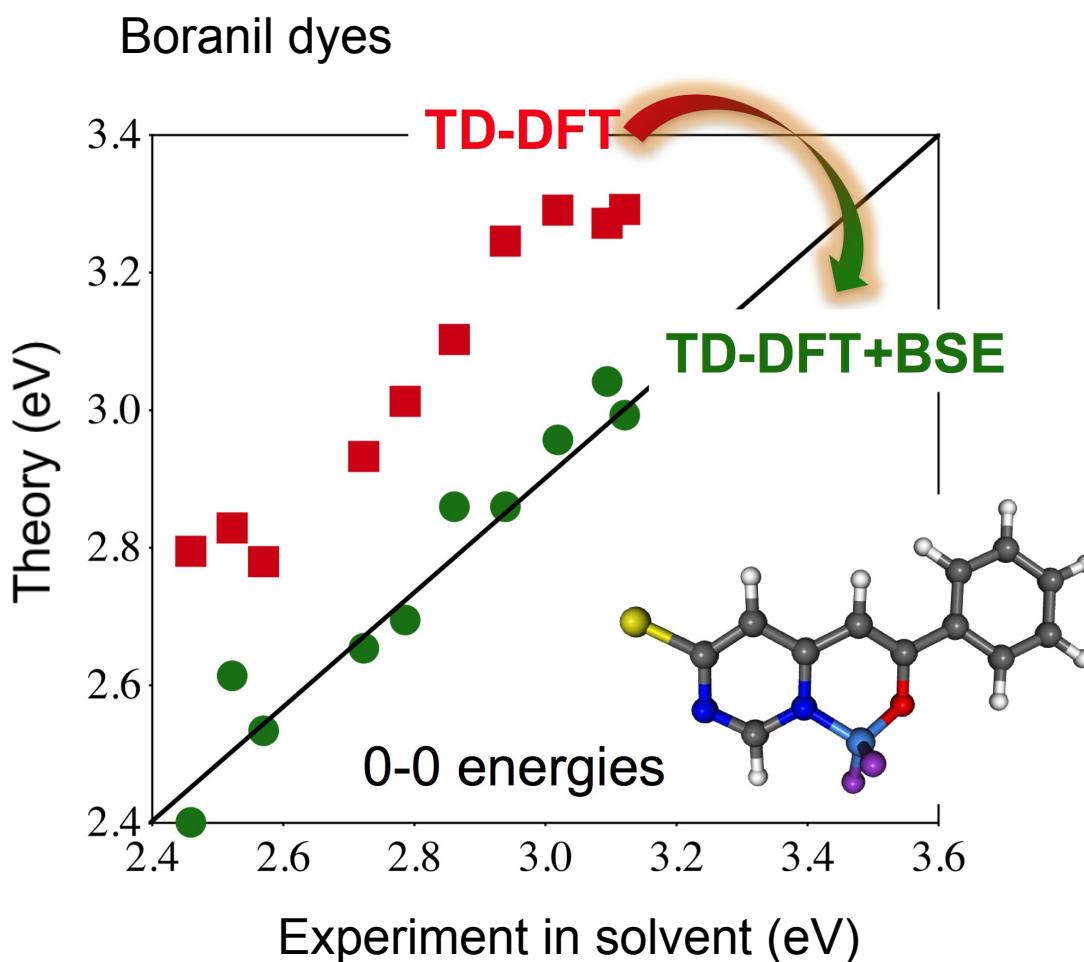
$$\Sigma_c^{GW}(\mathbf{r}, \mathbf{r}'|E) = \sum_n \phi_n(\mathbf{r})\phi_n^*(\mathbf{r}')\mathcal{V}_n(\mathbf{r}, \mathbf{r}'|E)$$

$$\begin{aligned} \mathcal{V}_n(\mathbf{r}, \mathbf{r}'|E) &= \tilde{W}(\mathbf{r}, \mathbf{r}'|\varepsilon_n - E) [\theta(E - \varepsilon_n) - \theta(E_F - \varepsilon_n)] \\ &\quad - \int_0^{+\infty} \frac{d\omega}{\pi} \frac{E - \varepsilon_n}{(E - \varepsilon_n)^2 + \omega^2} \tilde{W}(\mathbf{r}, \mathbf{r}'|i\omega) \end{aligned}$$



