Electronic and Optical Excitations in Confined Nanostructures: Density Functional versus Many-body Methods

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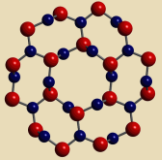
Outline



- Introduction
  - Achievements and Deficiencies of DFT
  - Many-Body Theory Alternative to DFT
- GW & BSE for Electronic and Optical Excitations
  - Levels of Approximation
  - Excitons
- Examples (Benzene, Si_nH_m)
- Comparison of Many-Body vs DFT methods for Ag Clusters
  - ΔSCF vs GW
  - TDLDA vs BSE

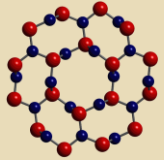
Collaborators

M. Tiago

J. C. Idrobo

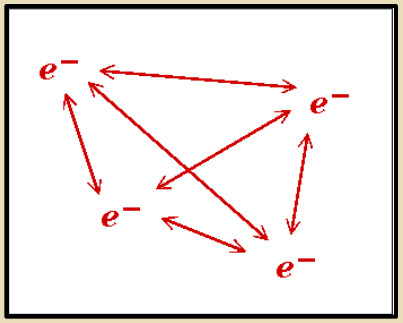
K.Baishya

Density-Functional Theory

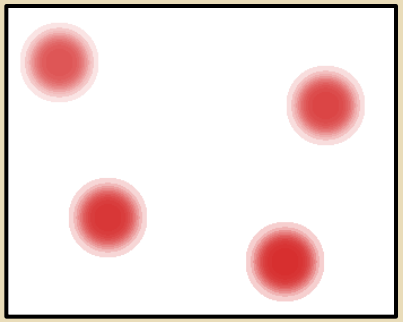


- Self-consistent mean-field theory.

A generic electronic system is fully described by a single scalar function, the electron density $n(\mathbf{r})$.



$|\Psi\rangle$



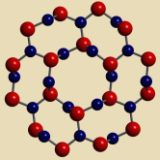
$n(\mathbf{r})$

- Formally exact.

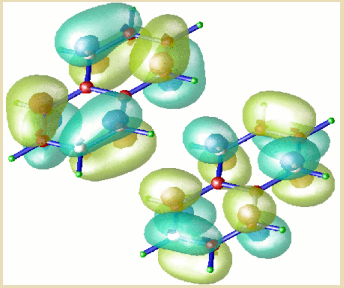
In practice, the exchange-correlation functional is modeled.

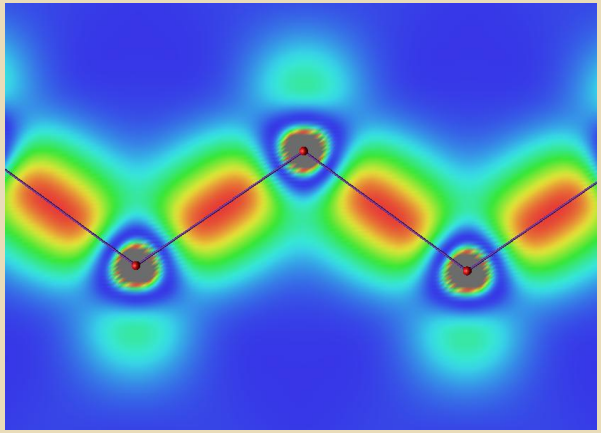
- Good description of weakly correlated, homogeneous systems.

Achievements of DFT



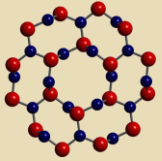
- First-principles electronic band theory.
- Quantum molecular dynamics.
- Quantum chemistry.



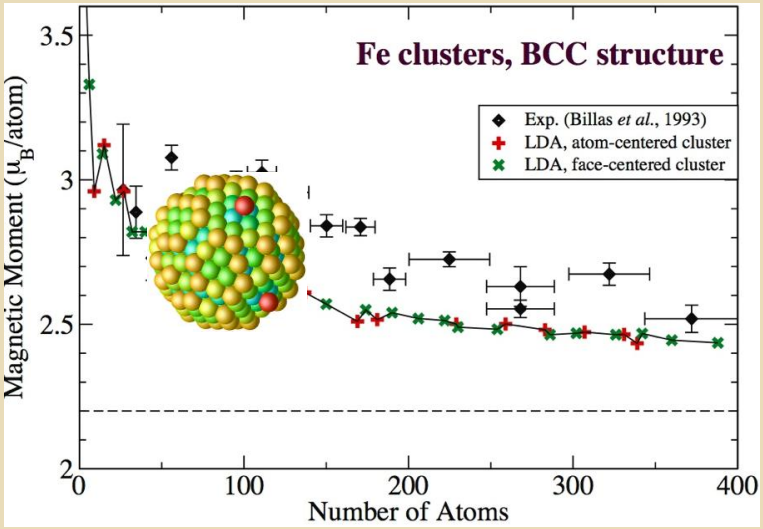


In 1998, Walter Kohn shared the Nobel Prize in Chemistry, “for his development of the density-functional theory”.

