

# Electronic structure

C. Delerue

IEMN – Dept. ISEN

UMR CNRS 8520

Lille – France

[christophe.delerue@isen.fr](mailto:christophe.delerue@isen.fr)

## Ground state properties

Structure, phonons, molecule adhesion, surface reconstructions

- Total energy tight-binding (moments)
- Ab initio Density Functional Theory (DFT)

## Single-particle excitations

Ionization potential (I) , electron affinity (A), “electrical” gap (I-A)

- Semi-empirical methods: tight-binding, pseudopotential, k.p, effective mass
- Ab initio DFT ( $\Delta_{\text{SCF}}$ , hybrid functionals)
- Beyond DFT: GW

## Two-particle excitations

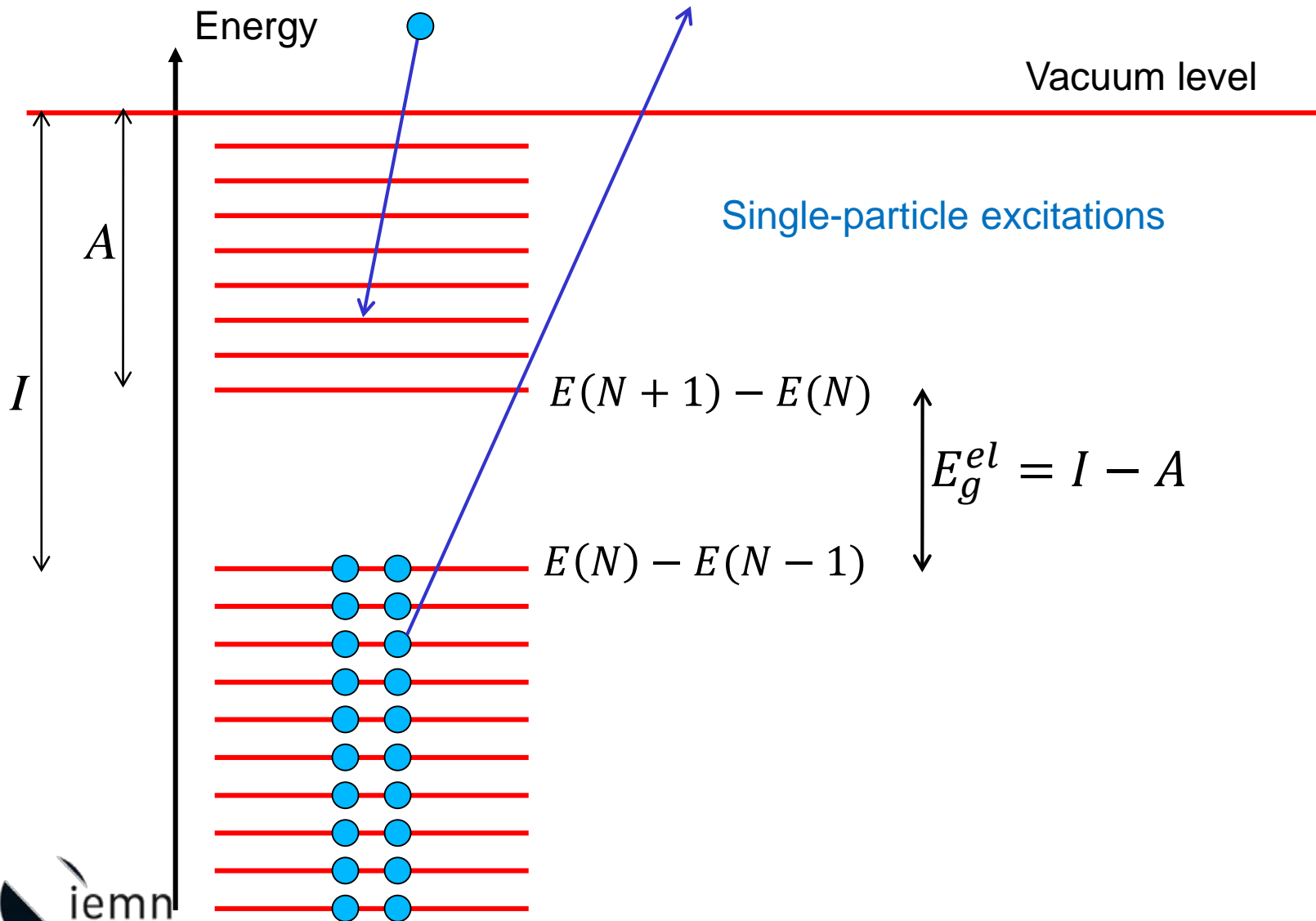
Optical gap, excitons, absorption spectra

- Semi-empirical methods + corrections, + Configuration Interaction (CI)
- Ab initio Quantum Chemistry (Hartree-Fock, CI...)
- Ab initio DFT (hybrid functionals), Time-Dependent-DFT (TDDFT)
- Beyond DFT: GW + Bethe Salpeter

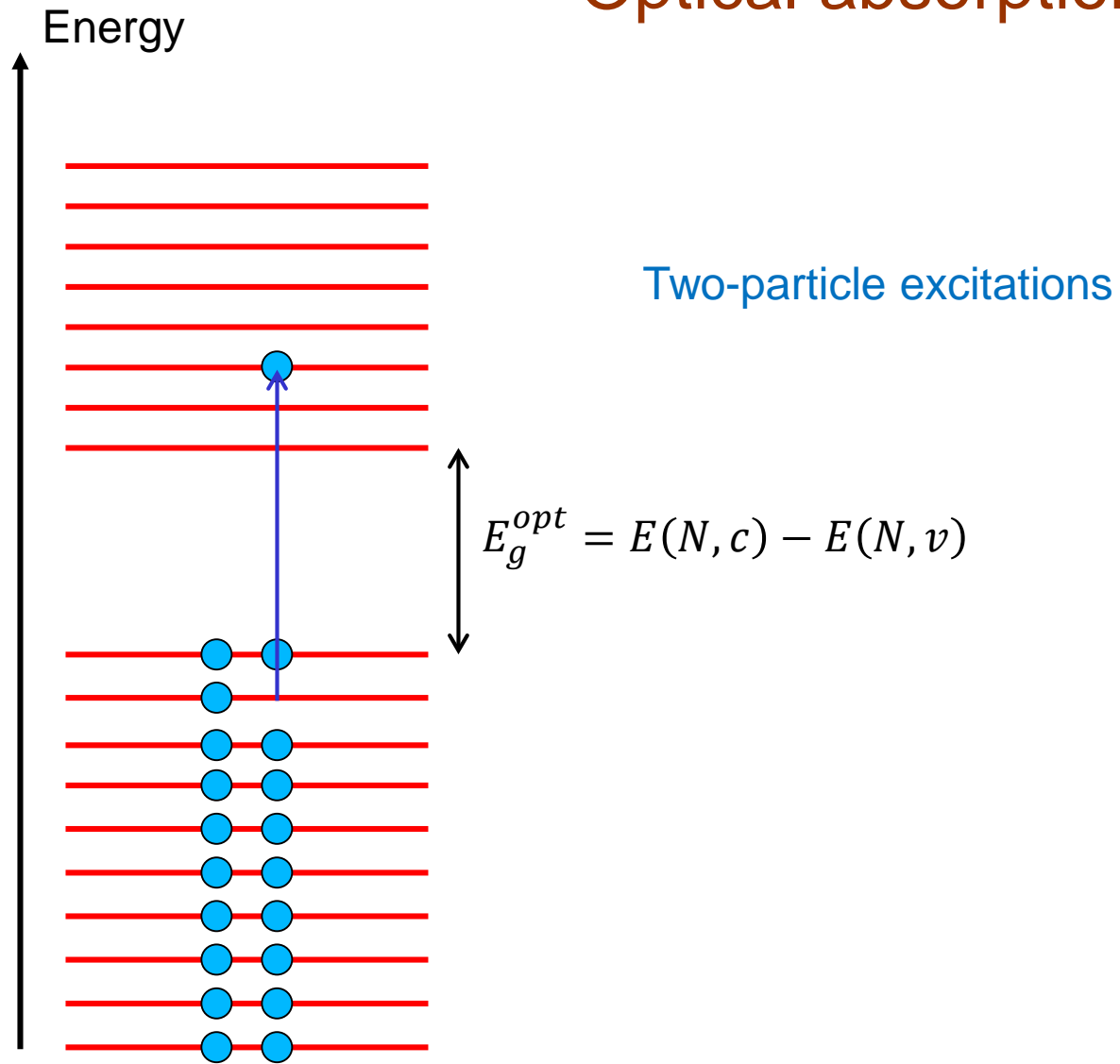
## Strong correlations

- DFT+U, DMFT (GW, hybrid functionals?)

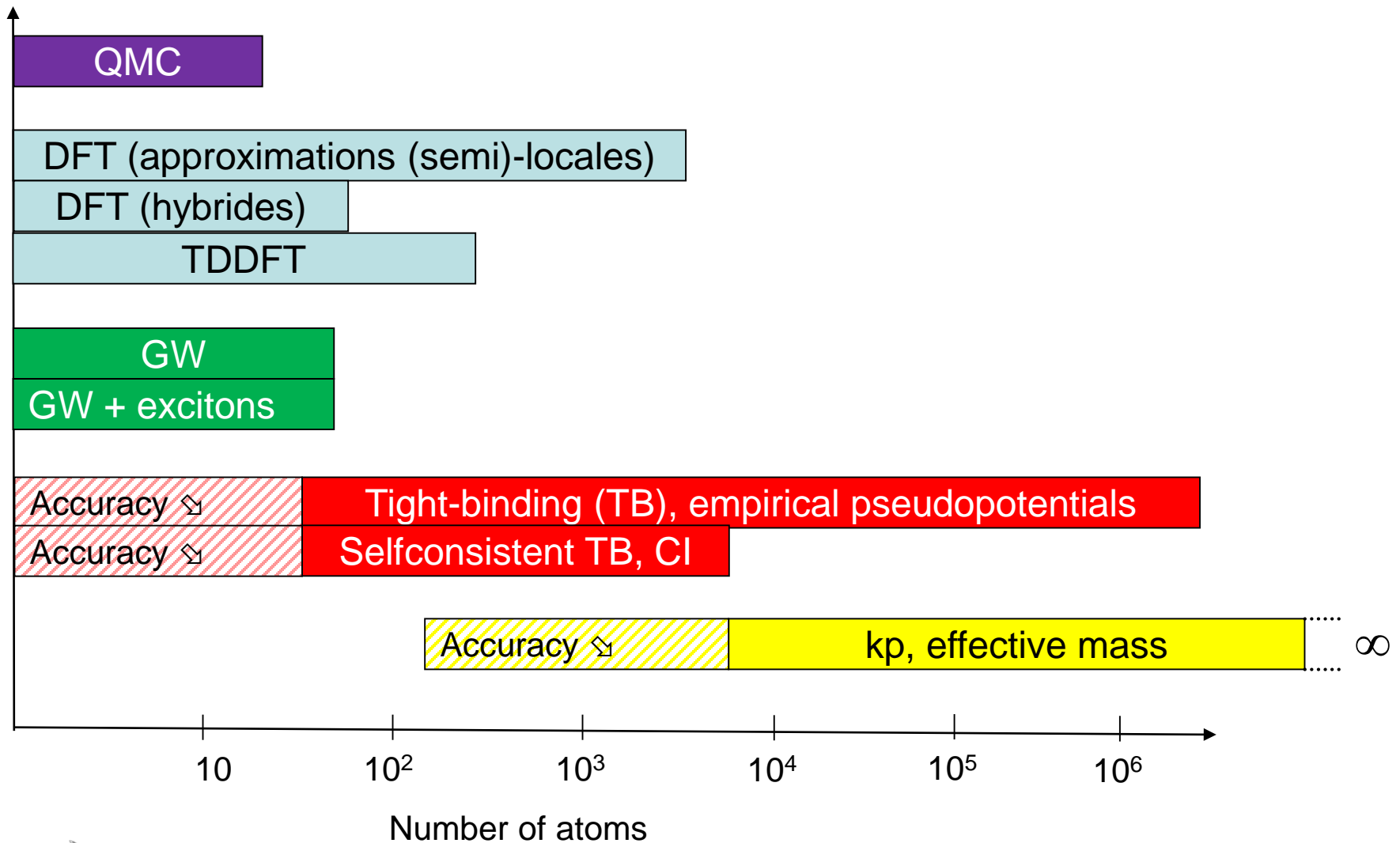
# (Inverse)-Photoemission



# Optical absorption



# Range of applicability



## Ab initio methods

Quantum Monte Carlo

Hartree

Hartree-Fock

DFT

GW

GW + Bethe-Salpeter

TDDFT

## Semi-empirical methods

Tight-binding

# General problem

General problem of  $N$  electrons in the potential  $\Phi_{ext}$  of fixed ions.

$$H = \sum_{i=1}^N \left( \frac{p_i^2}{2m} + \Phi_{ext}(\vec{r}_i) \right) + \frac{1}{2} \sum_{i,j=1}^N \frac{e^2}{r_{ij}}$$

$$H\Psi(\vec{r}_1, \vec{r}_2 \dots \vec{r}_N) = E\Psi(\vec{r}_1, \vec{r}_2 \dots \vec{r}_N) \quad (3N \text{ variables} + \text{spin})$$

Electron motions are correlated due to e-e interactions  
Electrons are fermions  $\rightarrow$  antisymmetric wavefunction

# Quantum Monte Carlo methods

## Resolution of the many-body wavefunction using a Monte Carlo approach

QMC has been applied to:

3D and 2D electron gas.

Band structures of insulators

Defects in semiconductors

Reconstruction of a crystalline surface and molecules on surfaces

Transition metal oxide chemistry

Quantum dots

Optical band gaps of nanocrystals

Solid-state structural phase transitions

Binding of molecules and their excitation energies

Studies of exchange–correlation

Review: R.J. Needs et al, J. Phys.: Condens. Matter 22, 023201 (2010)



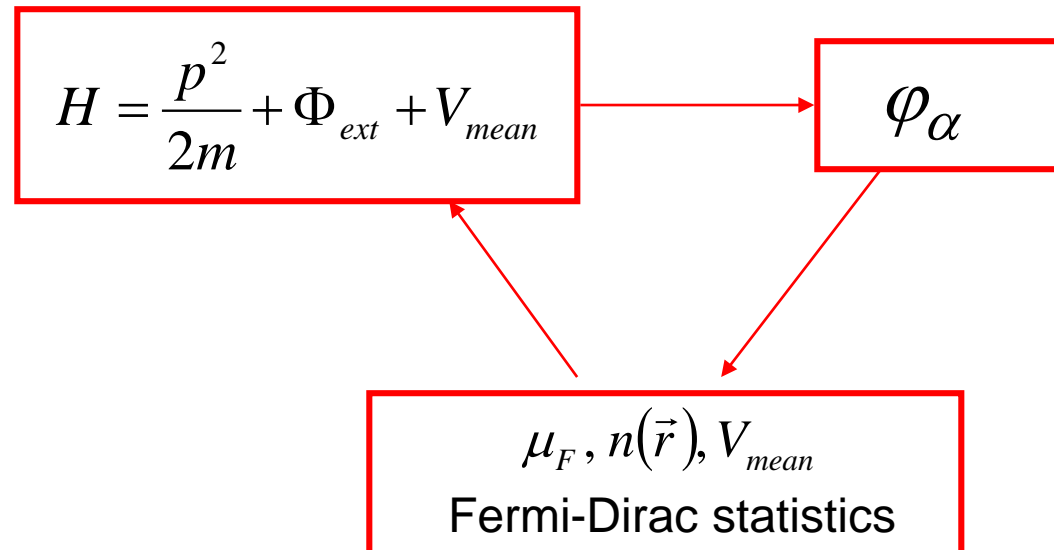
# Mean-field theory

General simplification: mean-field theory

Single-particle moving in a mean (self-consistent) potential.

$$\{h_0 + V_{mean}(\vec{r})\}\varphi_\alpha(\vec{r}) = \varepsilon_\alpha \varphi_\alpha(\vec{r})$$

$$h_0 = \frac{p^2}{2m} + \Phi_{ext}(\vec{r})$$



# Hartree

Hartree approximation:

$$\{h_0 + V_H(\vec{r})\}\varphi_\alpha(\vec{r}) = \varepsilon_\alpha \varphi_\alpha(\vec{r})$$

⇒ Schrödinger-Poisson

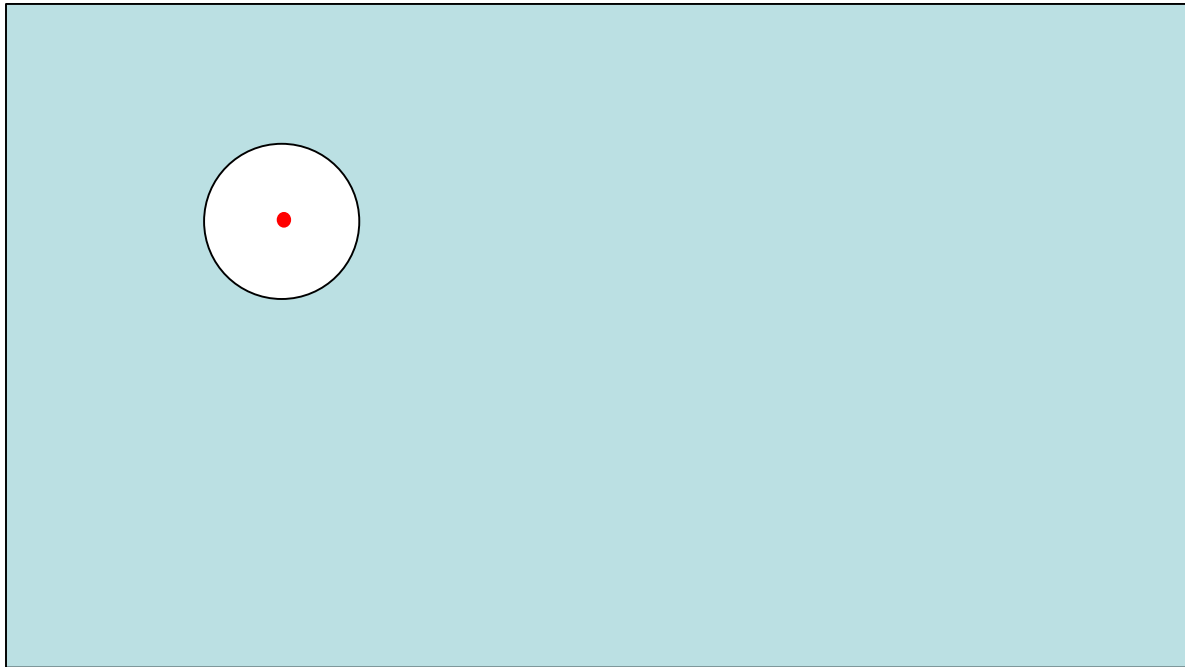
$$V_H(\vec{r}) = e^2 \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} dv' \quad (\text{solution of Poisson equation})$$

$$n(\vec{r}) = \sum_{\beta \text{ OCC.}} |\varphi_\beta(\vec{r})|^2 \quad (\text{electron density})$$

**Electron motions are not correlated:** crude approximation  
**Self-interaction of the electron**

# Exchange & correlation hole

Each electron is surrounded by a XC hole (other electrons are repelled).