Combining the BSE Formalism with TD-DFT Excited-State Forces

(Boulanger, Chibani, Le Guennic, Blase, Jacquemin, JCTC 2014)



Vertical transitions => GW/BSE

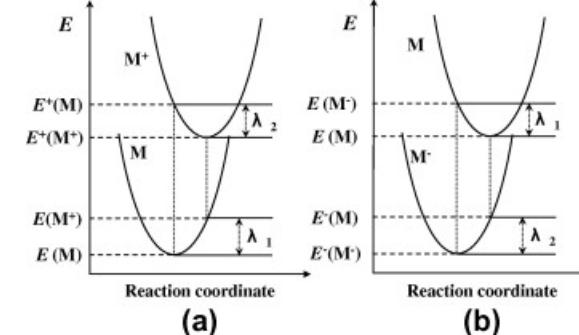
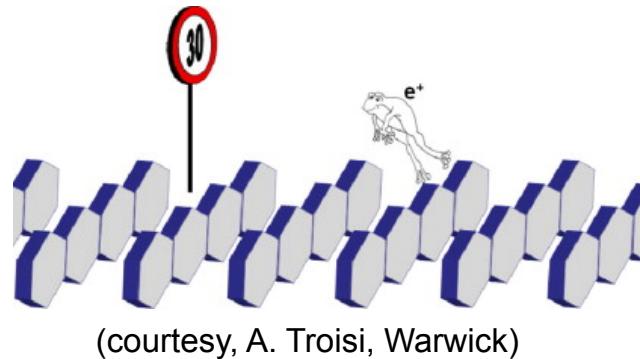
ZPVE + relaxation + embedding
=> TDDFT (M06-2X) and PCM

Challenges for GW/BSE formalism: excited states forces* and phonons and embedding

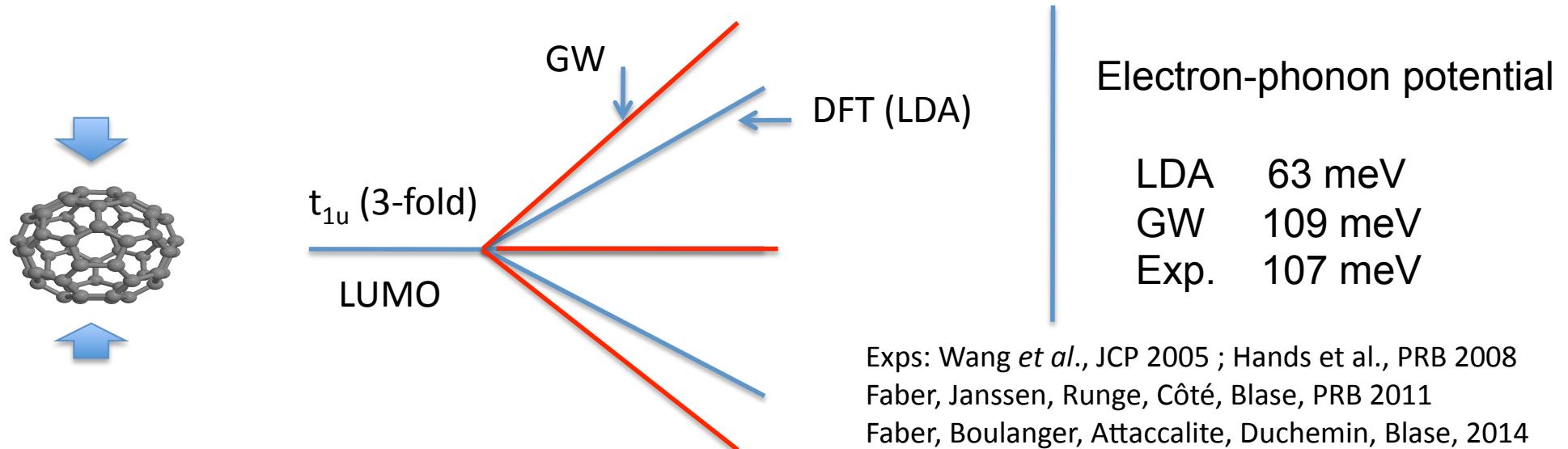
*BSE excited states forces: Ismael-Beigi and Louie, PRL 2003

Parenthesis: Electron-phonon or vibronic coupling in molecular systems

When a charge arrives onto a molecule, the structural relaxation of the molecule traps the charge and strongly limits the mobility of the carriers (polaronic coupling).