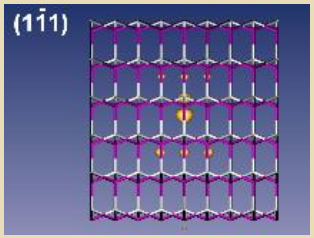
Achievements of DFT

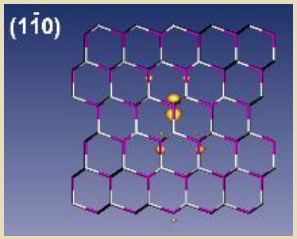


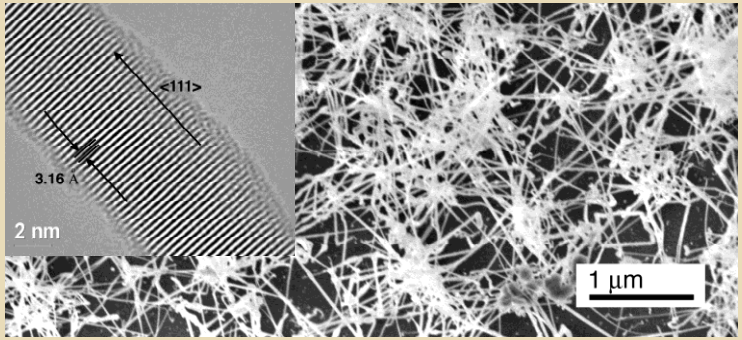
Magnetization in iron clusters



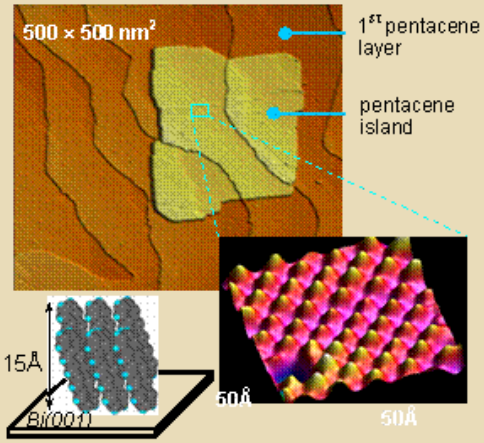
Doped semiconductor nanowires



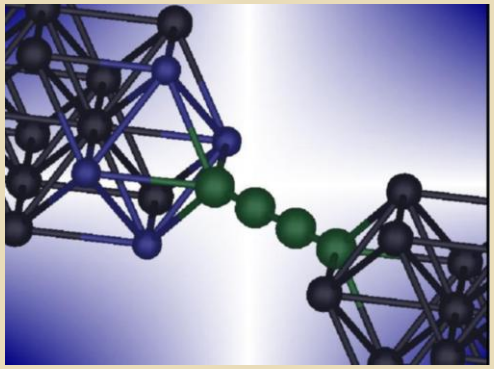




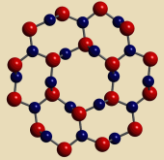
Growth of organic crystals



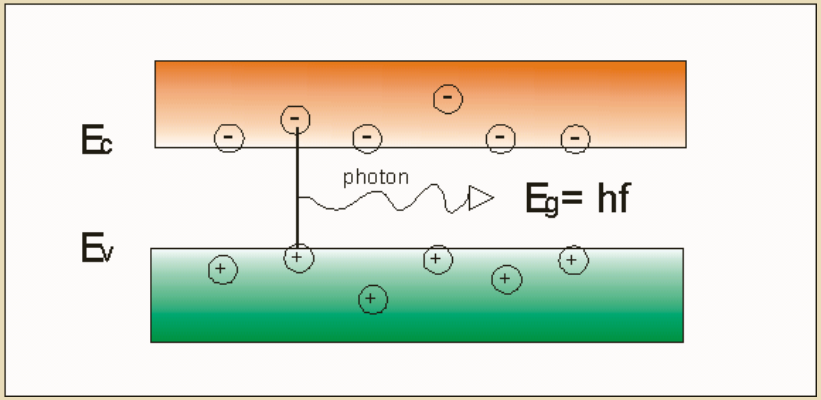
Transport through nanojunctions



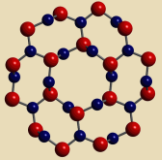
Deficiencies of DFT



- Exchange-correlation functional cannot be improved systematically.
- Complex magnetic ordering is still a challenge.
- Band gap is systematically underestimated.
- It does not give excitation energies: no optical spectroscopy.



Are there alternatives to DFT?

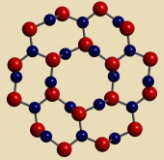


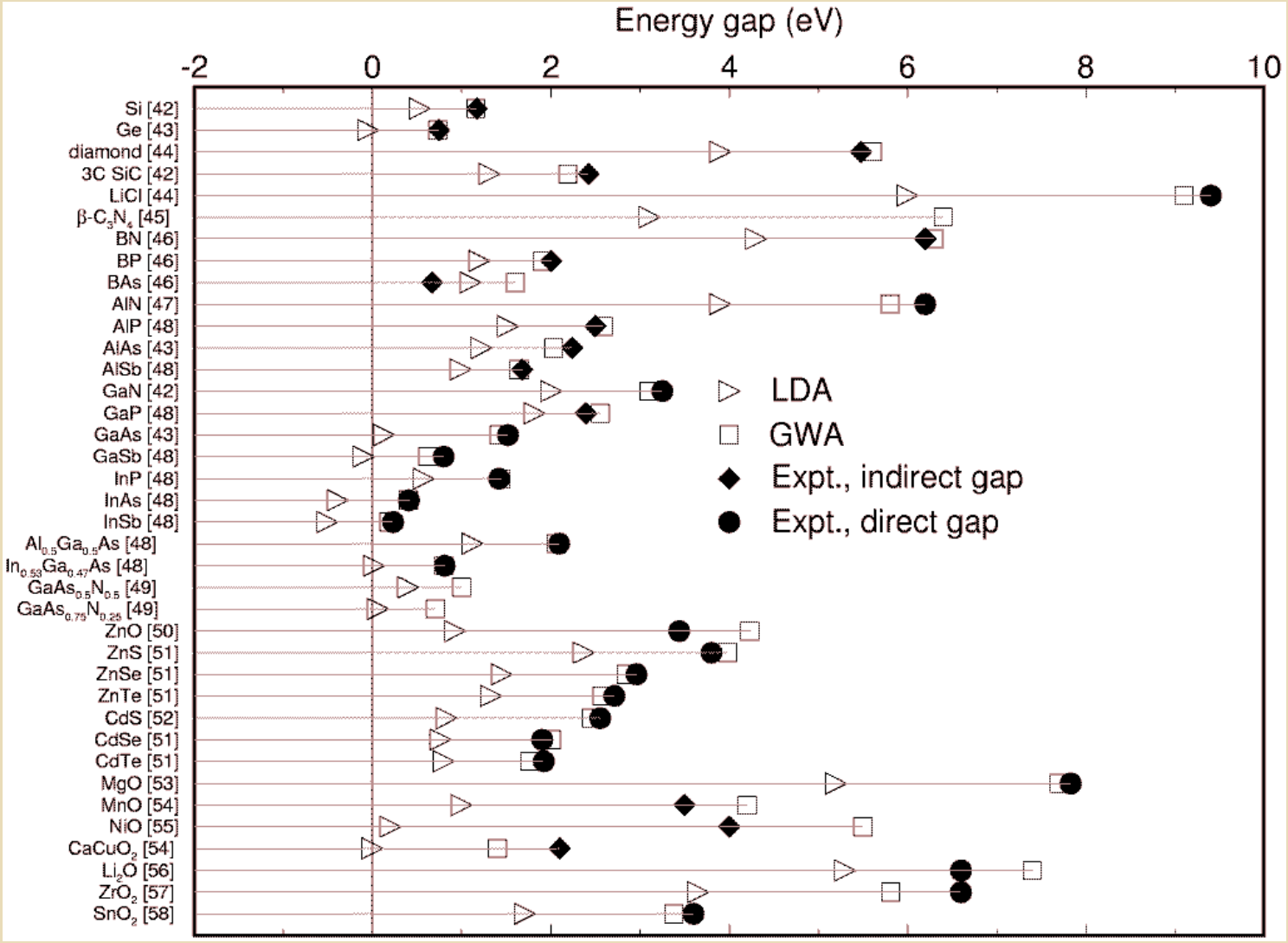
Yes! Many

Many-body Green's function methods

- Gives band gap greatly improved from DFT.
- Does not require phenomenological parameters.
- Exact. If you manage to sum up all Feynman diagrams.
- Amenable to high-performance computing.

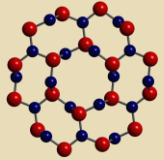
Band gaps of semiconductors

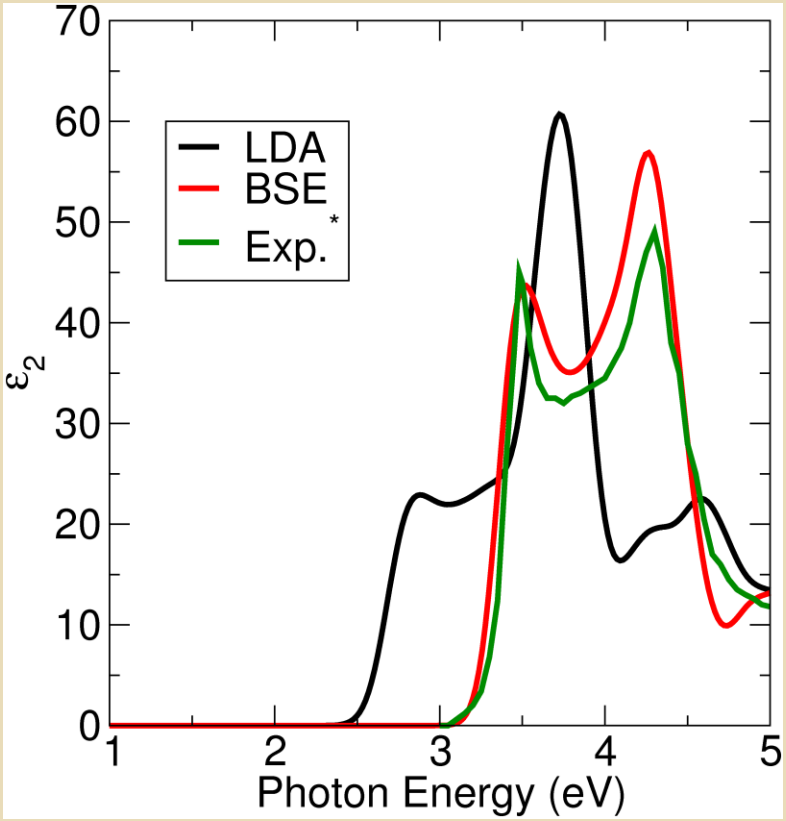




Compiled by Aulbur, Jönsson, Wilkins, Solid State Phys. **54**, 1(2000)