Dynamical response of the other electrons: in principle, can be calculated via the frequency-dependent dielectric constant

→ GW

→ Simplified description of the Coulomb hole: [Thomas-Fermi theory](#)

# Exchange & correlation hole

Origin of the hole?

**Correlation (Coulomb) hole:** consequence of the e-e repulsion

**Exchange hole:**

Indiscernable fermions:  $\Psi(\dots\vec{r}_i\dots\vec{r}_j\dots) = -\Psi(\dots\vec{r}_j\dots\vec{r}_i\dots)$

The probability to find two electrons ( $r_i \rightarrow r_j$ ) with same spin at the same position is vanishing.

# Hartree-Fock

Slater determinant as a variational trial function  
⇒ Exchange interaction

$$\{h_0 + V_H(\vec{r})\}\varphi_\alpha(\vec{r}) + \int \Sigma_x(\vec{r}, \vec{r}')\varphi_\alpha(\vec{r}')d\vec{r}' = \varepsilon_\alpha\varphi_\alpha(\vec{r})$$

$$\Sigma_x(\vec{r}, \vec{r}') = - \sum_{\beta \text{ occ.}} \frac{e^2 \varphi_\beta(\vec{r})\varphi_\beta^*(\vec{r}')}{|\vec{r}' - \vec{r}|}$$

Exchange, but no correlation → strong under-binding

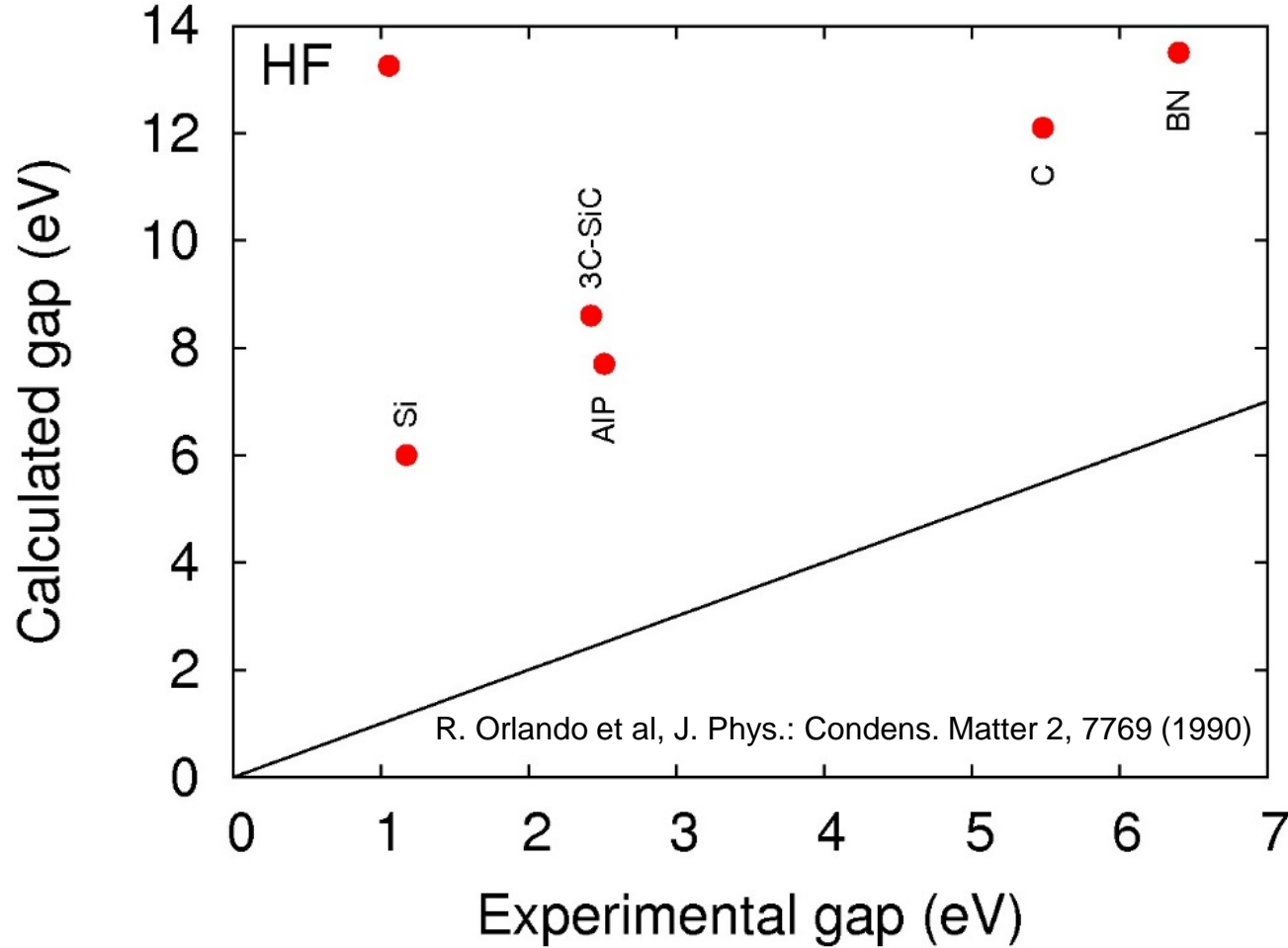
No self-interaction

Complex to implement because

$$\Sigma_x(\vec{r}, \vec{r}') = \text{non-local long-range term}$$

HF not too bad for small molecules, poor for solids

# Hartree-Fock



Poor results for solids: absence of correlation  
HF very problematic for metals

# Configuration interaction

HF + CI:

$$\Phi = a_0\Psi_0 + \sum_{v,c} a_{c,v}\Psi_{c,v} + \sum_{v,c,v',c'} a_{c,v,c',v'}\Psi_{c,v,c',v'} + \text{triple excitations...}$$

Computational difficulty  $\propto e^N$

Provides very accurate results for very small molecules.

# Density functional theory

## DFT



$N$ -electron system of electron density  $n(\vec{r})$ :

$$\int n(\vec{r}) d^3\vec{r} = N$$

Hohenberg, Kohn:

One-to-one mapping between  $n(\vec{r})$  and  $\Phi_{ext}(\vec{r})$

All the observables can be computed from  $n(\vec{r})$

The total energy  $E$  is a functional of the density  $E = E[n]$

Minimization of the energy functional yields the ground-state density.

Kohn, Sham:

Map the interacting system to a non-interacting one with the same density  $n(\vec{r})$

$$n(\vec{r}) = \sum_{\beta \text{ occ.}} |\varphi_{\beta}(\vec{r})|^2$$

KS equation:

$$\{h_0 + V_H(\vec{r}) + V_{xc}[n](\vec{r})\} \varphi_{\alpha}(\vec{r}) = \varepsilon_{\alpha} \varphi_{\alpha}(\vec{r}) \quad E = \sum_{\beta \text{ occ.}} \varepsilon_{\beta}$$

Exchange-correlation potential, universal functional of  $n$   
(but its expression is not known)

Local density approximation (LDA):  $V_{xc}(\vec{r}) = V_{xc}^{hom}[n(\vec{r})]$   
 $V_{xc}^{hom}$  = exchange-correlation potential for the homogeneous gas

Gradient approximation (GGA: PBE...):  $V_{xc}(\vec{r}) = V_{xc}[n(\vec{r}), \vec{\nabla}n(\vec{r})]$

## Assessment of DFT-LDA or GGA

### Good:

Many efficient softwares

Structural properties: 2-3% error

Elastic constants: 10%

Phonons: 10%

### Bad:

Strongly correlated systems (e.g., transition metal oxides)

Van der Waals bonding missing

Band gap problem

Description of electronic excitations

## Cohesive energy of elemental crystals (GGA/PBE)

$\Delta E_{\text{coh}}$

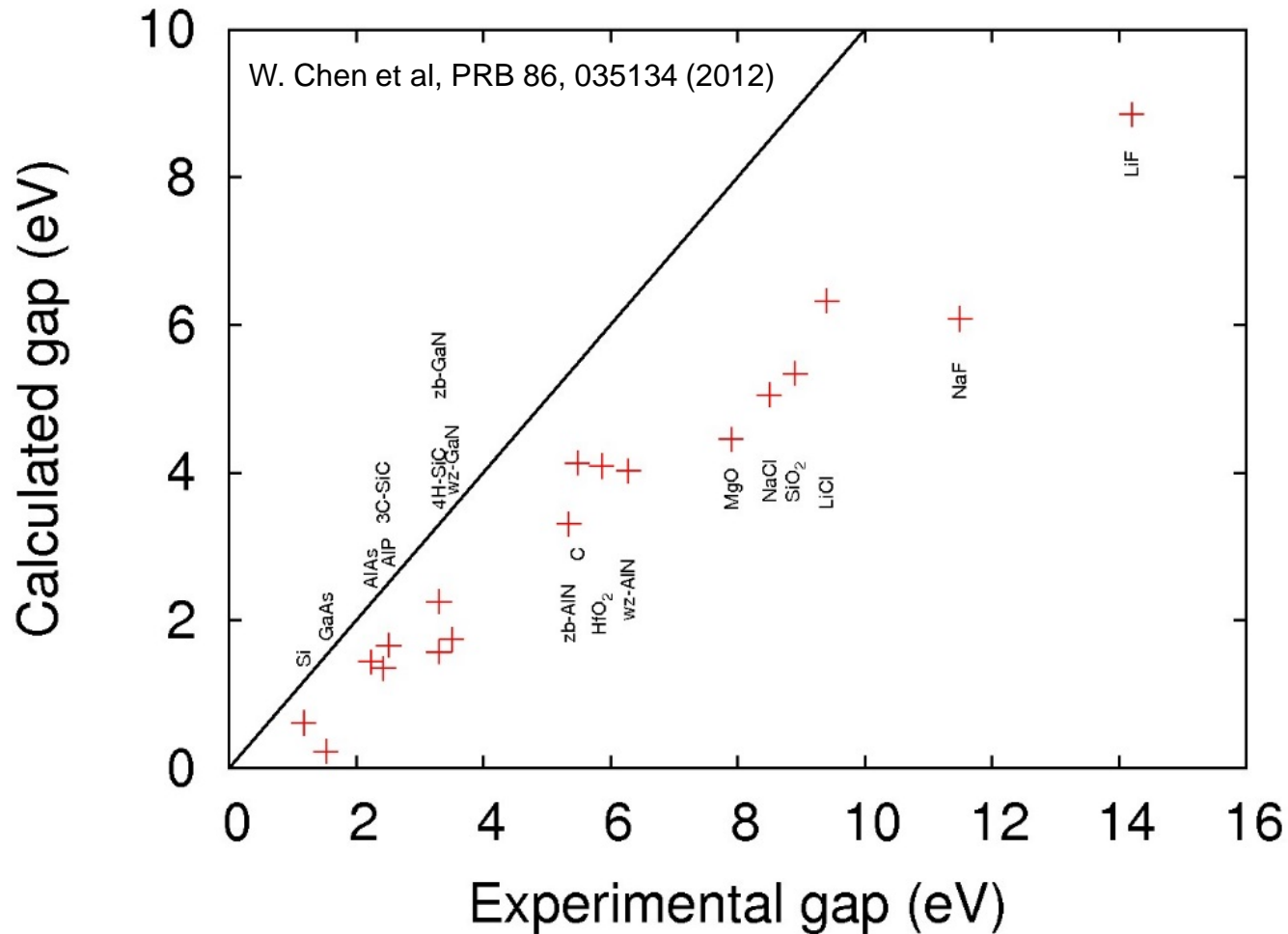
H																	He
Li	Be											B	C	N	O	F	Ne
4%	8%											6%	5%	6%	17%	40%	31%
Na	Mg											Al	Si	P	S	Cl	Ar
4%	2%											0%	3%	1%	6%	3%	7%
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
8%	3%	5%	12%	11%	3%	30%	12%	16%	8%	1%	20%	7%	4%	1%	6%	10%	80%
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
10%	7%	5%	0%	9%	9%	1%	2%	2%	6%	16%	37%	9%	0%	2%	10%	15%	84%
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
11%	1%	8%	3%	2%	1%	2%	3%	0%	9%	19%	69%	20%	4%	5%	8%		81%

K. Lejaeghere et al, Critical Reviews in Solid State and Materials Sciences 39, 1 (2014)

# Gap problem in DFT

(Kohn-Sham gap, from M. Hybertsen and S.G. Louie)

	LDA	Experimental
C	3.9	5.48
Si	0.5	1.17
Ge	-0.26	0.74
GaAs	0.12	1.52
AlAs	1.28	2.24
LiCl	6.0	9.4



DFT-LDA (GGA) strongly underestimates the bandgap of insulators

# Failure of (semi-)local approximations of DFT

## DFT: theory for the ground state

In principle, it cannot be used to describe excitations

## Problems:

The eigenvalues of the KS equation have no physical meaning

The exchange-correlation potential is approximated

(true exchange-correlation potential must be discontinuous across the gap)

Self-interaction problem

## Solutions:

Many-body theory beyond DFT: GW, Bethe-Salpeter

Time-dependence: TDDFT

Hybrid functionals

# Experimental situation / theory

## Different types of excitations

- 1) Single-particle excitations: (inverse)-photoemission, tunneling...  
quasi-particle approach (GW), hybrid functionals
- 2) Two-particle excitations: optical absorption...  
GW+e-h interaction (Bethe-Salpeter), TDDFT, hybrid functionals
- 3) Collective electronic excitations, plasmons: EELS  
TDDFT
- 4) Collective electronic + nuclei excitations: dissociation of molecules,  
Coulomb explosion of clusters, chemical reactions  
TDDFT + nuclei dynamics (classical or quantum)



# GW

## Basic principles

[Further information](#)

References:

Onida et al, Rev. Mod. Phys. 74, 601 (2002).

L. Hedin & S. Lundqvist, Solid State Physics 23, Academic Press (1969)

# Self-energy

## Quasiparticle approach

Low-lying excitations can be described as single-particle excitations

Dressed particle = particle + its polarization cloud

## Exact equation:

$$\{h_0 + V_H(\vec{r})\}f_\alpha(\vec{r}) + \int \Sigma(\vec{r}, \vec{r}', \varepsilon_\alpha^{qp})f_\alpha(\vec{r}')dr' = \varepsilon_\alpha^{qp} f_\alpha(\vec{r})$$

$\Sigma(\vec{r}, \vec{r}', \varepsilon)$  is the self-energy  
= non-local, non-Hermitian, energy-dependent operator  
= effective potential (beyond Hartree) for an electron or hole added to the system

Exact expression  $\Sigma$  of is not known!