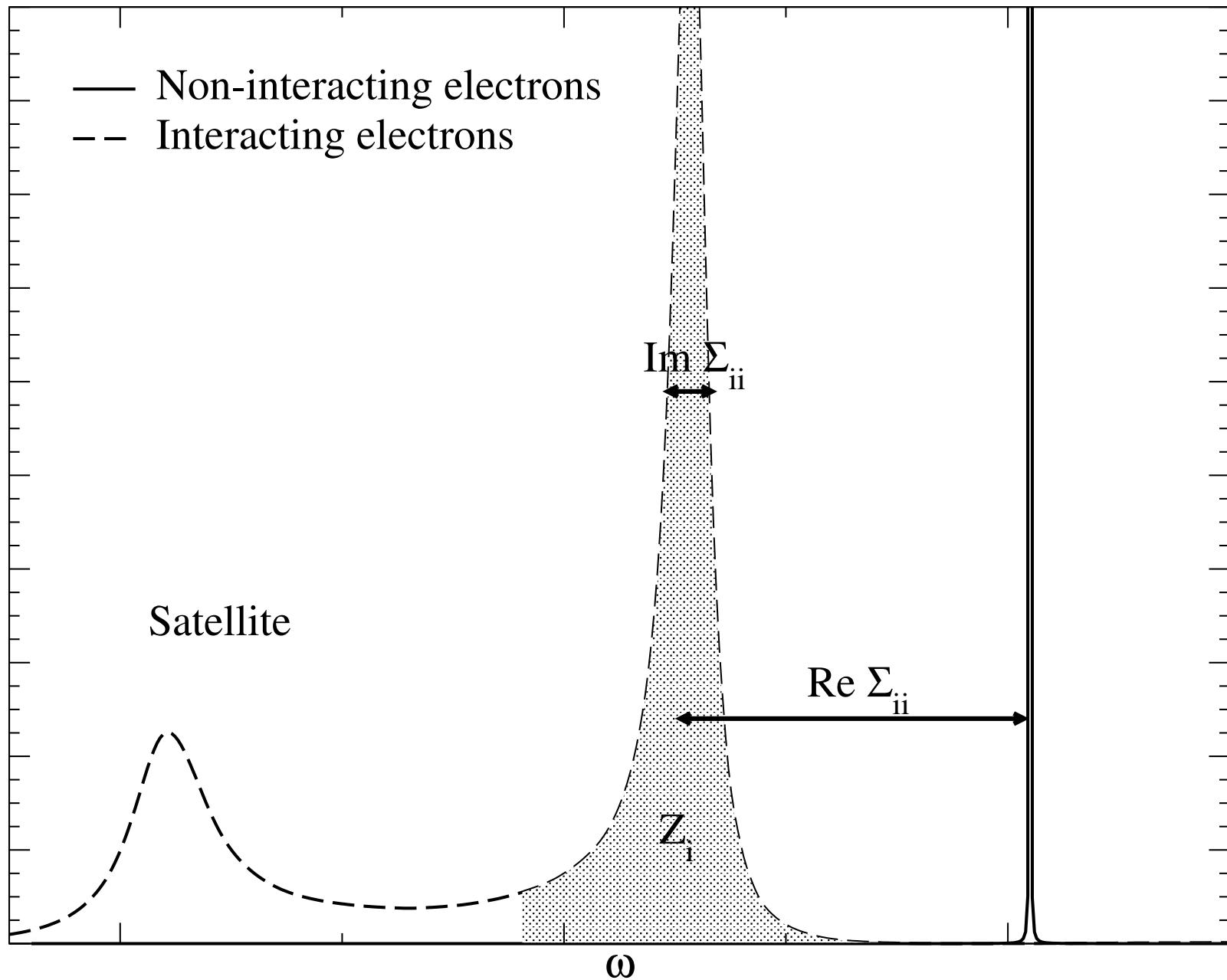


The relaxation energy is closely related to the electron-phonon coupling strength.



(Implications in superconductivity, inelastic scattering, resonant Raman, etc.)