Bulk Si: Imaginary part of the dielectric function



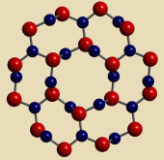


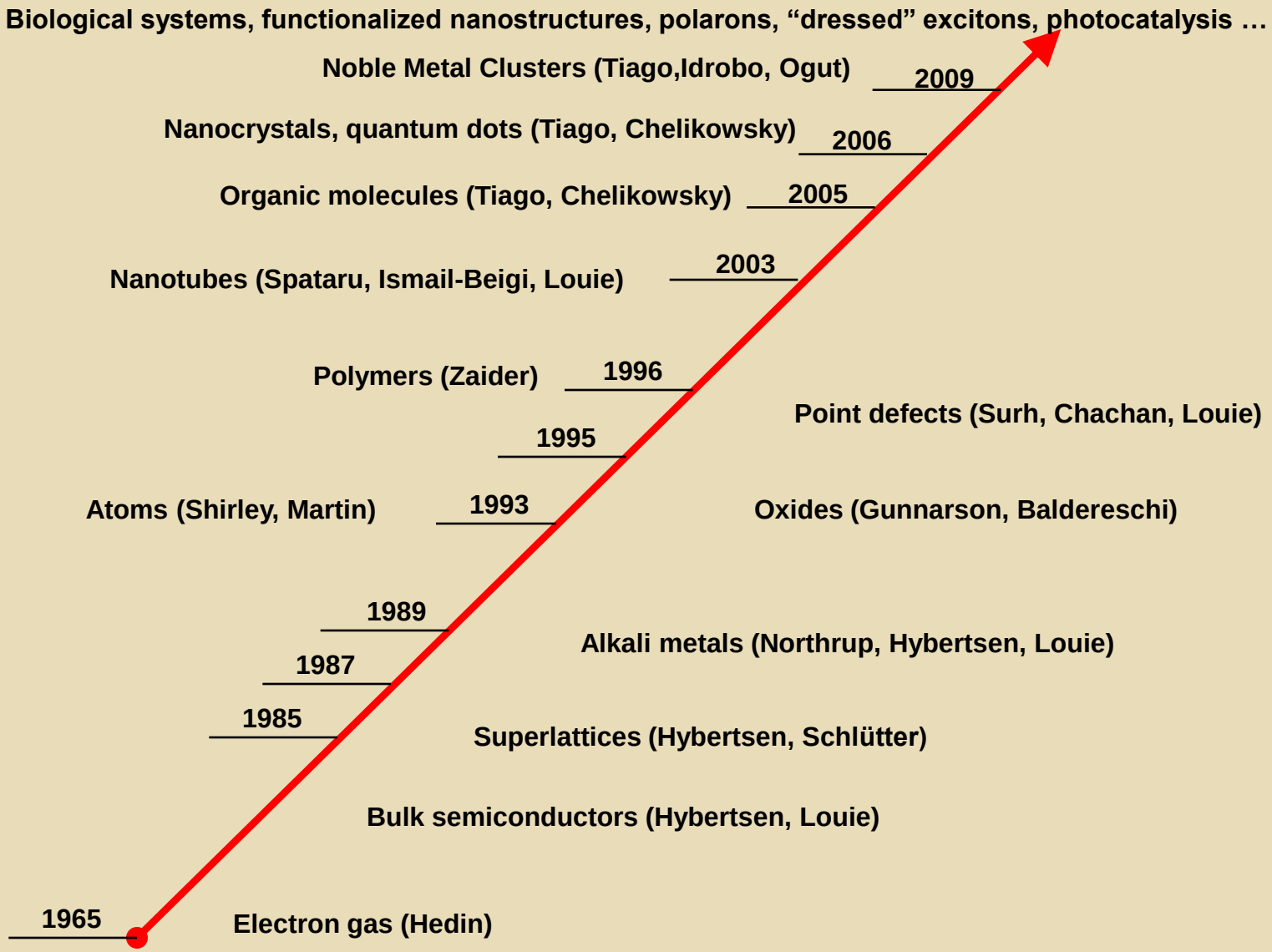
	E_{gap}	$\Gamma^{v}_{25'} \rightarrow \Gamma^{c}_{15}$	$\Gamma^{v}_{25'} \rightarrow X^{c}_{1}$
DFT	0.46	2.52	0.60
GW†	1.29	3.35	1.44
Exp.*	1.17	3.35	1.3

† Hybertsen and Louie (1986).
*Lautenschlager *et al*. (1987).

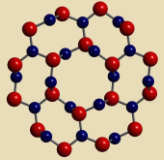
- Photoluminescence
- Exciton dynamics
- Photoemission spectroscopy
- Transport in doped materials

Many-body Green's functions: timeline



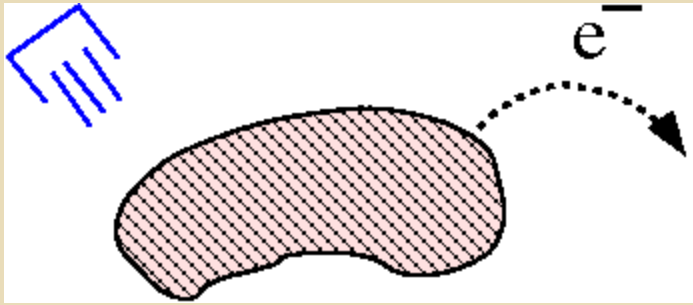


Electronic Band Structure: GW theory



Quasi-particle approximation:

$$G(\mathbf{r},\mathbf{r}';E) = \sum_n \frac{\varphi_n(\mathbf{r})\varphi_n^\star(\mathbf{r}')}{E-\varepsilon_n}$$



Eigenvalue problem:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{ion} + V_H + \Sigma\right]\varphi_n(\mathbf{r}) = \varepsilon_n\varphi_n(\mathbf{r})$$

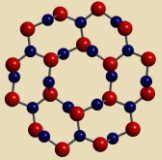
In DFT:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{ion} + V_H + V_{xc}\right]\psi_n(\mathbf{r}) = E_n\psi_n(\mathbf{r})$$

Perturbation theory:

$$\left[H_{DFT} + \Sigma - V_{xc}\right]\varphi_n = \varepsilon_n\varphi_n$$

Levels of approximation:



0-th order: “DFT”

$$\Sigma = V_{xc}$$

Hartree-Fock

$$\Sigma = iGV$$

1-st order: G_0W_0 approximation

$$\Sigma = iG_0W_0$$

1-st order + vertex: G_0W_f approximation

$$\Sigma = iG_0W_0\Gamma_0$$

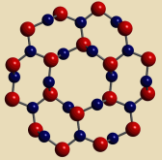
Self-consistent: GW approximation

$$\Sigma = iGW$$

Exact: Hedin’s equations

$$\begin{cases} W = V + VPW \\ P = -iGG\Gamma \\ \Sigma = iG\Gamma W \\ \Gamma = 1 + \frac{\delta\Sigma}{\delta G}GG\Gamma \end{cases}$$

Requirements



1. DFT Green's function:

$$G_0(\mathbf{r},\mathbf{r}';E) = \sum_n \frac{\psi_n(\mathbf{r})\psi_n^\star(\mathbf{r}')}{E - E_n}$$

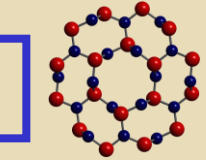
sum over occupied *and* unoccupied energy levels

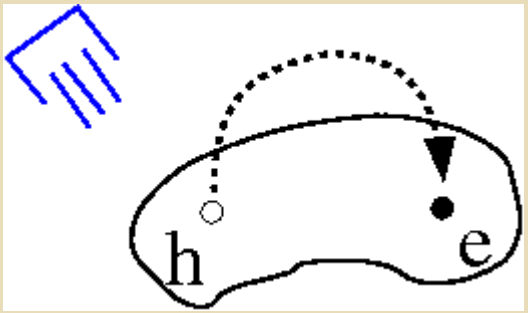
2. G_0W_0 and G_0W_f approximations rely on DFT as a "good starting point".