## Many-Body Perturbation Theory

Expansion of  $\Sigma$  in terms of the dynamically screened e-e interaction

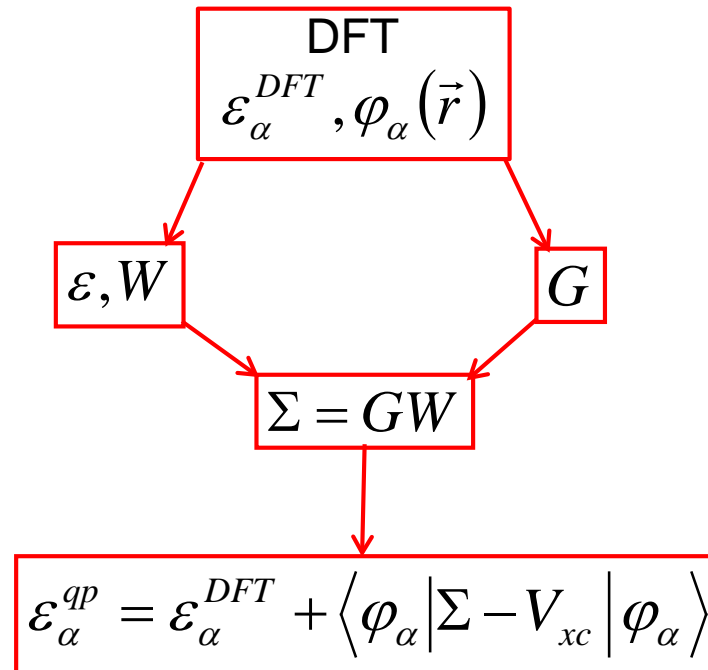
$$\Sigma \equiv GW$$

$G$  = many-body Green's function

$$W(\vec{r}, \vec{r}', \omega) = \int \varepsilon^{-1}(\vec{r}, \vec{r}'', \omega) v(\vec{r}'', \vec{r}') dr''$$

with

$$v(\vec{r}, \vec{r}') = \frac{e^2}{|\vec{r} - \vec{r}'|}$$

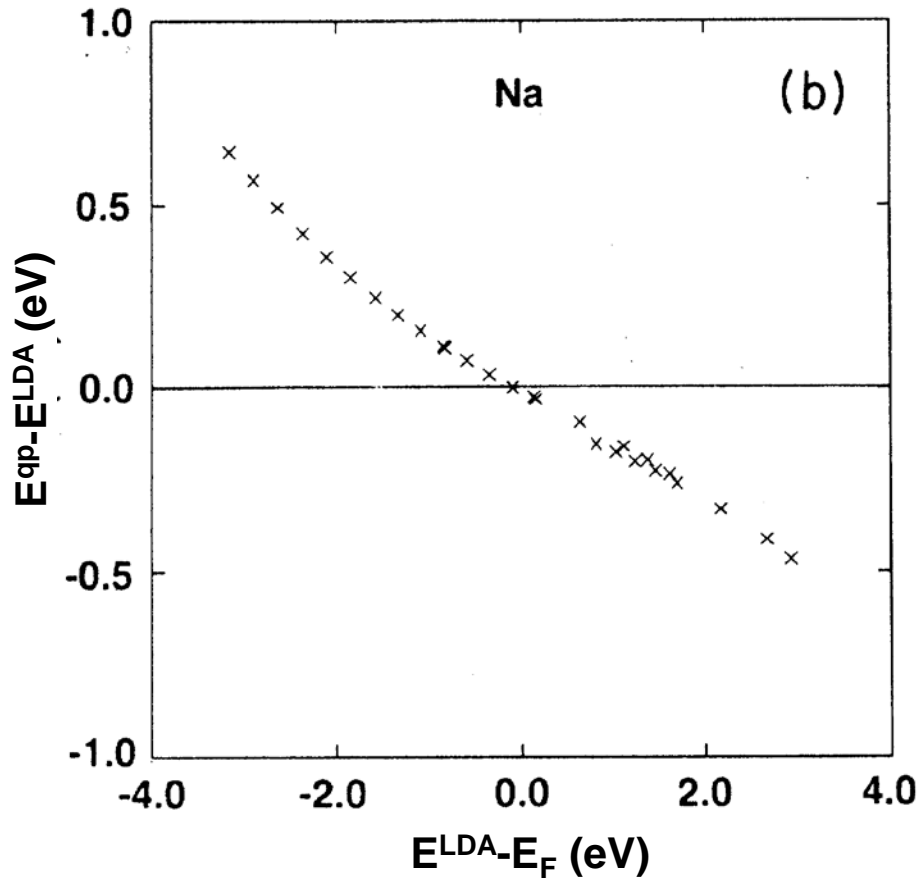


Self-consistent schemes also exist but are very costly:

- Self-consistency over the energies
- Self-consistency over the energies and the wave-functions

# Quasiparticle correction

Case of a nearly-free-electron metal: Na



Occupied bandwidth (eV)

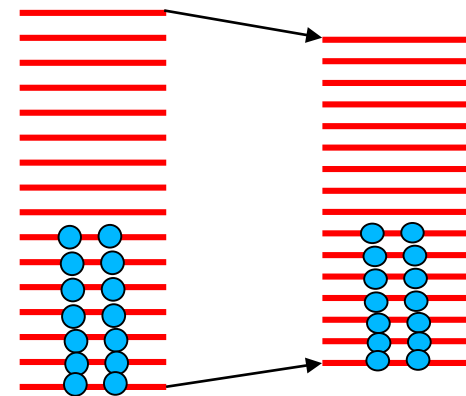
LDA: 3.15

GW: 2.52\*, 2.81\*\*

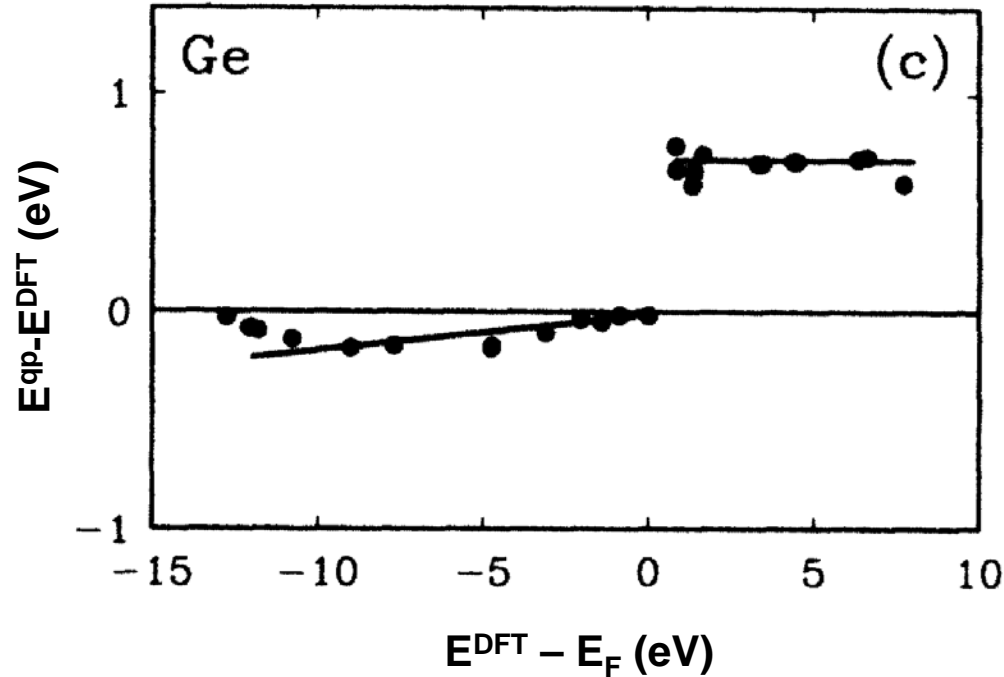
Exp: 2.65

\* Nothrup et al, PRB 39, 8198, 1989

\*\* Cazzaniga et al, PRB 77, 035117, 2008



# Quasiparticle correction

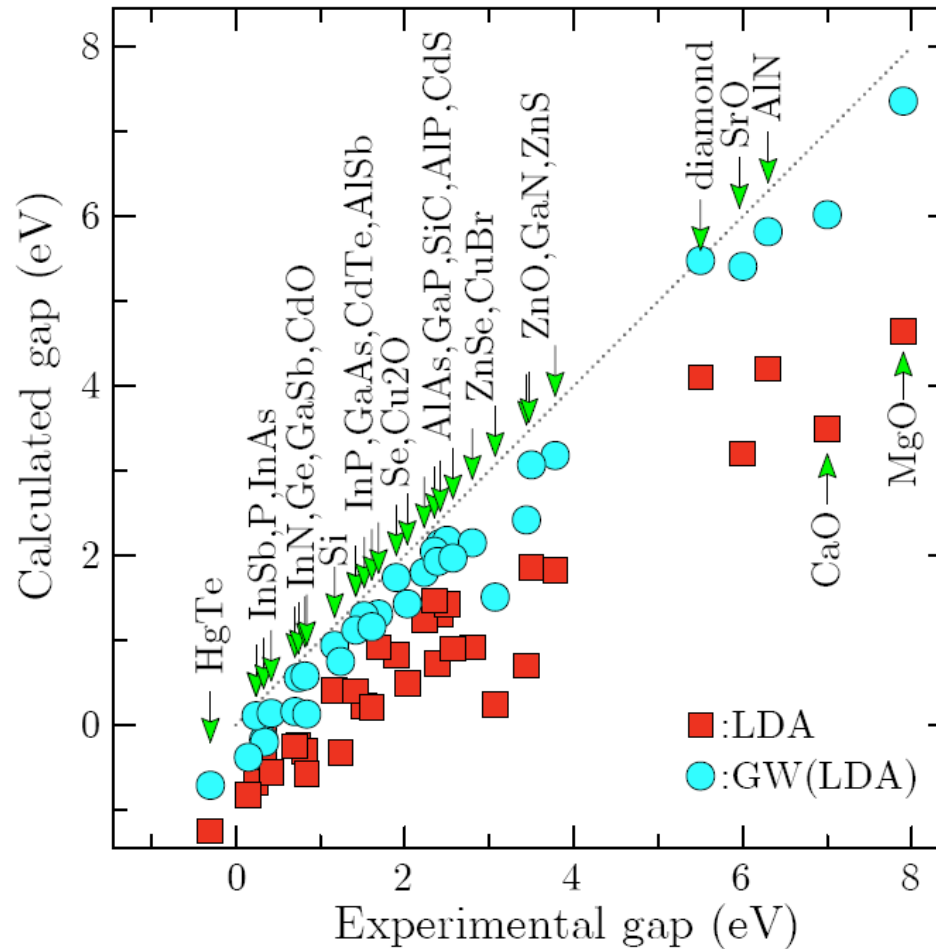


Hybertsen et al, Phys. Rev. B 34, 5390–5413 (1986)

In semiconductors and insulators:

Discontinuity of the quasiparticle correction at the gap  $\Rightarrow$  opening of the gap.

# Quasiparticle correction



Non self-consistent  
scheme  $\equiv G_0W_0$

[adapted from van Schilfgaarde et al., PRL **96**, 226402 (2006)]

# Excitonic effects

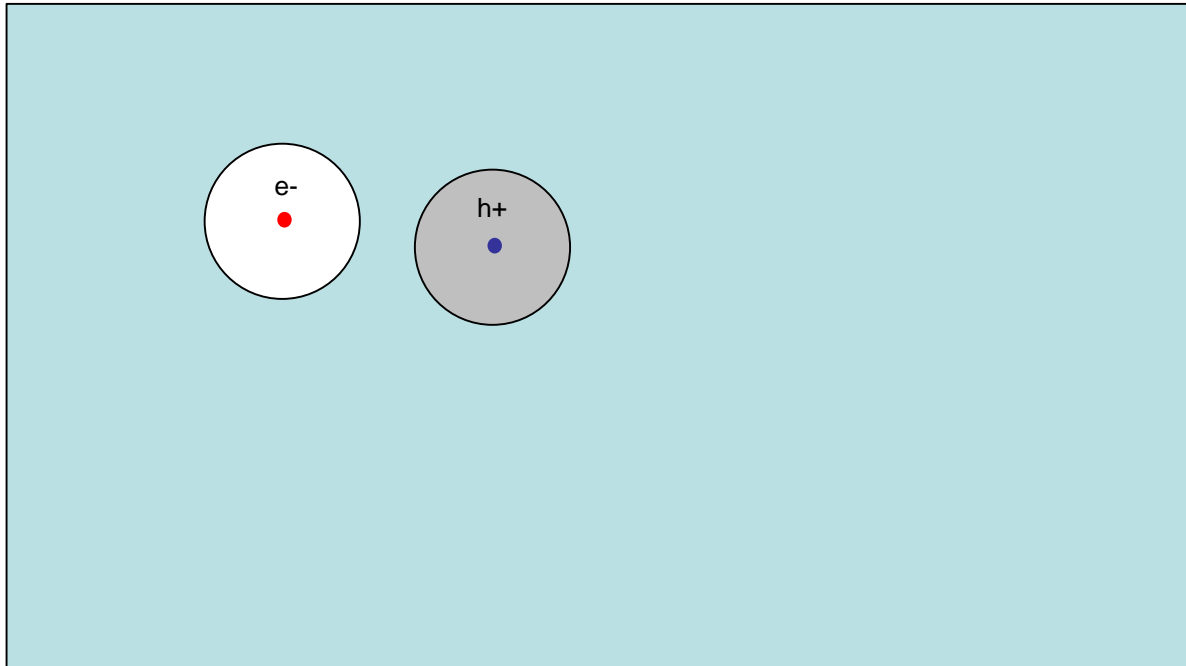
## Bethe-Salpeter equation

### Basic principles

Reference:  
Onida et al, Rev. Mod. Phys. 74, 601 (2002).



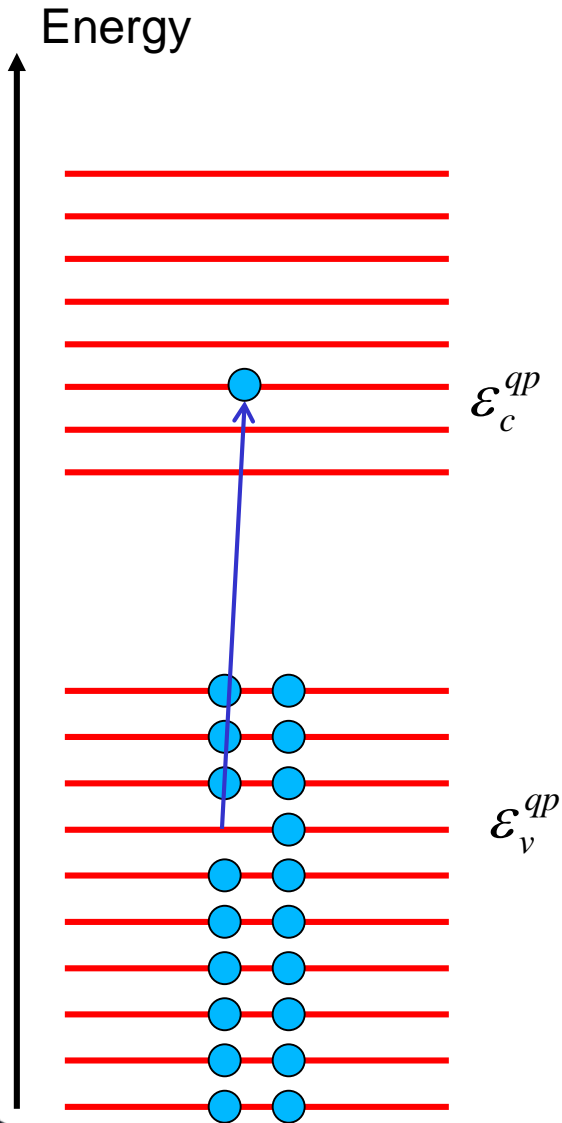
# Excitonic effects



Two-particle problem  $\Rightarrow$  Bethe-Salpeter equation

Includes the dynamically screened interaction between the quasiparticles

# Excitonic effects



## Practical implementation

- 1) Calculate the wave-functions in DFT
- 2) Calculate quasiparticle corrections in GW
- 3) Consider a set of pair states  $|vc\rangle$
- 4) Build an excitonic hamiltonian  $H^{qp} + H^{eh}$
- 5) Diagonalization
- 6) Calculation of the optical matrix elements

$$\begin{array}{cccc}
 & \dots & |vc\rangle & |v'c'\rangle & \dots \\
 \dots & \left( \begin{array}{cccc}
 \dots & \dots & \dots & \dots \\
 |vc\rangle & \dots & \mathcal{E}_c^{qp} - \mathcal{E}_v^{qp} + \langle vc | H^{eh} | vc \rangle & \langle vc | H^{eh} | v'c' \rangle & \dots \\
 |v'c'\rangle & \dots & \langle v'c' | H^{eh} | vc \rangle & \mathcal{E}_{c'}^{qp} - \mathcal{E}_{v'}^{qp} + \langle v'c' | H^{eh} | v'c' \rangle & \dots \\
 \dots & \dots & \dots & \dots & \dots
 \end{array} \right) & \dots & \dots & \dots
 \end{array}$$

# Excitonic effects

$$\begin{array}{cccc}
 & \dots & |vc\rangle & |v'c'\rangle & \dots \\
 \dots & \left( \begin{array}{ccc}
 \dots & \dots & \dots \\
 \dots & \varepsilon_c^{qp} - \varepsilon_v^{qp} + \langle vc|H^{eh}|vc\rangle & \langle vc|H^{eh}|v'c'\rangle & \dots \\
 \dots & \langle v'c'|H^{eh}|vc\rangle & \varepsilon_{c'}^{qp} - \varepsilon_{v'}^{qp} + \langle v'c'|H^{eh}|v'c'\rangle & \dots \\
 \dots & \dots & \dots & \dots
 \end{array} \right) & & \dots
 \end{array}$$