Spectral function of G



Green's function for non-interacting systems (can be found in the Cohen-Tannoudji/Diu/Laloé)

Time evolution operator $|\psi(t)\rangle = \hat{U}(t, t_0)|\psi(t_0)\rangle$

For a time-independent Hamiltonian: $\hat{U}(t, t_0) = e^{-i\hat{H}(t-t_0)/\hbar}$

Let's define the causal (retarded) single-particle Green's function.

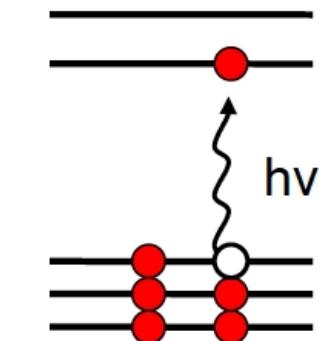
$$\begin{aligned} i\hbar G^T(\mathbf{r}_2 t_2, \mathbf{r}_1 t_1) &= \theta(t_2 - t_1) \langle \mathbf{r}_2 | \hat{U}(t_2 - t_1) | \mathbf{r}_1 \rangle \\ &= \theta(t_2 - t_1) \sum_n \phi_n(\mathbf{r}_2) \phi_n^*(\mathbf{r}_1) e^{-i\varepsilon_n(t_2 - t_1)/\hbar} \end{aligned}$$

Then G^R verifies the following equation:

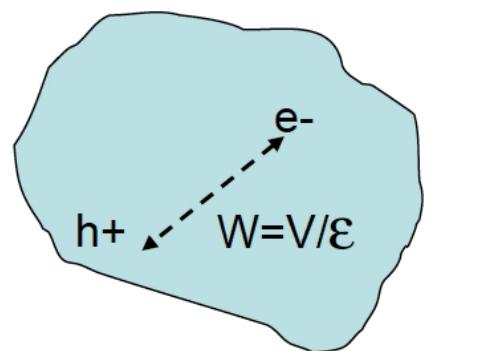
$$\left(i\hbar \frac{\partial}{\partial t_2} - \hat{H}(\mathbf{r}_2, \nabla_2) \right) G^R(\mathbf{r}_2 t_2, \mathbf{r}_1 t_1) = \delta(t_2 - t_1) \delta(\mathbf{r}_2 - \mathbf{r}_1)$$

One recovers the mathematical definition of Green's function as the solution of a linear differential equation with the right hand-side as a delta-function.

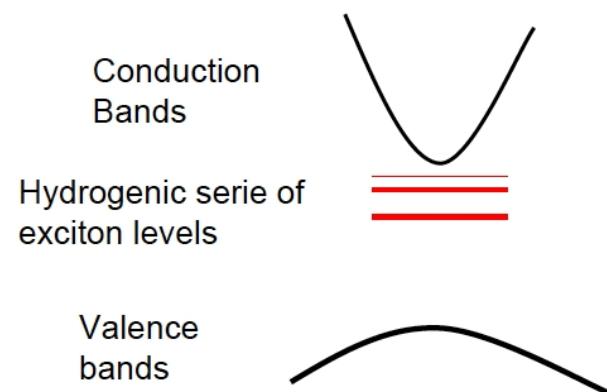
Part II: Optical absorption



Optical absorption



Electron-hole interaction



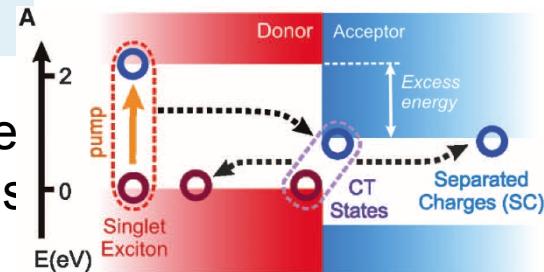
Bound (in gap) exciton binding energy

In a solid (Mott-Wannier): $E_n^{e-h} = \frac{-1}{n^2} \left(\frac{\mu}{\epsilon^2 m_e} \right) \left(\frac{m_e e^4}{2\hbar^2} \right)$ = a few tens of meV (Silicon)

On a molecule, localized exciton (Frenkel): E^{e-h} = several 100 meV !!