3. Local, dynamic dielectric screening must be known.

$$W \approx \epsilon^{-1}\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}$$

Optical Excitations: Bethe-Salpeter Equation



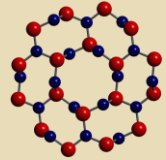


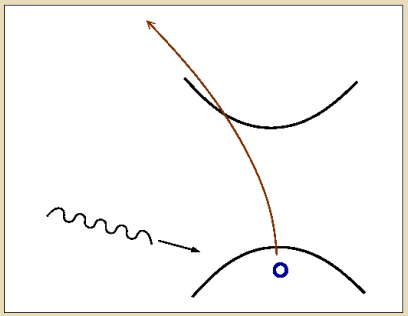
Eigenvalue problem:

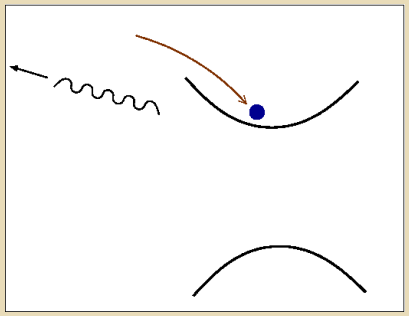
$$\left(\varepsilon_c^{GW} - \varepsilon_v^{GW}\right) A_{cv}^S + \sum_{c'v'} \langle vc|K^{BSE}|c'v'\rangle A_{c'v'}^S = \Omega^S A_{cv}^S$$

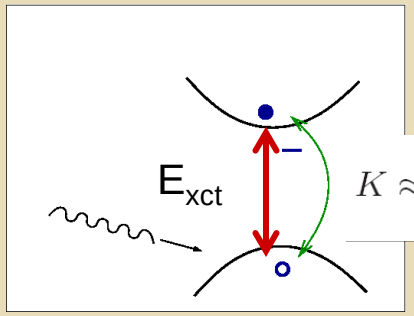
- Many-body expansion of the electron-hole propagator.
- Dynamics of electron-hole excitation obtained by solving the Bethe-Salpeter equation (BSE).
- Requires knowledge of quasiparticle orbitals (get from GW).

Excitons









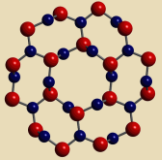
$h\omega = -E_{VBM}$

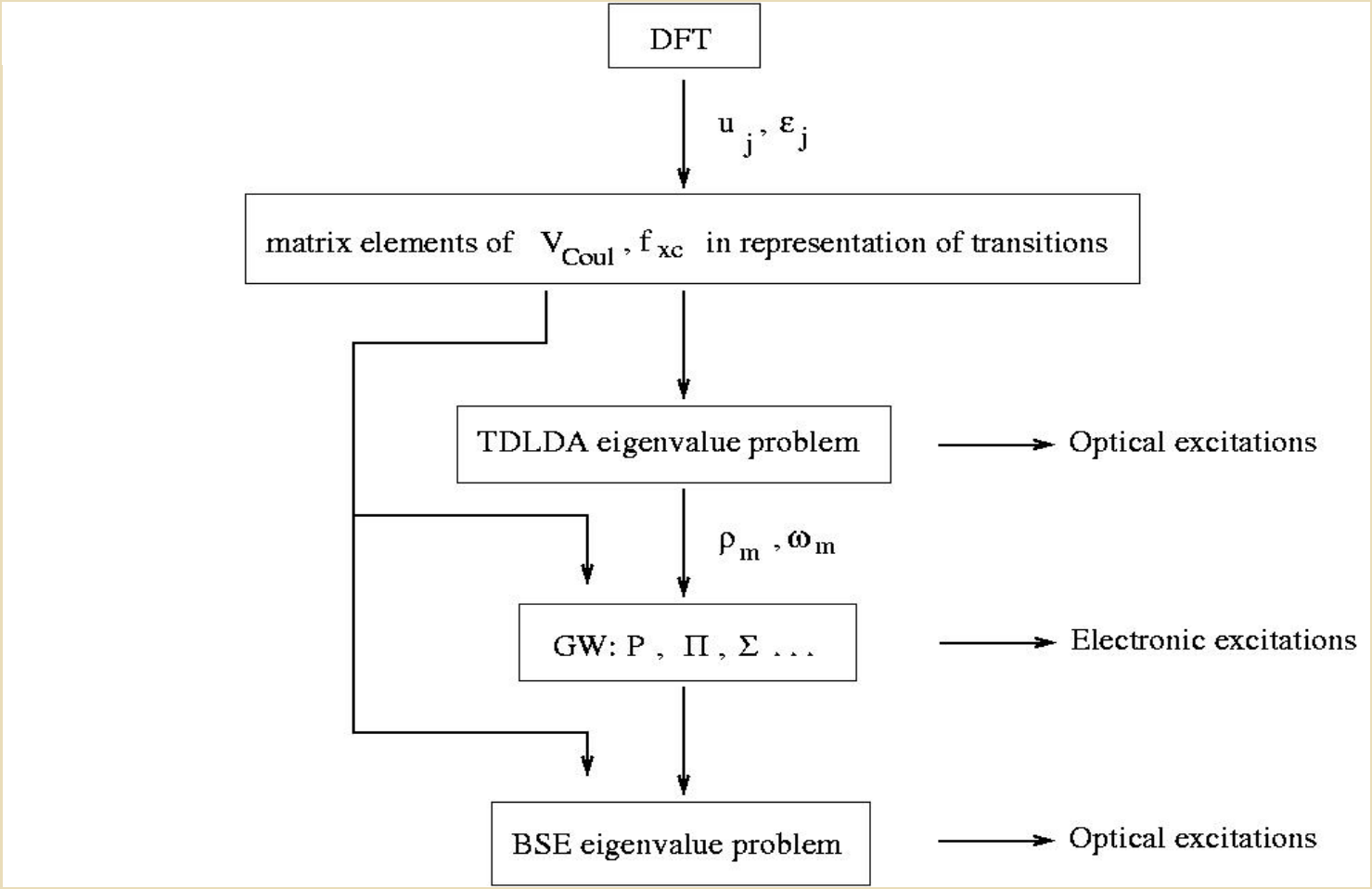
$h\omega = -E_{CBM}$

$h\omega = E_{xct}$

Exciton binding energy : $(E_{CBM} - E_{VBM}) - E_{xct} > 0$

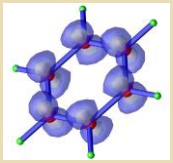
GW/BSE from DFT

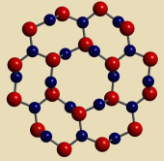




RGWBS Package (free software)