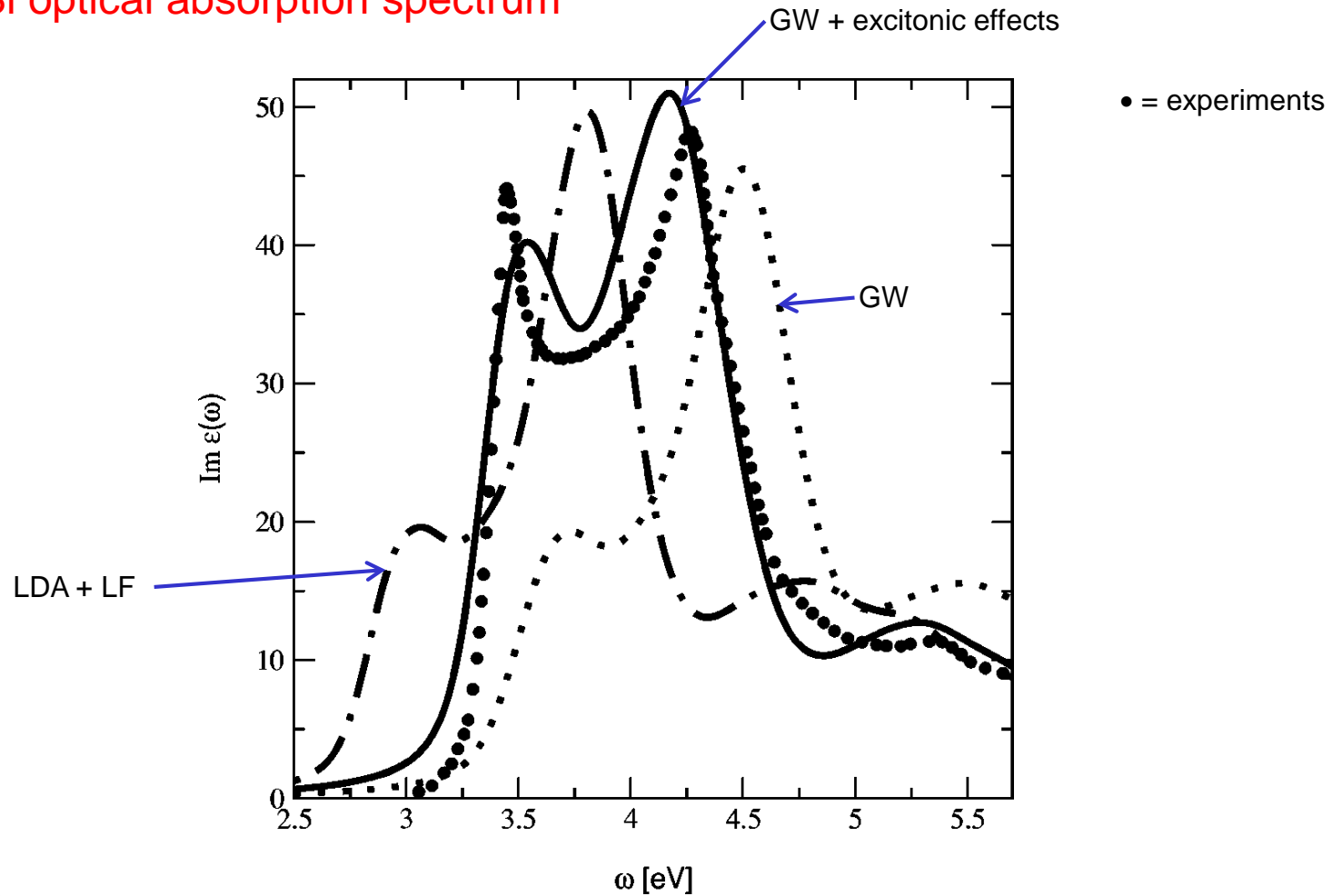
Exchange term

$$\begin{aligned}
 \langle vc|H^{eh}|v'c'\rangle &= \int d^3r d^3r' \varphi_c^*(\vec{r})\varphi_v(\vec{r})v(\vec{r},\vec{r}')\varphi_{c'}(\vec{r}')\varphi_{v'}^*(\vec{r}') \\
 &- \int d^3r d^3r' \varphi_c^*(\vec{r})\varphi_{c'}(\vec{r})W(\vec{r},\vec{r}',\varepsilon^{exc})\varphi_v(\vec{r}')\varphi_{v'}^*(\vec{r}')
 \end{aligned}$$

Direct coulomb interaction term

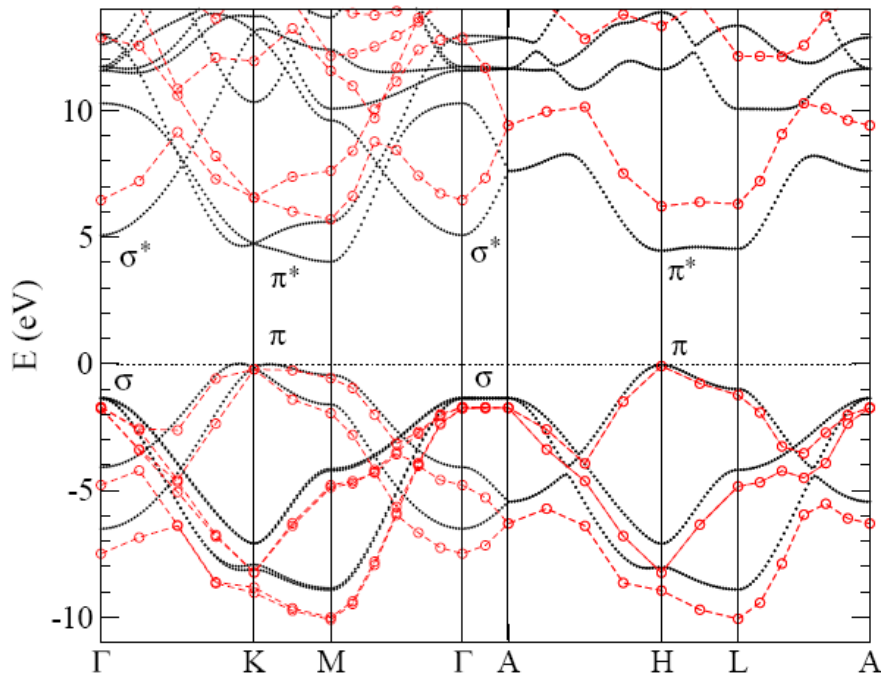
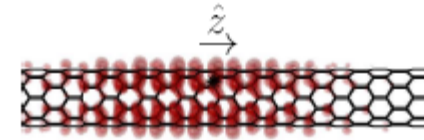
# Excitonic effects

## Si optical absorption spectrum



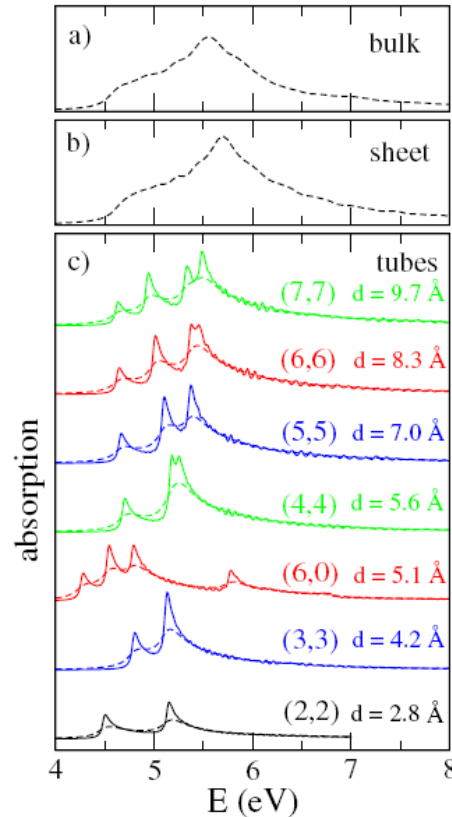
# Excitonic effects

## Bulk BN and BN nanotubes

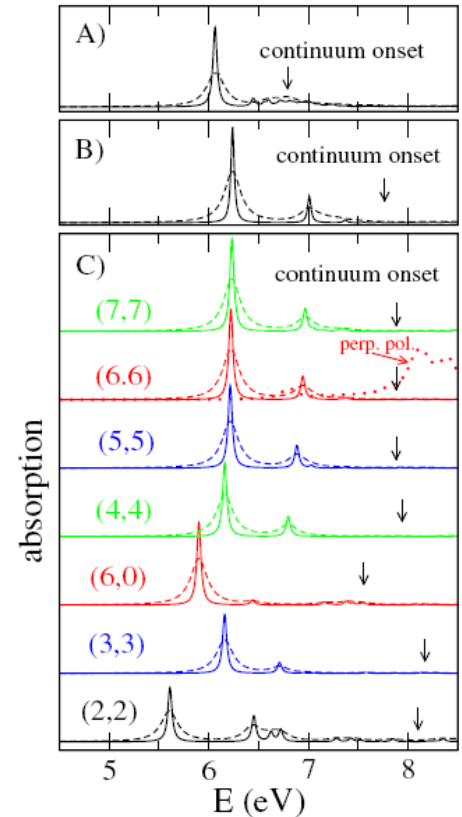


Band structure of hBN  
 — LDA (gap = 4.47 eV)  
 - - - GW (gap = 6.26 eV)

### RPA



### GW + Bethe Salpeter



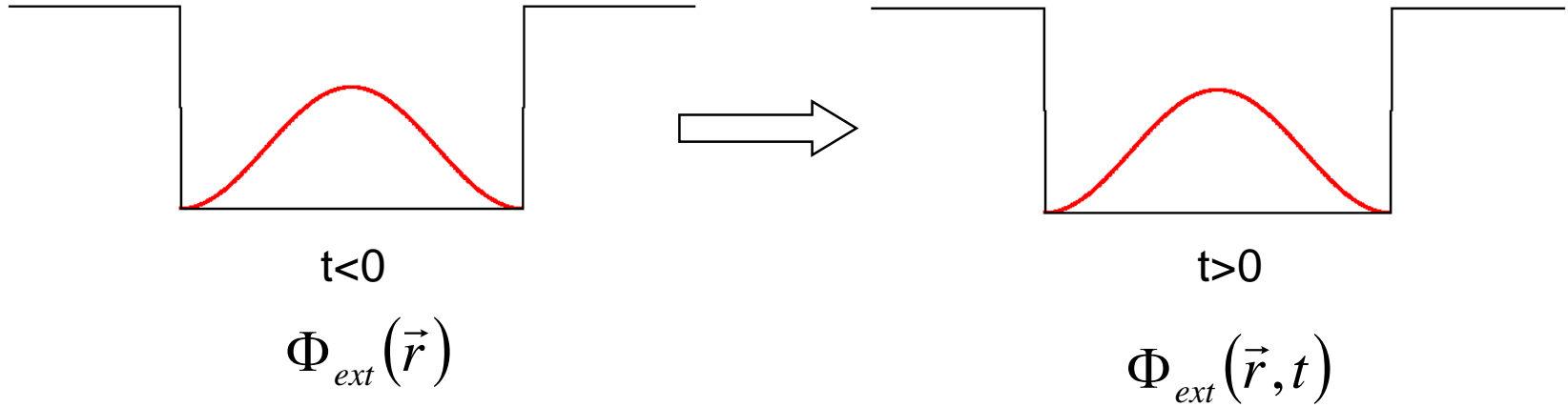
L. Wirtz et al, PRL 96, 126104 (2006)

# TDDFT

## Basic principles

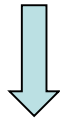
Reference: Time-dependent density functional theory, edited by M.A.L. Marques, C.A. Ullrich, F. Nogueira, A. Rubio, K. Burke, and E.K.U. Gross, Springer Lecture Notes in Physics, Vol. 706 (2006).

# TDDFT



Simplest idea:

$$\{h_0 + V_H(\vec{r}) + V_{xc}[n](\vec{r})\}\varphi_\alpha(\vec{r}) = \varepsilon_\alpha \varphi_\alpha(\vec{r})$$



$$\{h_0(t) + V_H(\vec{r}, t) + V_{xc}(\vec{r}, t)\}\varphi_\alpha(\vec{r}, t) = i\hbar \frac{\partial \varphi_\alpha(\vec{r}, t)}{\partial t}$$

Validity of this approach?  
XC potential?

# Runge-Gross theorem

Assuming an initial state  $\Psi(\vec{r}_1, \vec{r}_2 \dots \vec{r}_N, t = 0) \equiv \Psi_0$

**Runge-Gross theorem:**  $\Phi_{ext}(\vec{r}, t) \leftrightarrow n(\vec{r}, t)$

**Consequences:** all observables can be known from  $n(\vec{r}, t)$   
all observables are functional of  $\Psi_0$  and  $n(\vec{r}, t)$

Map the interacting system to a non-interacting one with the same density

**Time-dependent Kohn-Sham equation:**

$$\left\{ \frac{p^2}{2m} + e^2 \int \frac{n(\vec{r}', t)}{|\vec{r} - \vec{r}'|} d^3 r' + \Phi_{ext}(\vec{r}, t) + V_{xc}[n, \Psi_0](\vec{r}, t) \right\} \varphi_\alpha(\vec{r}, t) = i\hbar \frac{\partial \varphi_\alpha(\vec{r}, t)}{\partial t}$$

If  $\Psi_0 =$  ground state, no initial-state dependence since Hohenberg-Kohn.



# Adiabatic approximation

$V_{xc}[n](\vec{r}, t)$  is a functional of  $n(t' < t)$ : **memory dependence**

**Adiabatic approximation:**  $V_{xc}^{adiab}[n](\vec{r}, t) = V_{xc}^{gs}[n(t)](\vec{r})$

**ALDA:**  $V_{xc}^{ALDA}[n](\vec{r}, t) = V_{xc}^{hom}[n(\vec{r}, t)]$

Almost all calculations today use an adiabatic approximation.

When a system is subject to a time-dependent external perturbation, its response is directly related to the N-particle excited states ( $\varepsilon_{\alpha}^{exc}$ ).

Linear-response function  $\chi$ :

$$\delta n(\vec{r}, \omega) = \int \chi(\vec{r}, \vec{r}', \omega) \delta \Phi_{ext}(\vec{r}', \omega) d^3 r'$$

$$\chi(\vec{r}, \vec{r}', \omega) \equiv \sum_{\alpha} \frac{A(\vec{r}, \omega) A^*(\vec{r}', \omega)}{\omega - \varepsilon_{\alpha}^{exc} / \hbar}$$

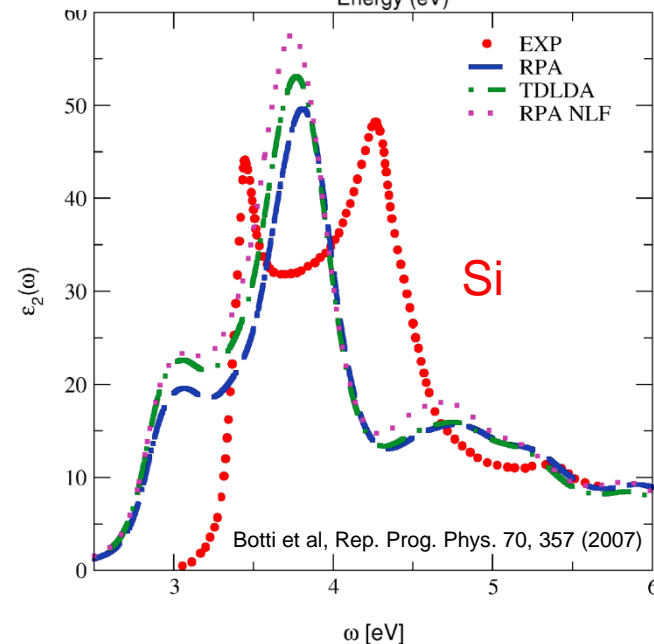
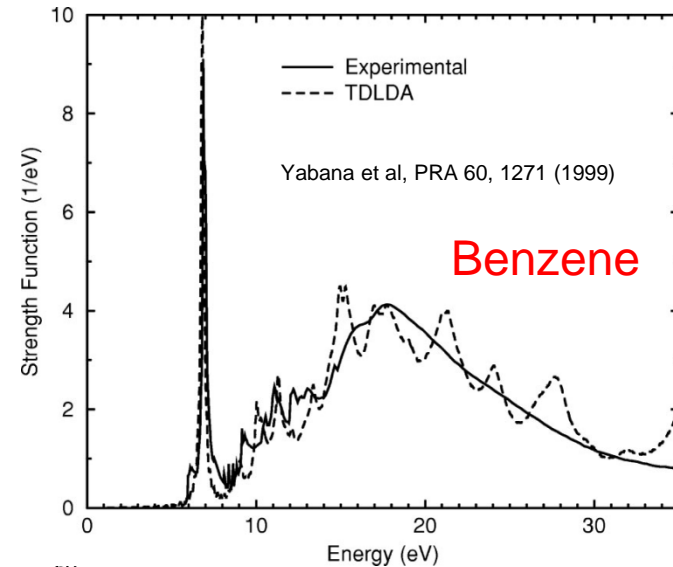
Optical spectra can be calculated from the linear-response function or by a direct resolution of the time-dependent KS equation.