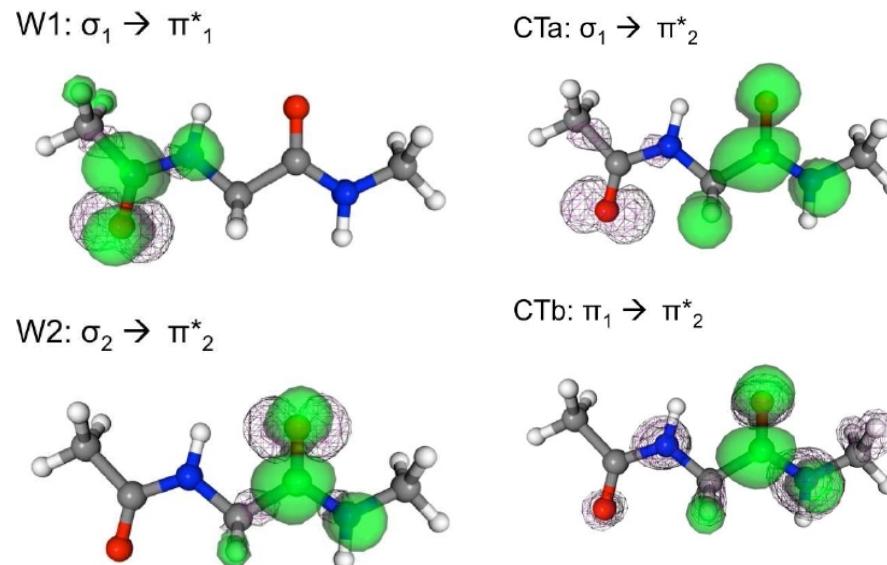
TD-DFT versus Bethe-Salpeter for charge-transfer excitations

Charge-transfer excitations requiring long-range electron-hole interaction is a well known failure of TD-DFT with local kernels
Similar situation in solids with extended Wannier excitons.

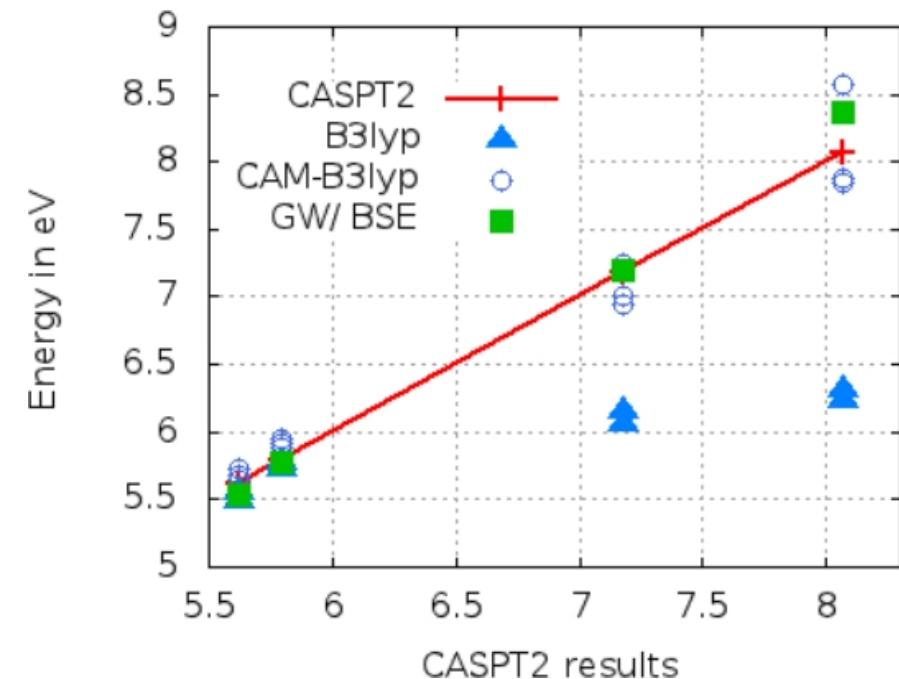


Drew and Head-Gordon, JACS 2004 => organic donor-acceptor complexes
Botti *et al.*, PRB 2004 => long range kernel for semiconductors

A very simple example: dipeptide intramolecular charge-transfer states



(excitonic states: electrons are green, holes are grey)



(Faber, Boulanger, Duchemin, Blase, JCP 2013)