Benzene, C_6H_6

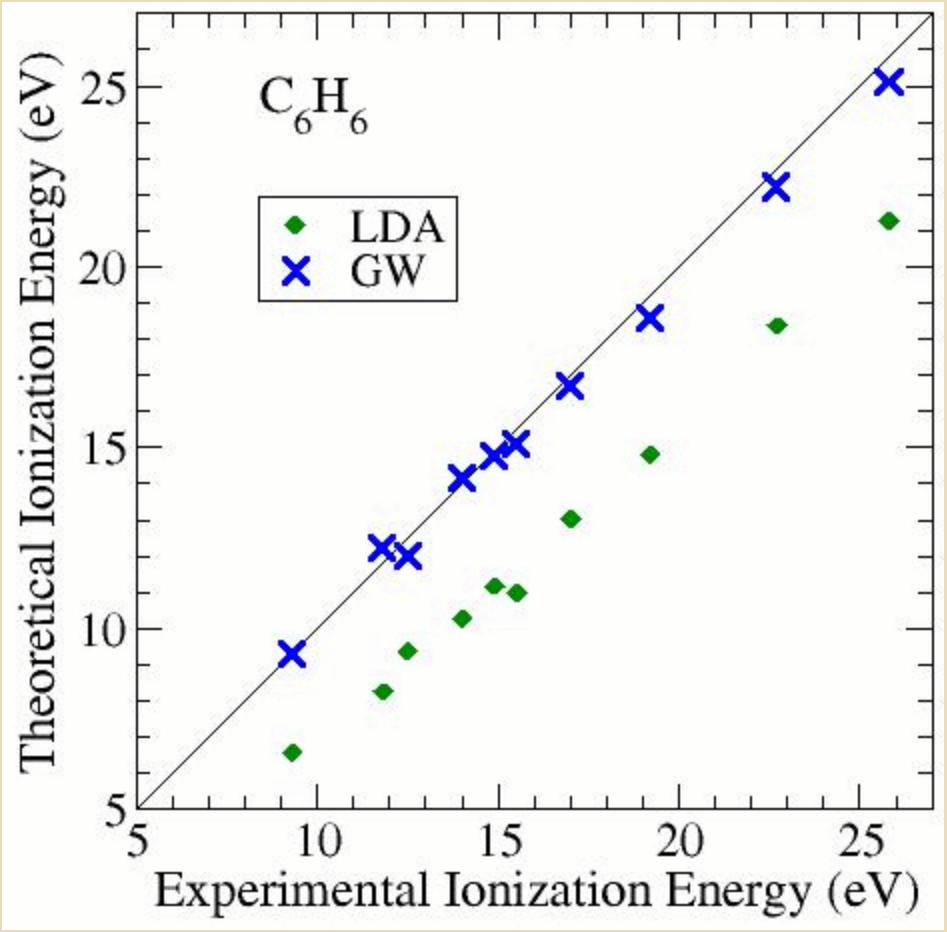




1st Ionization Potential:

	IP (eV)
ΔSCF	9.55
GW	9.31
Exp.*	9.25

* Koch & Otto (1972).

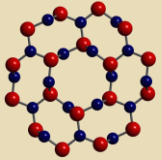


Electron Affinity:

	EA (eV)
ΔSCF	-
GW	-0.99
Exp.*	-1.12

* Resonant transmission: Barrow *et al.* (1987).

Singlet and Triplet Excitations in Benzene

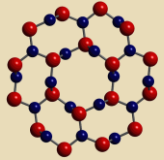


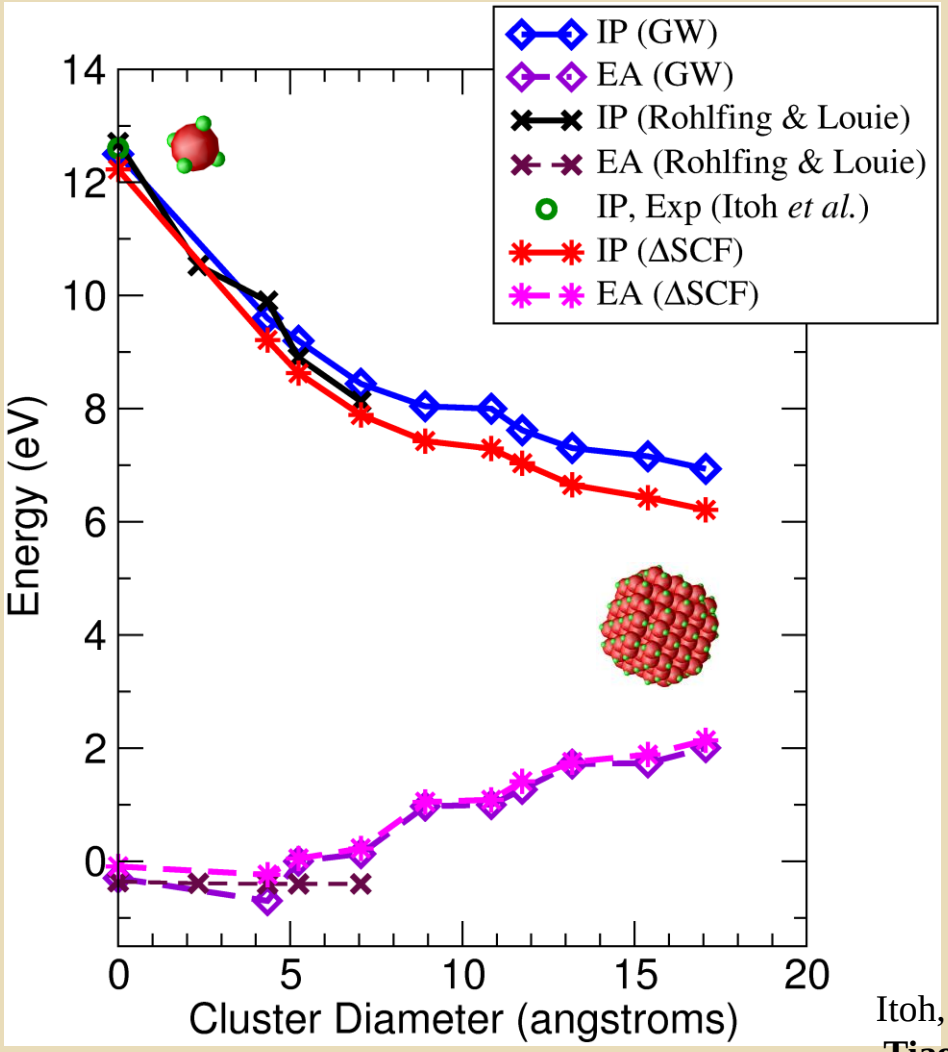
		TDLDA	BSE	Exp.* (eV)	
Triplet	B_{1u}	4.53	3.59	3.9	
Singlet	B_{2u}	5.40	4.86	5.0	dark
	B_{1u}	6.23	6.14	6.2	dark
	E_{1u}	6.9-7.2	7.23	6.9	bright

* Resonant transitions: Doering *et al.* (1969).

- Low-energy excitations are better described within BSE.
- Strong electron-hole binding is missing in TDLDA excitations.