# Strengths & weaknesses of TDDFT

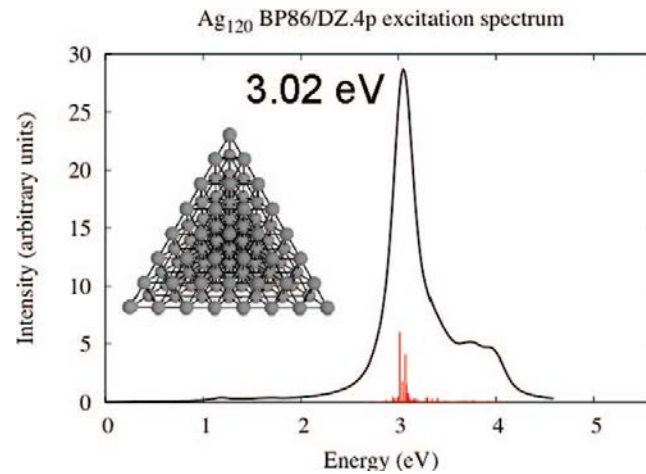
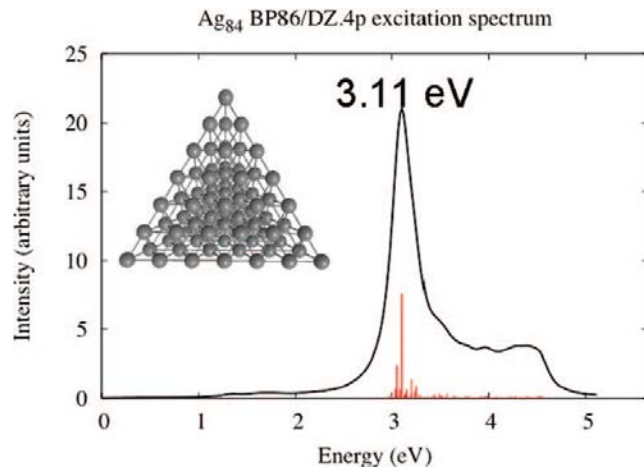
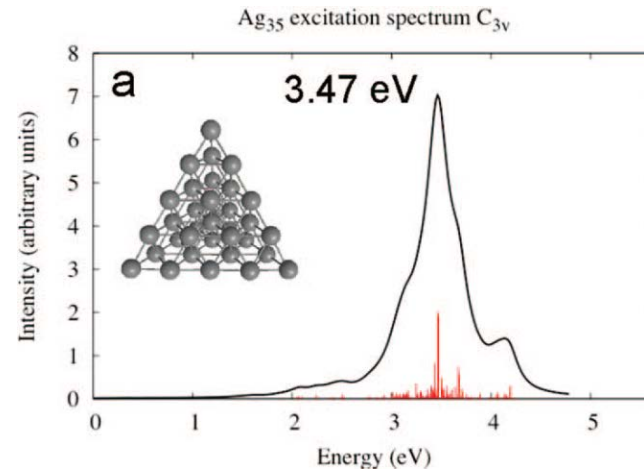
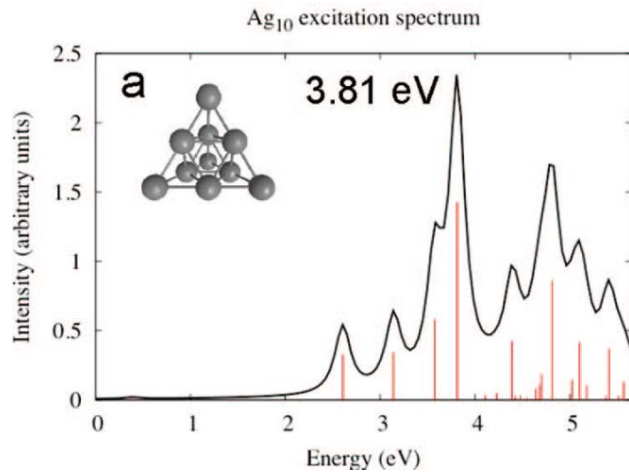
Compared to GW+BS: computational simplicity.

TDLDA describes quite well excitons, collective excitations and plasmons in molecules, clusters.  
Nanocrystals?

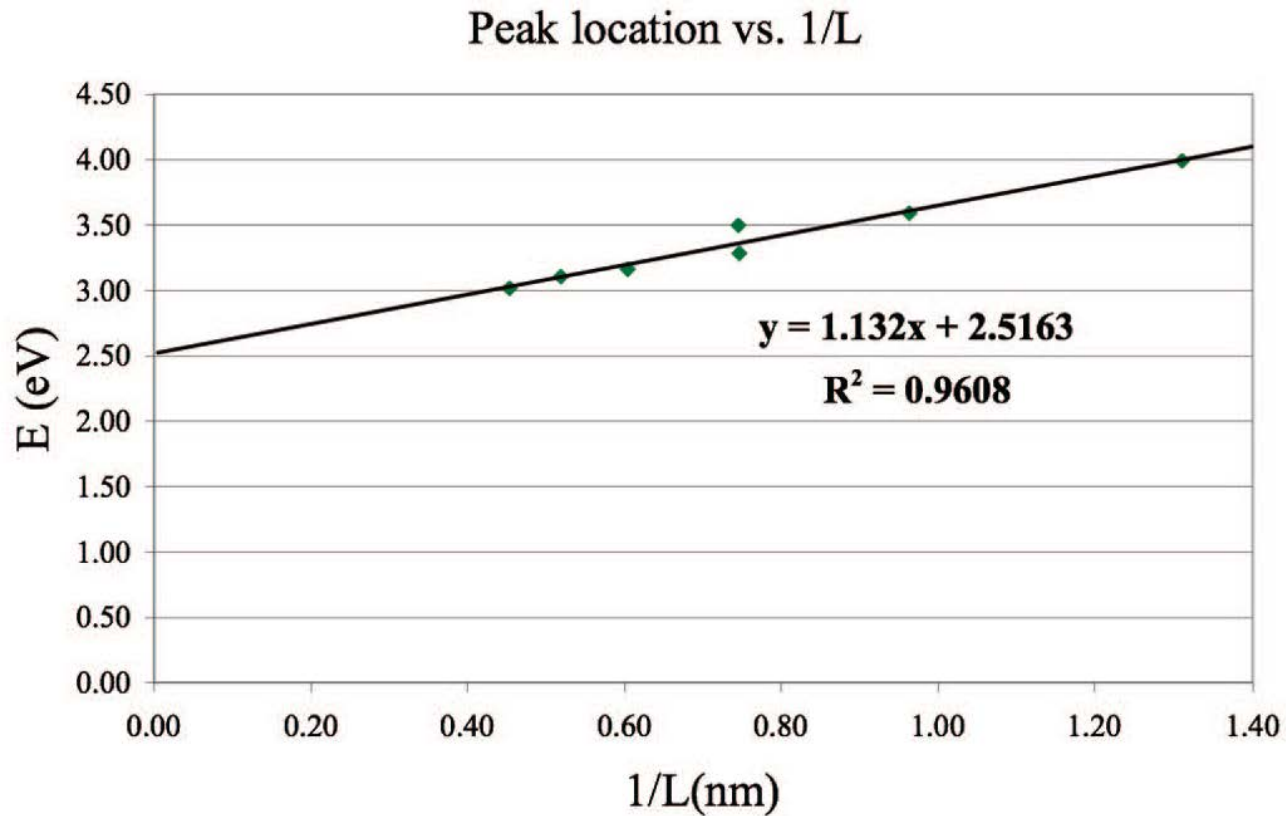
In bulk materials, TDLDA works well for EELS but not for optical absorption spectra.



# Absorption spectra of Ag clusters

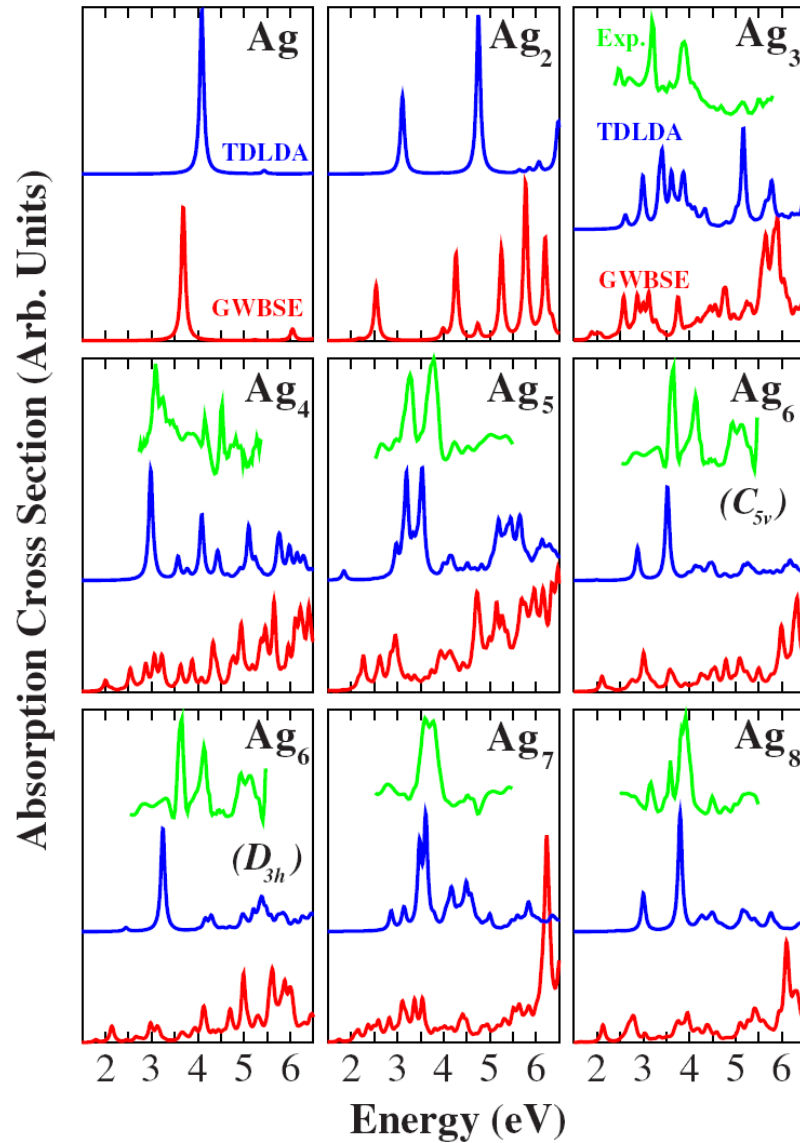


# Absorption spectra of Ag clusters



Aikens et al, J. Phys. Chem. C 112, 11272 (2008)

# Absorption spectra of Ag clusters



In that case, TDLDA results are in better agreement with experiments than GWBSE results.

However better results would be probably obtained using a self-consistent scheme for GW.

# Hybrid functionals

Reference:

AD. Becke J. Chem. Phys. 98, 5648 (1993).

A. Seidl et al, Phys. Rev. B 53, 3764 (1996).

S. Kümmel and L. Kronik, Rev. Mod. Phys. 80, 3 (2008).

Janesko et al, Phys. Chem. Chem. Phys. 11, 443 (2009).

# General principle

Admixture of a certain amount of nonlocal Fock exchange energy to a part of (semi)-local density functional exchange energy.

Different types:

PBE0 [1] (parameter-free)

HSE03 [2] (one parameter)

B3LYP [3], B3PW91 (3 parameters)

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).



# General principle

## PBE0

$$E_{xc}^{PBE0} = \frac{1}{4} E_x^{HF} + \frac{3}{4} E_x^{PBE} + E_C^{PBE}$$

PBE: GGA functional

**HSE** (same but only short-range HF)

$$E_{xc}^{HSE} = \frac{1}{4} E_x^{HF,SR} + \frac{3}{4} E_x^{PBE,SR} + E_x^{PBE,LR} + E_C^{PBE}$$

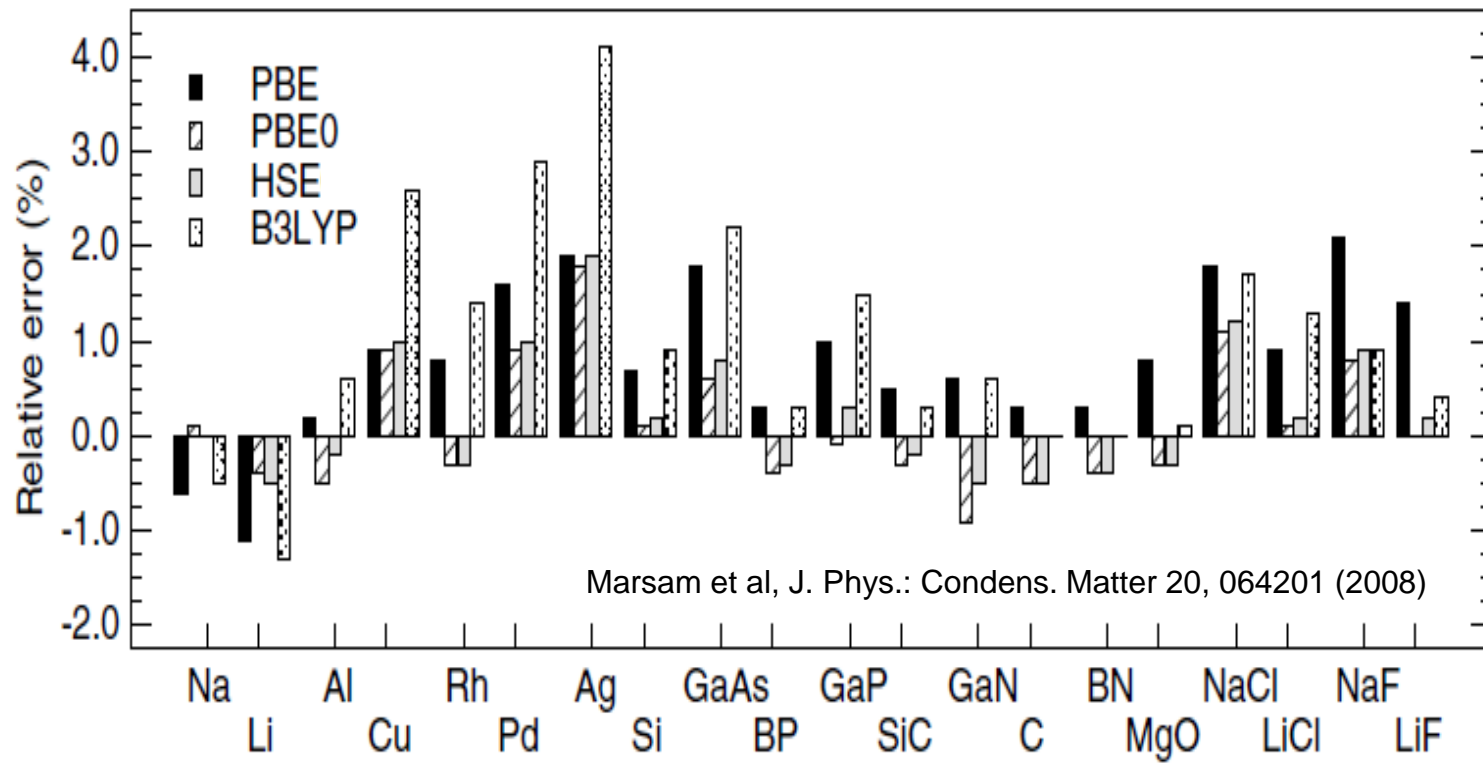
including range-separation  $\mu$

$$\frac{1}{r} = SR + LR = \frac{\text{erfc}(\mu r)}{r} + \frac{\text{erf}(\mu r)}{r}, \quad r = |\vec{r} - \vec{r}'|$$

## B3LYP

A three parameter functional – fitted to atomization energies, ionization potentials, proton affinities of a test set of molecules

# Accuracy: lattice constant

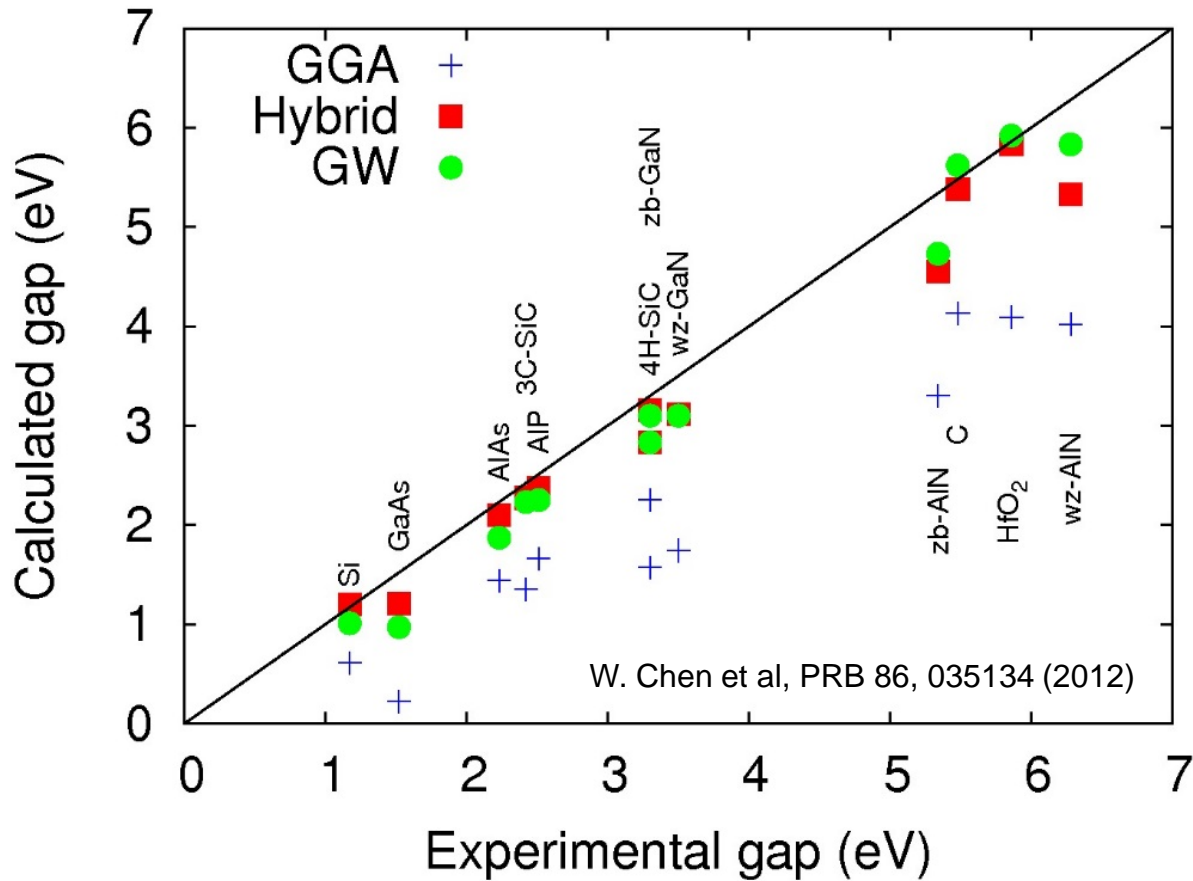


GGA (PBE) already quite good.