Si_nH_m: Electron Affinity and First Ionization Potential



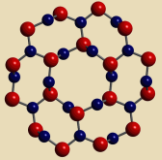


$$\Sigma = i\,\mathbf{GW}\Gamma_{\mathbf{LDA}}$$

- ΔSCF predicts the correct EA.
- IP differs by ~0.7 eV:
  - self-interaction effects;
  - wrong asymptotic behaviour of V_{xc}.
- Same trend in Si nanoshells ($Si_{156}H_{184}$)

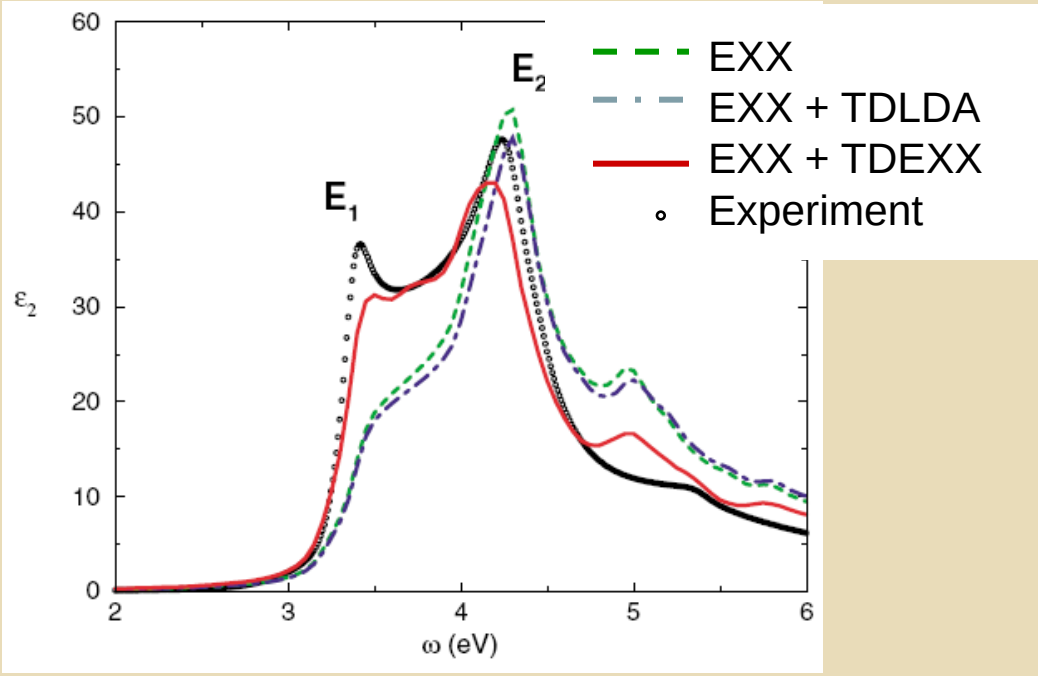
Rohlfing & Louie, Phys. Rev. Lett. **80**, 3320 (1998)
Itoh, Toyoshima & Onuki, J. Chem. Phys. **85**, 4867 (1986)
Tiago and Chelikowsky, Phys. Rev. B 73, 205334 (2006)

TDDFT vs GWBSE



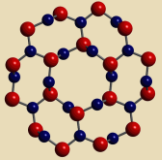
- Two of the state-of-the-art computational techniques for calculating optical excitations in materials: Time-dependent linear response theory using DFT (TDDFT) and adiabatic LDA (TDLDA), and Green's function many-body perturbation methods such as GW+Bethe-Salpeter Equation (GWBSE).

- Computational demand for TDLDA considerably smaller compared to GWBSE. GWBSE, however, gives much more accurate excitation energies in extended systems (excitonic effects).



Kim and Görling, PRL (2002)

TDDFT vs GWBSE



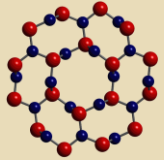
The two methods mostly applied to *sp*-bonded clusters with considerable success.

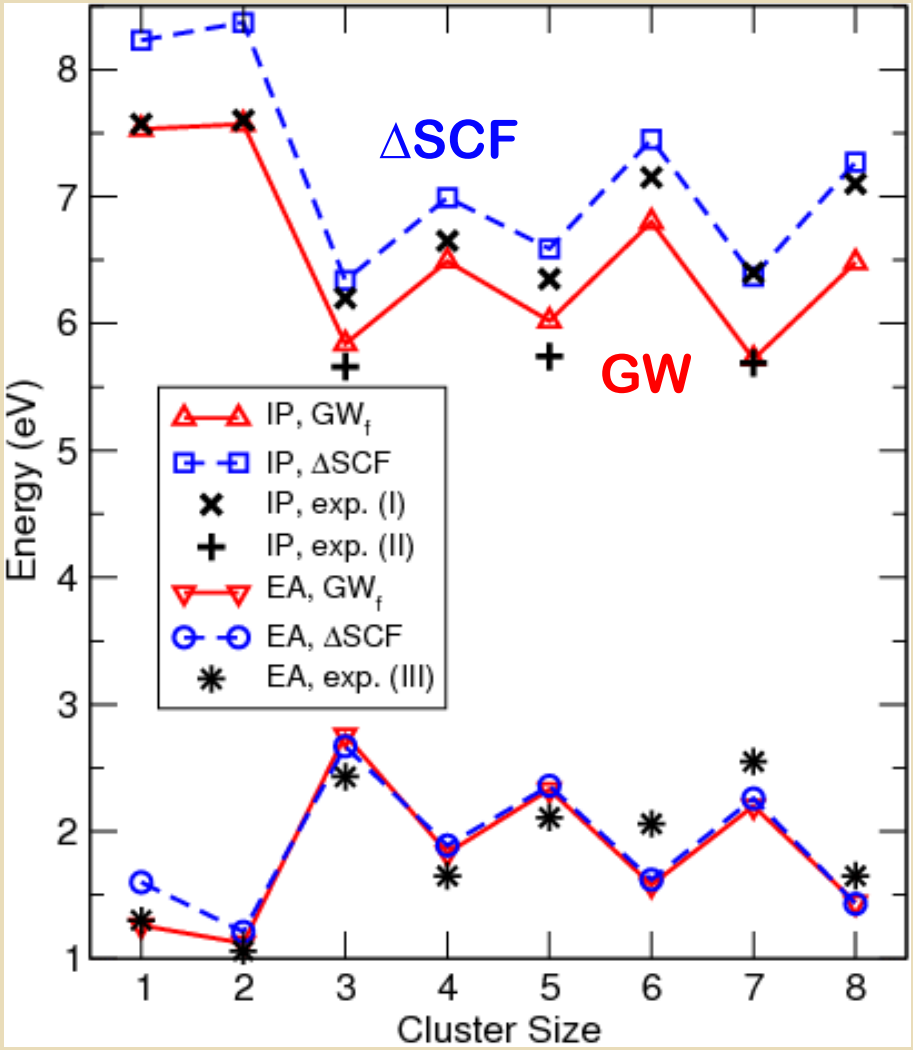
OUR GOAL

Systematic application and comparison of TDLDA and GWBSE in finite systems with tightly bound *d* electrons to investigate the role of *d* electrons in optical excitations.

Chose Ag_n (n = 1- 8) as prototype clusters with shallow (but filled) *d* orbitals. [Tiago, Idrobo, Ogut et al. PRB 79, 155419 (2009)]
Ongoing studies for Cu and Au clusters

Electronic Excitations (IP and EA) Comparison with ΔSCF and Experiment





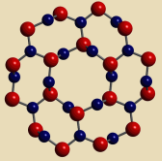
- Within ΔSCF *IP = E(n-1) - E(n)* and *EA = E(n) - E(n+1).*
- Within GW *IP = - HOMO* and *EA = - LUMO.*

- Generally quite good agreement of GW results with experiment (especially Ag and Ag_2). Agreement not so good with ΔSCF.
- Σ very sensitive to the number of virtual orbitals. Convergence accelerated by including a *static remainder* (estimate the numerical error by truncating the sum over virtual orbitals at the level of COHSEX).

	IP (eV)			EA (eV)		
	NS	ST	Exp	NS	ST	Exp
Ag	7.12	**7.53**	**7.57**	0.92	**1.26**	**1.30**
Ag_2	6.27	**7.54**	**7.60**	0.82	**1.12**	**1.06**

(700 orbitals included in Σ)

Electronic Excitations: Case of Ag^+



- Observed good agreement at this level of theory due to the fact that HOMO and LUMO of Ag_n ($n \leq 8$) have almost entirely *sp* character (little or no *d* character). For example, in Ag_2, HOMO is 92% *sp*, 8 % *d*, LUMO is 98 % *sp*, and 2% *d*.

- Singly ionized Ag atom, Ag^+, is a good test case for a system with large (entirely) *d* character in HOMO (and purely *s* character in LUMO!). IP of Ag^+ is the double IP of Ag, which is experimentally available. EA of Ag^+ is the IP of neutral Ag!

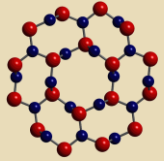
	IP (eV)			EA (eV)		
	NS	ST	Exp	NS	ST	Exp
Ag^+	16.64	**18.92**	**21.50**	7.34	**7.64**	**7.57**

- 2.6 eV underestimate of IP in Ag^+ (4*d* level) due to core-valence separation in the pseudopotential construction (standard $4d^{10}5s^15p^0$ reference). Though 4*s* and 4*p* levels are ~ 80 and 50 eV below the 4*d* level, due to their strong *spatial* overlap with 4*d* levels, exchange and correlation among 4*s*, 4*p*, and 4*d* electrons are not described properly by a Slater type exchange-correlation [Rohlfing et al. PRL 75, (1995)]

- Remedy: Create semi-core pseudopotentials by keeping 4*s* and 4*p* levels in the valence. Use the reference $4s^24p^64d^{10}$ with *sp* core radii ~ 1.1 a.u. Very deep pseudopotentials. Use $h = 0.2$ a.u (limited tests)

	NS	ST	Exp	NS	ST	Exp
Ag^+(semicore)	20.67	**21.85**	**21.50**	7.04	**7.30**	**7.57**

Optical Excitations within GWBSE and TDDFT: Ag and Ag_2



Ag

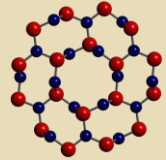
	TDLDA	GWBSE	Experiment
5s → 5p	4.09	3.68	3.74
5s → 6p	5.44	6.05	6.01

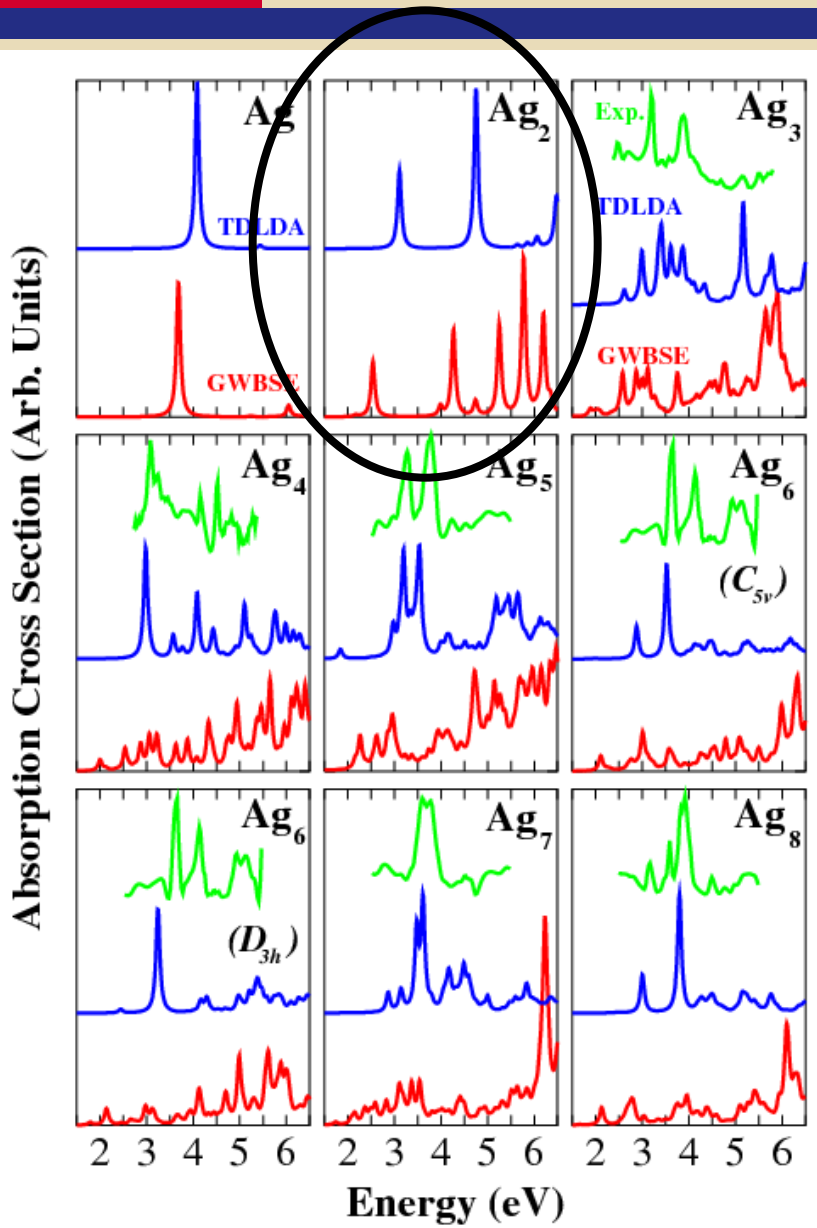
Ag_2

	TDLDA	GWBSE	Experiment
A - X	3.11	2.54	2.85
B - X	3.96	3.99	4.44
C - X	4.75	4.27	4.67

GWBSE clearly performs well for Ag atom. In Ag_2, agreement with experiment not as good. TDLDA in slightly better agreement (perhaps).

Optical Excitations within GWBSE and TDDFT & Comparison with Experiment





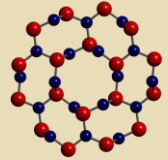
- For n >2, agreement between TDLDA and GWBSE very poor. At low energies, OS from GWBSE quenched significantly, above 5 eV, high OS transitions.

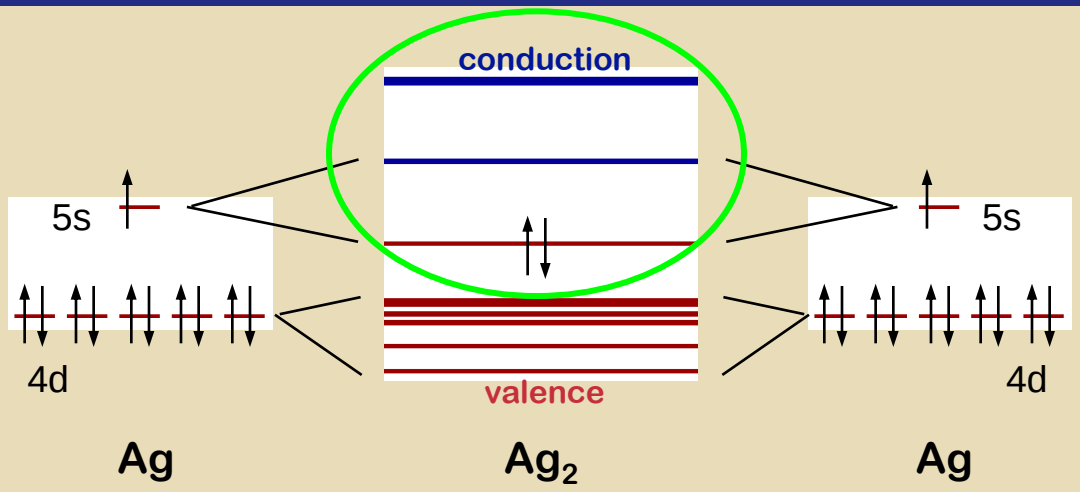
- TDLDA has clearly better agreement with experimental data (esp. $n = 5 - 8$).