Hybrid functionals PBE0 and HSE clearly improve upon GGA

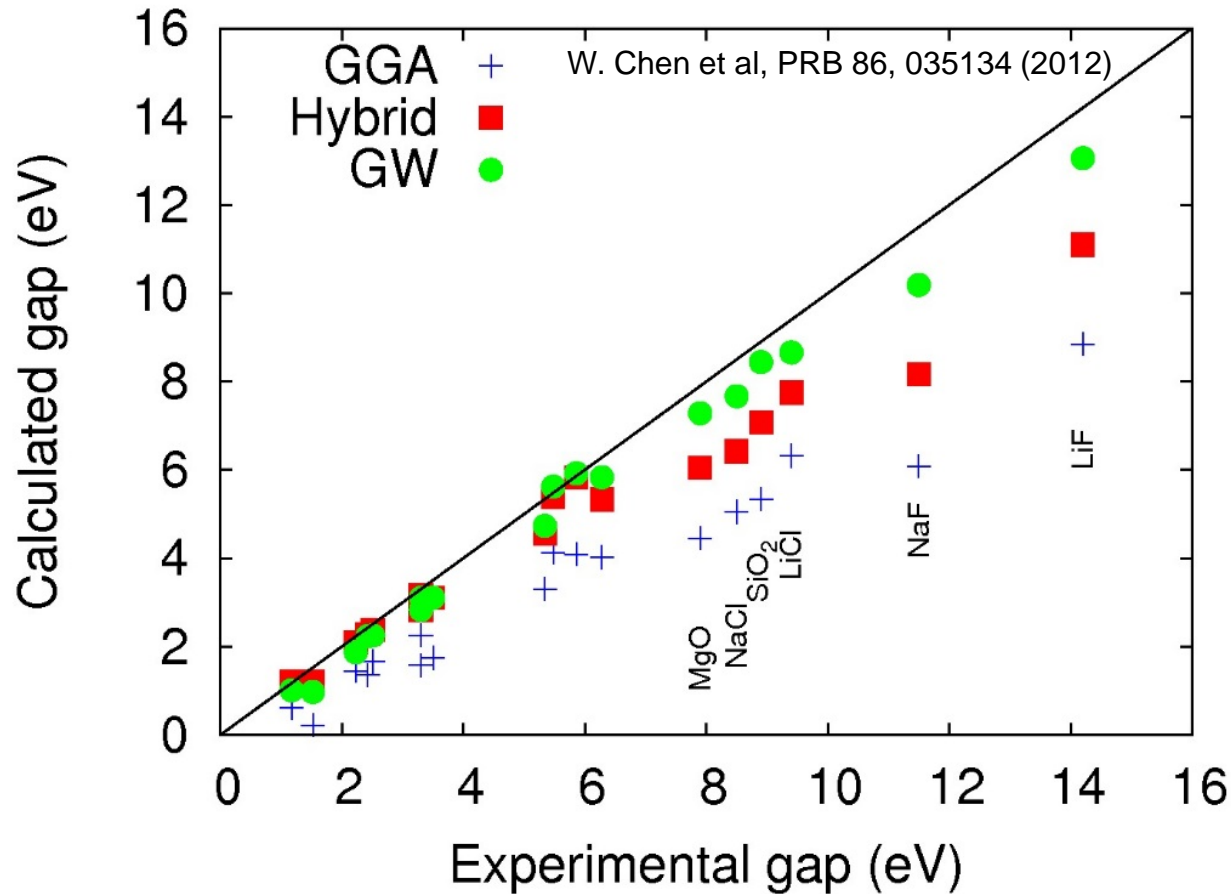
Larger errors for metals

# Accuracy: bandgap



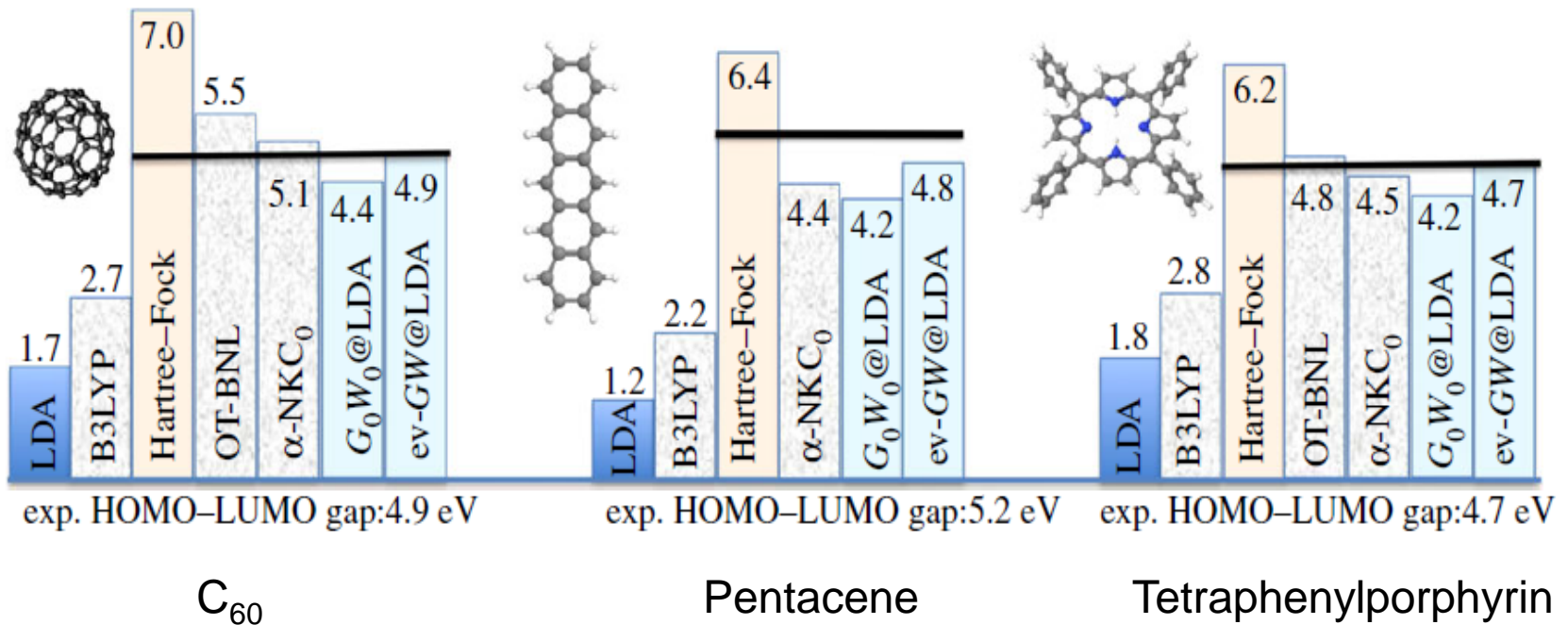
Hybrid functional HSE clearly improves upon GGA (PBE)

# Accuracy: bandgap



But HSE is not good for wide-bandgap (ionic) materials.

# Organic molecules: comparison of methods



The best results for the “electrical gap” obtained using self-consistent GW.  
Good results obtained with hybrid functionals OT-BNL.  
B3LYP not good for these molecules.

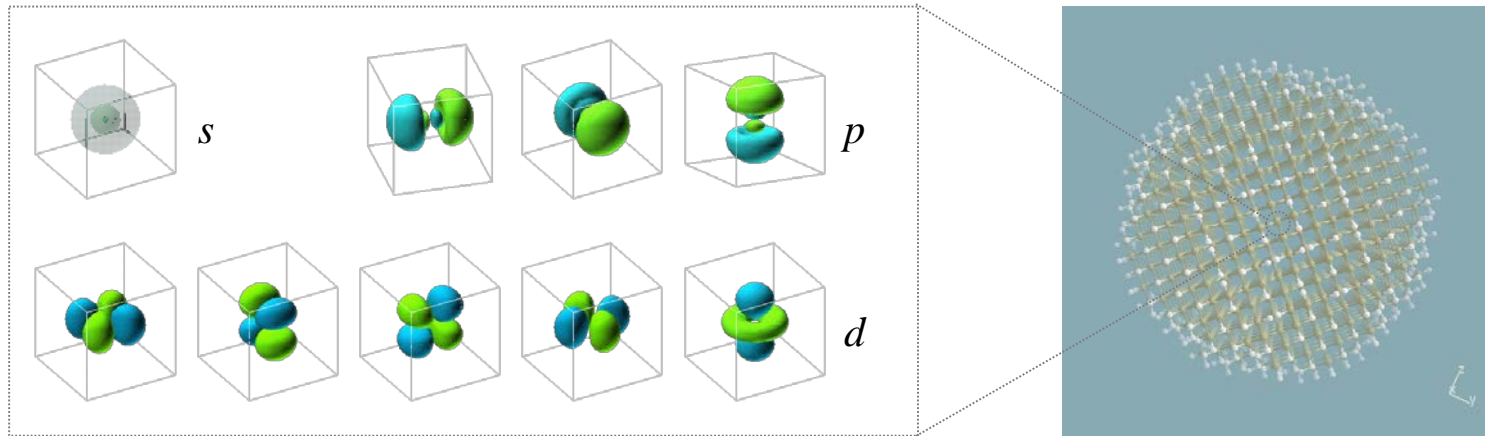
# Tight-binding

TB is also used to perform total-energy calculations: not described here.

## References:

- W.A. Harrison, *Electronic Structure and the Properties of Solids, The Physics of the Chemical Bond* (Freeman, New York 1980)
- C. Delerue & M. Lannoo, *Nanostructures: Theory & Modeling*, Springer (2004).
- *Tight Binding Approach to Computational Materials Science*, MRS Proceedings Vol. 491, ed. by P. Turchi, A. Gonis and L. Colombo (1998).

# TB: basic principles



The eigenstates of the single-particle Schrödinger equation are written as linear combinations of atomic orbitals:

$$|\Psi\rangle = \sum_{i=1}^N \sum_{\alpha=1}^{n_{orbs}} c_{i\alpha} |\varphi_{i\alpha}\rangle$$

Hamiltonian and overlap matrices:

$$\begin{cases} H_{i\alpha,j\beta} = \langle \varphi_{i\alpha} | H | \varphi_{j\beta} \rangle \\ S_{i\alpha,j\beta} = \langle \varphi_{i\alpha} | \varphi_{j\beta} \rangle \end{cases}$$

Overlap are neglected:

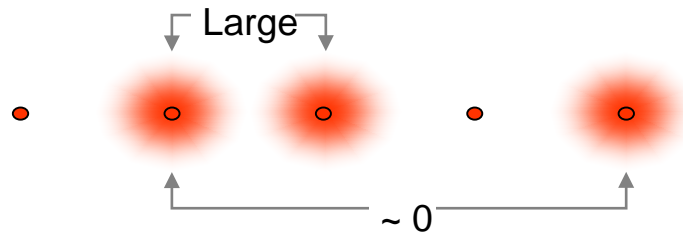
$$S_{i\alpha,j\beta} = \delta_{ij}\delta_{\alpha\beta} \Rightarrow S = I$$

Secular equation:

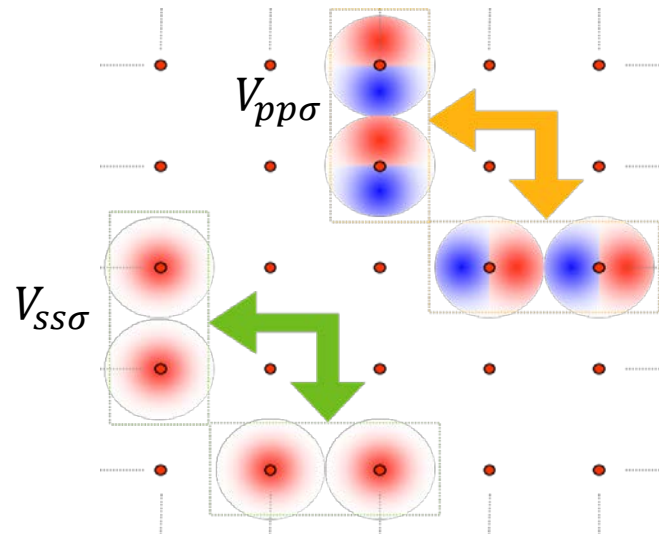
$$\det(H - EI) = 0$$



# TB: basic principles

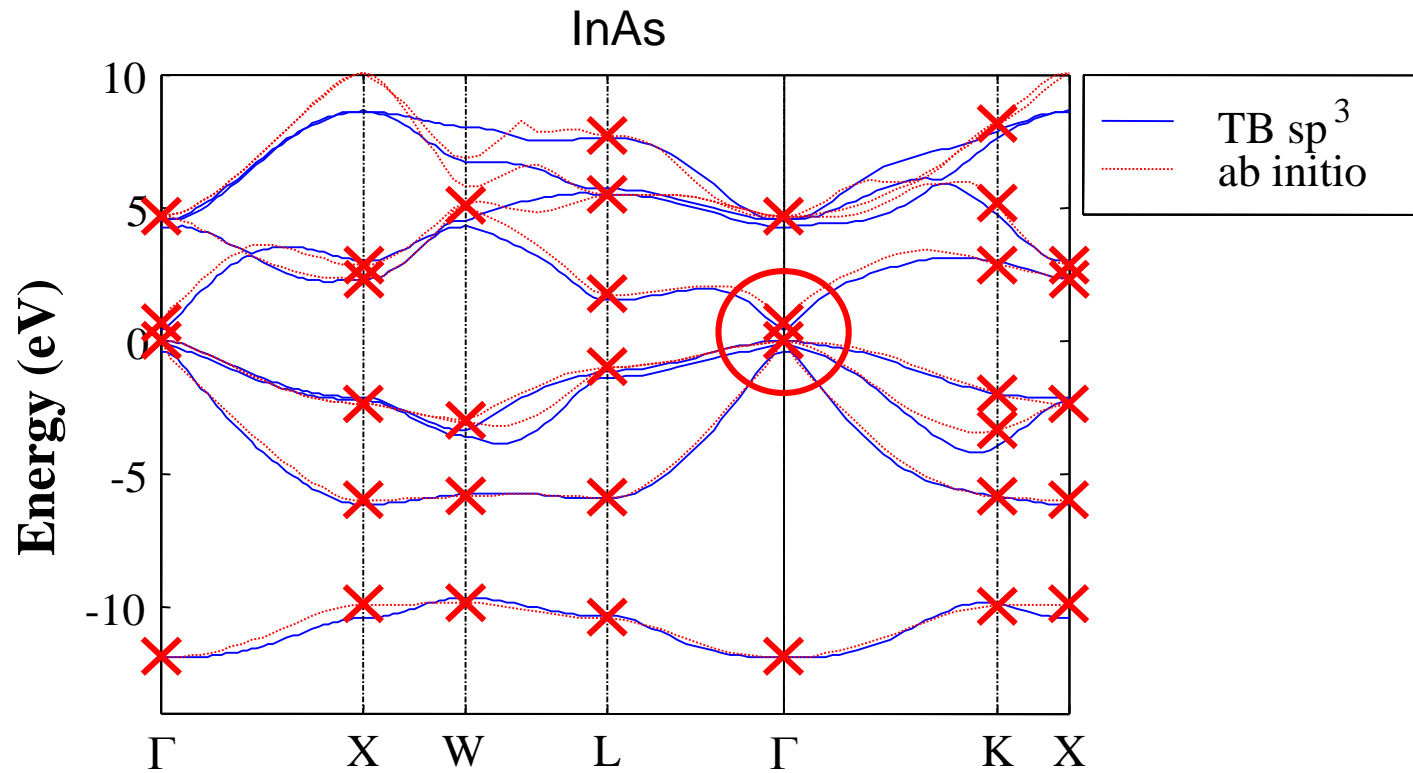


The matrix elements  $H_{i\alpha,j\beta}$  decay very quickly with inter-atomic distance. Restriction to first (second) nearest-neighbor terms.