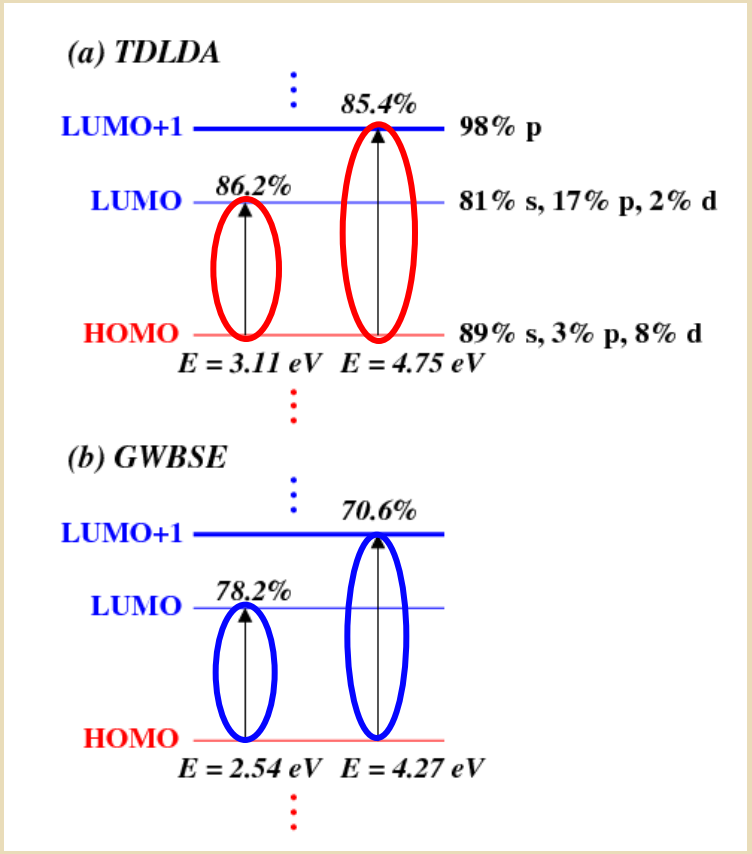
- Exchange-correlation effects involving 4*d* orbitals and strong non-locality of the BSE kernel are the main reasons for this behavior.

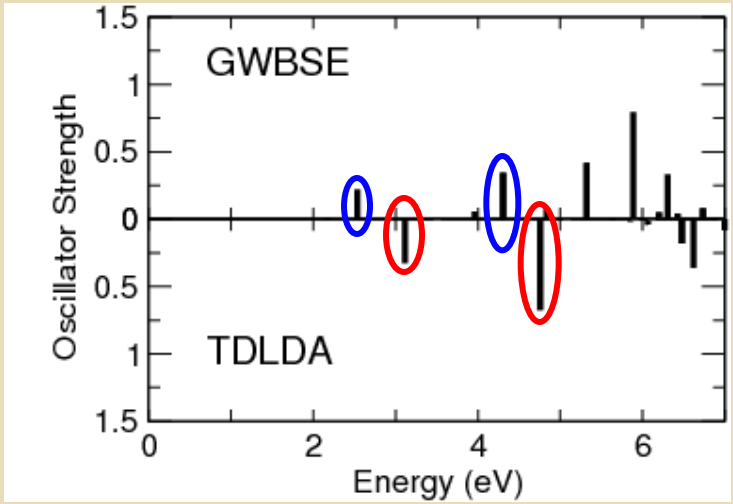
- Even a small mixture of *d* character results in significant quenching and red-shifting of the predicted transitions at the GWBSE level, as best illustrated for the case of Ag_2

Case Study: Ag_2



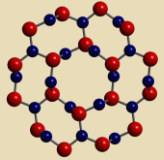




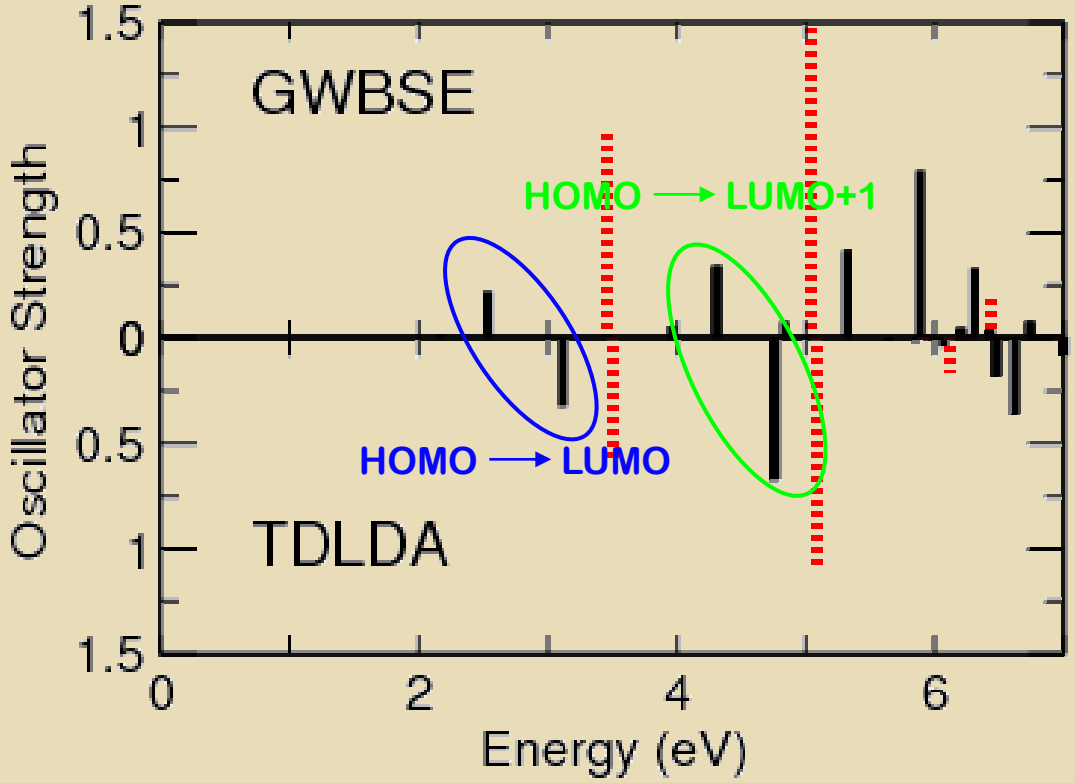


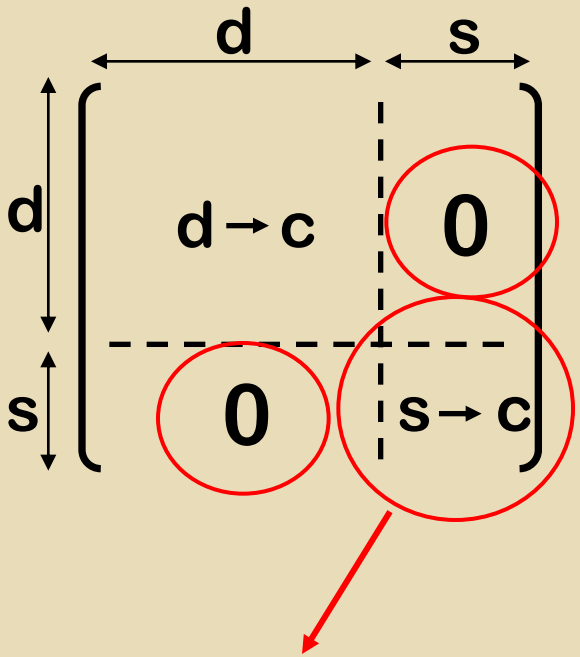
The increase in *d* character of optical excitations at the GWBSE level accompanied by a redshift and quenching of OS compared to TDLDA.

Thought experiment: "Remove" the *d* electrons



d: $v = 1 - 10$ *s*: $v = 11$ (HOMO)





Diagonalize this only

When *d* electrons are removed, very good agreement between TDLDA and GWBSE.