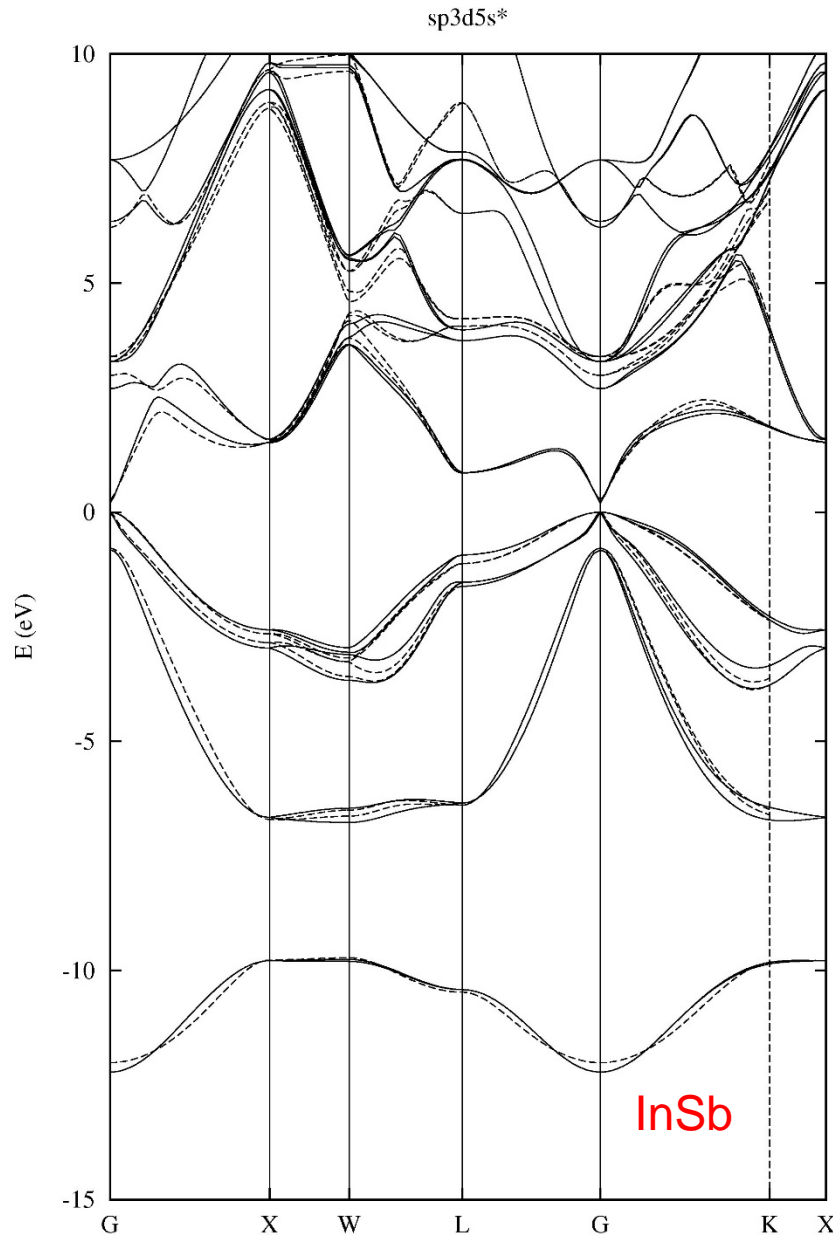


By symmetry, matrix elements function of a small number of parameters adjusted on the bulk band structure.

# TB: basic principles



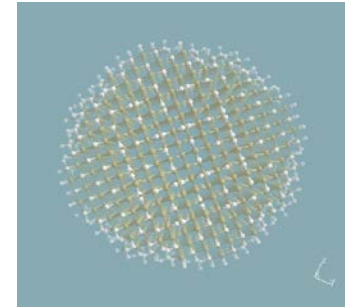
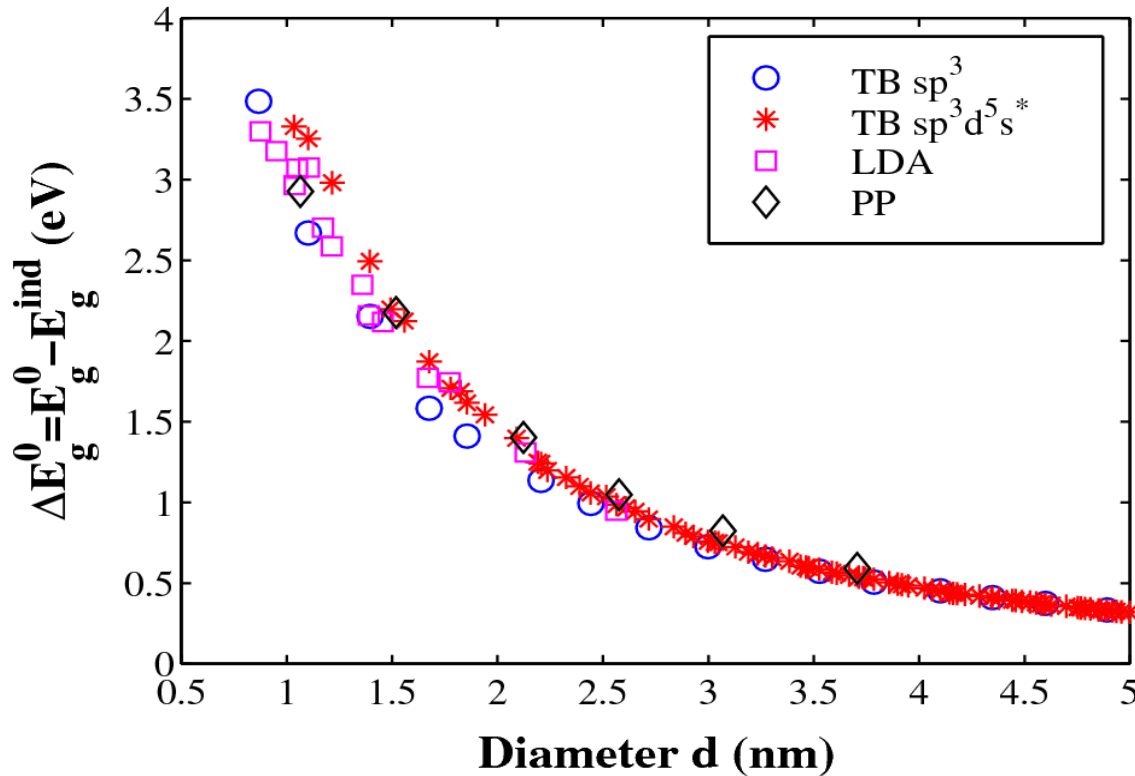
# TB: basic principles



— TB  
- - - GW (Kim et al, PRB 80, 035203, 2009)

Parameters fitted on the bulk can be safely used for nanostructure:  
Principle of **transferability**

# Confinement energy in Si nanocrystals



$$\Delta E_g^0 = E_g(d) - E_g(\text{bulk Si})$$

where  $E_g(\text{bulk Si}) = 1.17 \text{ eV}$

$sp^3$  tight-binding (TB) model

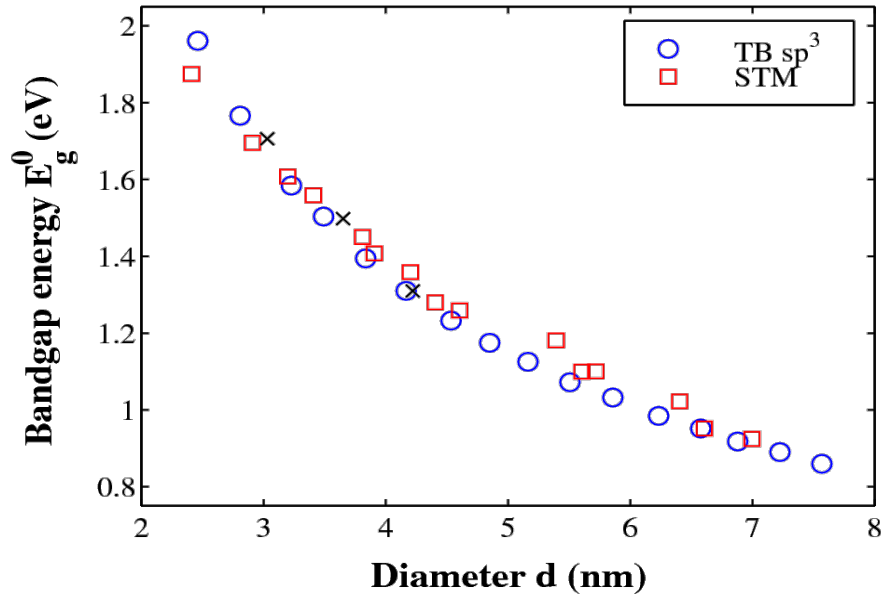
$sp^3d^5s^*$  TB model

Semi-empirical pseudopotential (PP) method

*Ab initio* local density approximation (LDA).

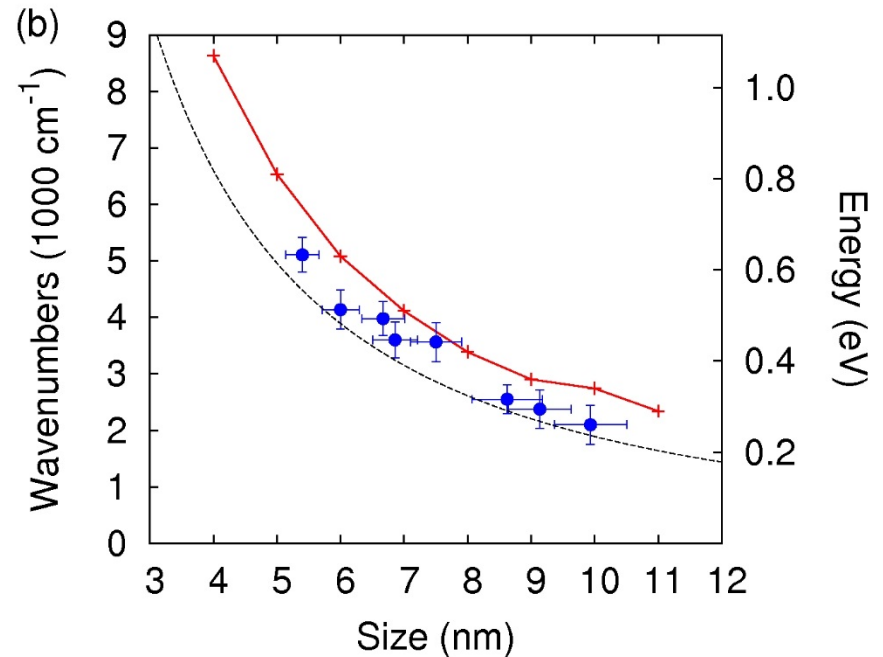
# Comparison with experiments

## Electrical gap of InAs nanocrystals



Y.M. Niquet et al, PRB 64, 113305 (2001)

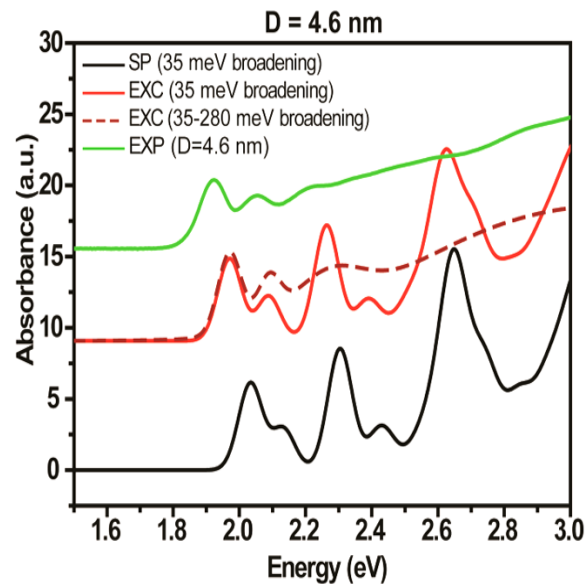
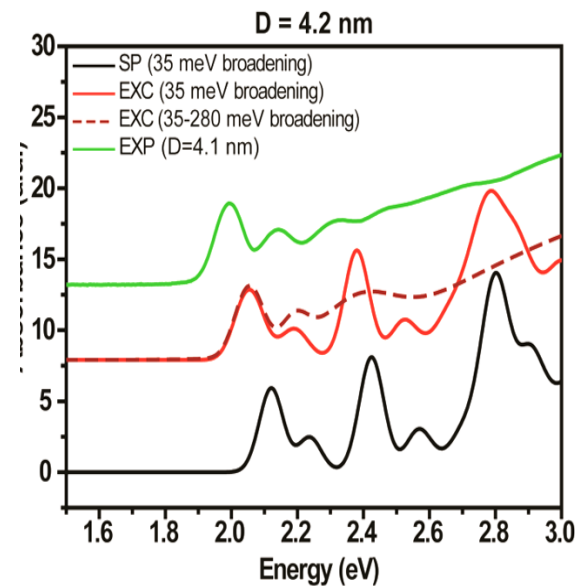
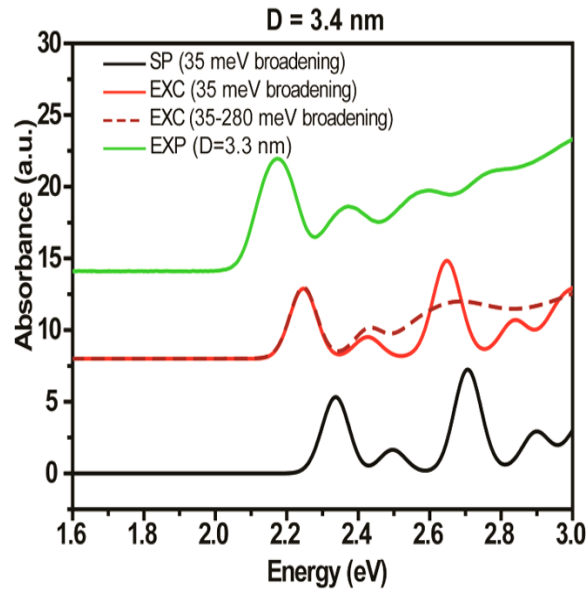
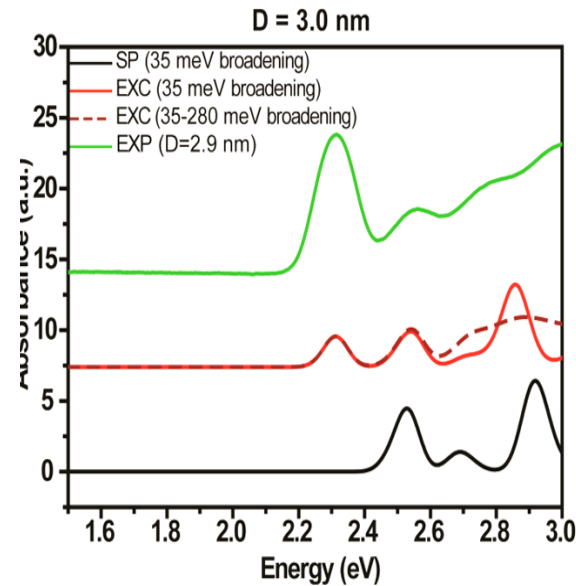
## Optical gap of HgTe nanocrystals



S.E. Keuleyan et al, ACS Nano 8, 8676 (2014)

# Comparison with experiments

Optical absorption spectra of CdTe nanocrystals.  
Tight-Binding + Configuration Interaction method for excitons



# Conclusion

DFT-GGA good for ground-state properties

GW: very good for “electrical” bandgap, affinity, ionization energy

GW-BSE: the most accurate for optical spectra but very heavy

TDDFT: computational simplicity, works well in finite systems  
but not in extended ones (except with ad-hoc functionals)

Hybrid functionals: HSE works well for solids, maybe a good compromise between accuracy and computation time – somehow empirical

Semi-empirical tight-binding: accurate and efficient for specific problems (graphene, carbon nanotubes, semiconductor nanostructures)

# Thomas-Fermi theory

Gives a simplified description of the Coulomb hole

Gives an estimate of the electron self-energy

A theory of the density preceding DFT

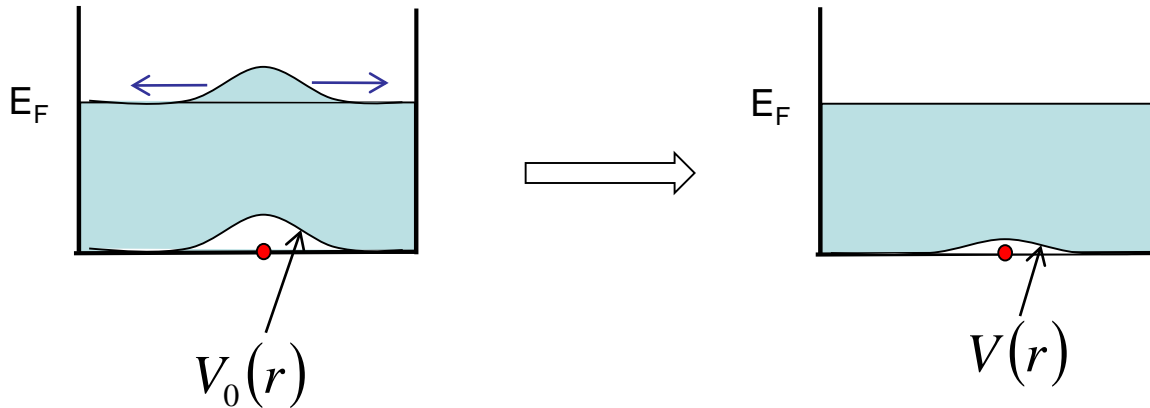


# Correlation (Coulomb) hole

Simplest description of the correlation hole in a metal: Thomas-Fermi

Charge  $-e$  in an homogeneous electron gas

$$V_0(r) = -\frac{e}{r} \quad V(r) = V_0(r) + V_{ind}(r) \equiv \frac{V_0(r)}{\epsilon(r)}$$



# Correlation (Coulomb) hole

Simplest description of the correlation hole in a metal: Thomas-Fermi

$$\Delta V = -4\pi\rho \quad \rho(r) = -e^2 V(r) n(E_F)$$

$$V(r) = -e \frac{e^{-\lambda r}}{r} \quad \lambda = 4\pi e^2 n(E_F) \approx 0.5 \text{ \AA}$$

$V$  totally screened for  $r \gg \lambda \Rightarrow$  coulomb hole charge =  $+e$

Not exactly the same in insulators, semiconductors or nanostructures: incomplete screening

## Self-energy in the Thomas-Fermi model

Energy needed to put the charge at point  $r$  and to create the Coulomb hole?

$$\Sigma = -\frac{e}{2}V_{ind}(r=0) = -\lambda \frac{e^2}{2} \approx -13 \text{ eV}$$

$$V_{ind}(r) = V(r) - V_0(r) = -e \frac{e^{-\lambda r} - 1}{r}$$

TF : crude estimation of the self-energy (static...)

The true self-energy should describe dynamical screening effects!

# GW

## Single-particle excitations

### Many-body theory

# Many-Body Green's functions

## Quasiparticle approach

Low-lying excitations can be described as single-particle excitations

Dressed particle = particle + its polarization cloud

## Many-Body Green's function theory

Single particle Green's function:  $G(\vec{r}, \vec{r}', \tau) = -i \langle N | T \{ \Psi(\vec{r}, \tau) \Psi^\dagger(\vec{r}', 0) \} | N \rangle$   
(correlation function)

$$G(\vec{r}, \vec{r}', E) = \frac{1}{2\pi} \int e^{iE\tau} G(\vec{r}, \vec{r}', \tau) d\tau = \sum_{\alpha} \frac{f_{\alpha}(\vec{r}) f_{\alpha}^*(\vec{r}')}{E - \varepsilon_{\alpha}^{qp}}$$

$$\text{Re}(\varepsilon_{\alpha}^{qp}) = E(N+1, \alpha) - E(N) \text{ or } \text{Re}(\varepsilon_{\alpha}^{qp}) = E(N) - E(N-1, \alpha)$$

(imaginary part = lifetime of the quasiparticle).

## Case of independent particles

$$f_{\alpha}(\vec{r}) = \Psi_{\alpha}(\vec{r}) \quad \varepsilon_{\alpha}^{qp} = \varepsilon_{\alpha}$$

## Many-Body Perturbation Theory

### Conventional approach

Expansion of  $\Sigma$  in terms of the bare e-e interaction  $v(\vec{r}, \vec{r}') = \frac{e^2}{|\vec{r} - \vec{r}'|}$   
 Convergence problems!

### GW approach

Expansion of  $\Sigma$  in terms of the dynamically screened e-e interaction

$$W(\vec{r}, \vec{r}', \omega) = \int \varepsilon^{-1}(\vec{r}, \vec{r}'', \omega) v(\vec{r}'', \vec{r}') dr''$$

Simplest approximation:

$$\Sigma(\vec{r}, \vec{r}', \varepsilon) = \frac{i}{2\pi} \int W(\vec{r}, \vec{r}', \vare' / \hbar) G(\vec{r}, \vec{r}', \vare + \vare') e^{i\delta\vare'} d\vare' \equiv GW$$

(Quinn, Ferrell, Hedin, Lundqvist...)

## Practical implementation

### In principle

$W$  and  $G$  must be computed self-consistently.

### Practically

DFT wave-functions are good starting point to build the Green's function

$$\{h_0 + V_H(\vec{r})\}f_\alpha(\vec{r}) + \int \Sigma(\vec{r}, \vec{r}', \varepsilon_\alpha^{qp})f_\alpha(\vec{r}')dr' = \varepsilon_\alpha^{qp} f_\alpha(\vec{r})$$

$$\{h_0 + V_H(\vec{r}) + V_{xc}[n](\vec{r})\}\varphi_\alpha(\vec{r}) = \varepsilon_\alpha^{DFT} \varphi_\alpha(\vec{r})$$

$$f_\alpha(\vec{r}) \approx \varphi_\alpha(\vec{r})$$

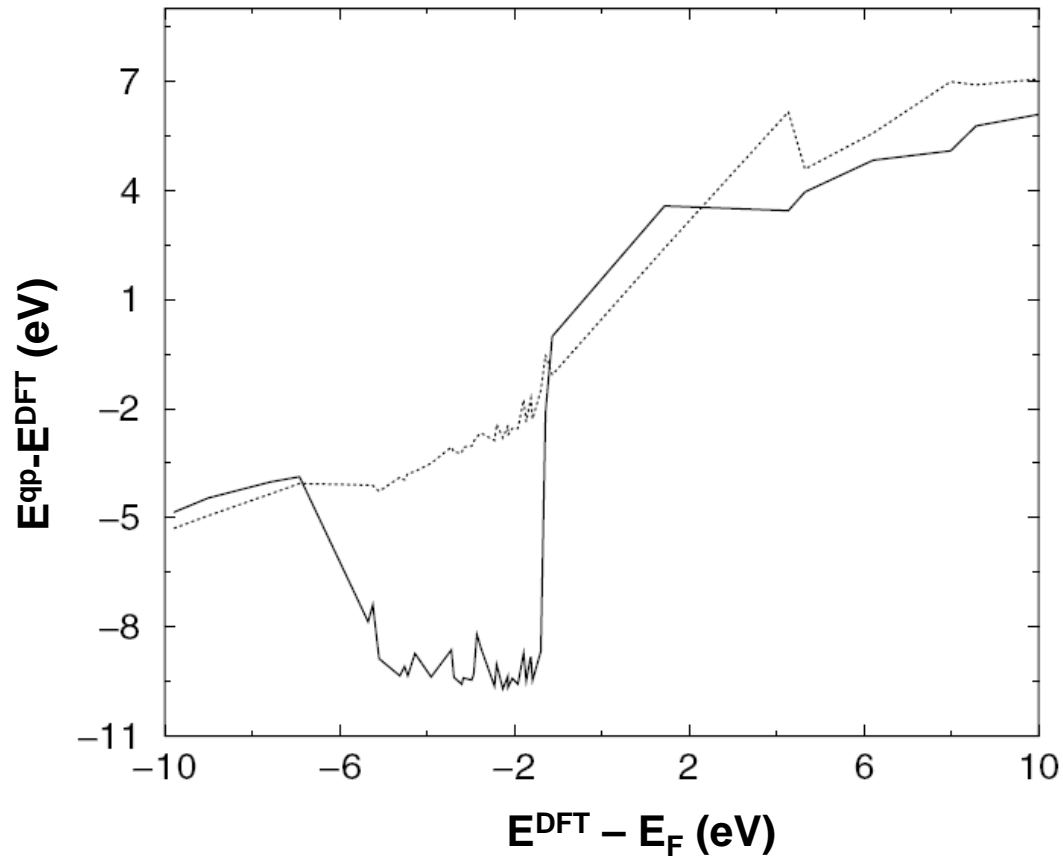
First-order perturbation:

$$\varepsilon_\alpha^{qp} = \varepsilon_\alpha^{DFT} + \langle \varphi_\alpha | \Sigma - V_{xc} | \varphi_\alpha \rangle$$

(quasiparticle correction)

# Quasiparticle correction

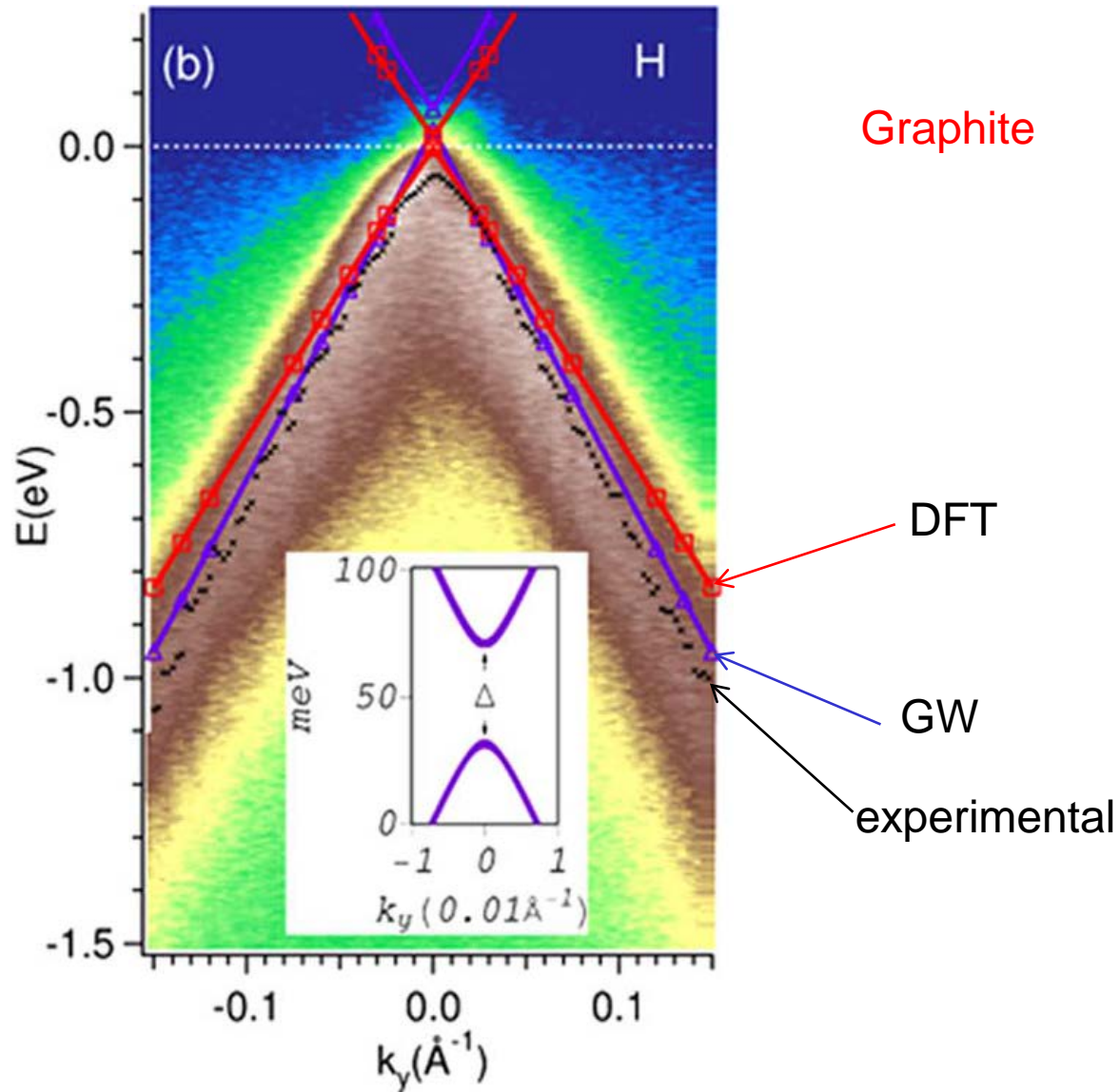
Case of a more complex metal: Cu



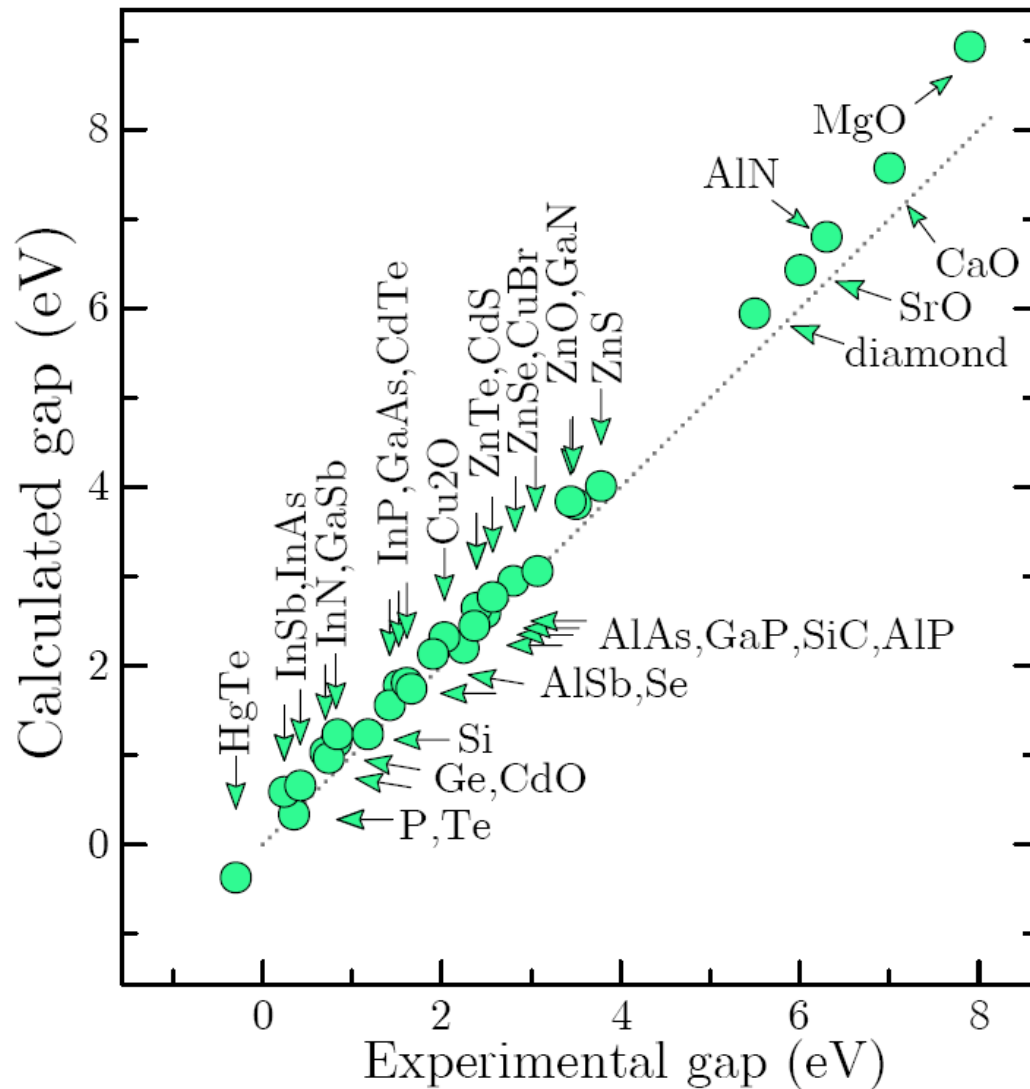
Marini et al, PRL 88, 016403 (2001)



# Quasiparticle correction



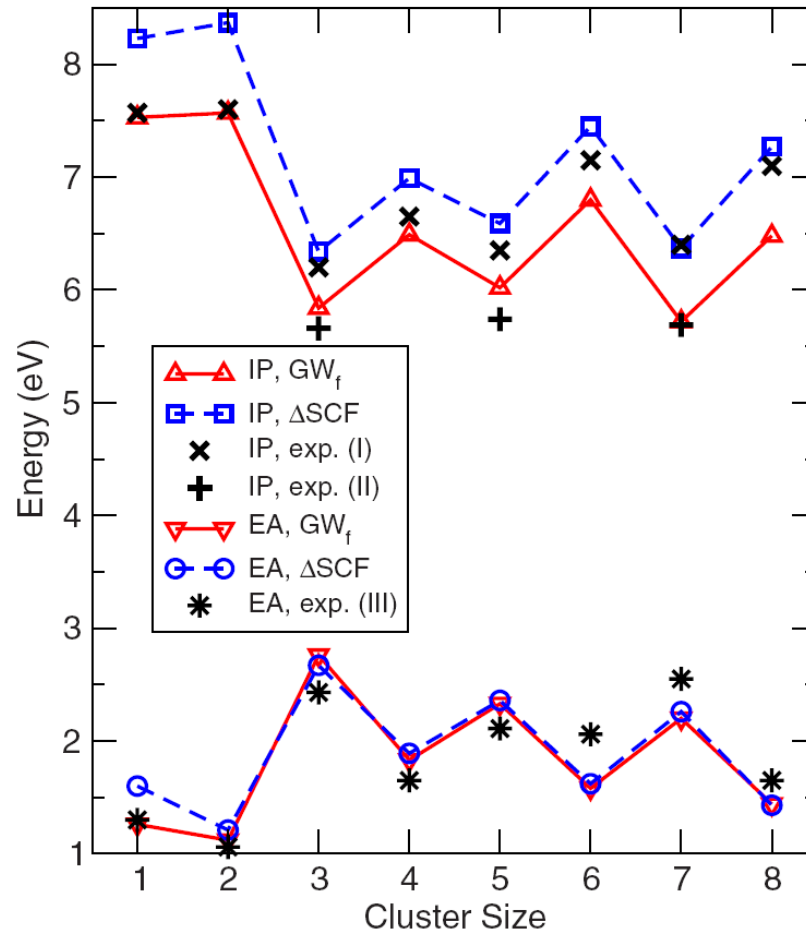
# Quasiparticle correction



Self-consistent GW

[adapted from van Schilfgaarde et al., PRL **96**, 226402 (2006)]

# IP & EA of Ag clusters



IP = Ionization Potential  
EA = Electron Affinity

Tiago et al, PRB 79, 155419 (2009)