

Electronic Excitations Successes and Failures of approximate DFT functionals and the GW approximation

Special lecture – Fudan University

April 20, 2010

Richard M. Martin

Electronic Excitations Successes and Failures of approximate DFT functionals and the GW approximation

OUTLINE

Electronic Excitations

Electron addition/removal - ARPES experiments
Excitation with fixed number – Optical experiments

Non-interacting particles

Electron addition/removal - empty (filled) bands
Excitation with fixed number – spectra are just combination of
addition/removal

Why are excitations harder than the ground state to approximate?

Leads us to explicit many-body methods

Many-body approaches

Addition/removal --GW approximation

Excitation with fixed number -- Bethe-Salpeter Eq.

TDDFT -- Time Dependent DFT

(In principle exact excitations from TD-Kohn-Sham!

Mentioned
briefly

Electronic Excitations – Rigorous Definitions

Consider a system of N electrons

1. Electron addition/removal

$$N \rightarrow N+1$$

or

$$N \rightarrow N-1$$

$$\Delta E = E(N+1) - E(N) - \mu$$

or

$$\Delta E = E(N) - E(N-1) - \mu$$

Note sign

$$\begin{aligned} \text{Minimum gap } E_{\text{gap}} &= [E(N+1) - E(N) - \mu] - [E(N) - E(N-1) - \mu] \\ &= E(N+1) + E(N-1) - 2 E(N) \end{aligned}$$

2. Electron excitation at fixed number N

$$\Delta E^* = E^*(N) - E_0(N)$$

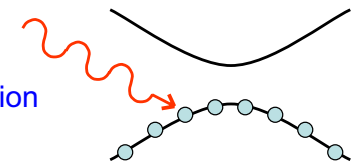
$$\text{In General } \Delta E^* < E_{\text{gap}}$$

Why?

(See book, Chapter 2, sections 2.10 and 2.11)

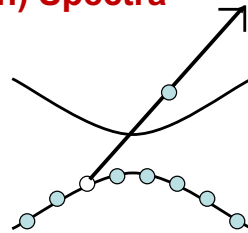
Electronic Removal (Addition) Spectra

- Excitations
- Electron removal (addition)
 - Experiment – Photoemission
 - Theory – Quasiparticles
“GW” Approximation



Electronic Removal (Addition) Spectra

- Excitations
- Electron removal (addition)
 - Experiment – Photoemission
 - Theory – Quasiparticles
“GW” Approximation



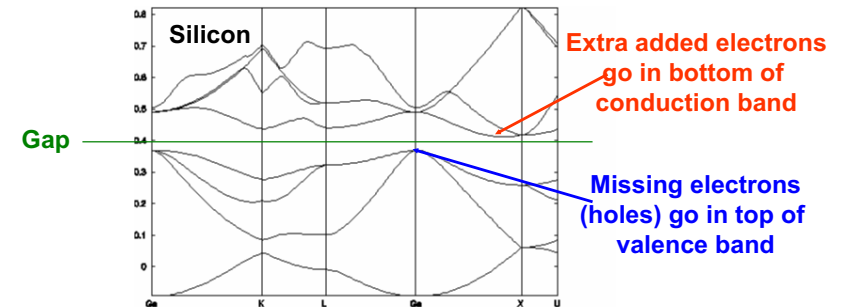
Inverse Photoemission – just the reverse
Electrons in -- photons out
Measures addition spectra

5

What really happens for removal (addition)

- Understood since the 1920's - independent electron theories predict that electrons form **bands of allowed eigenvalues**, with **forbidden gaps**

The gap and edges of conduction and valence bands are rigorously well-defined

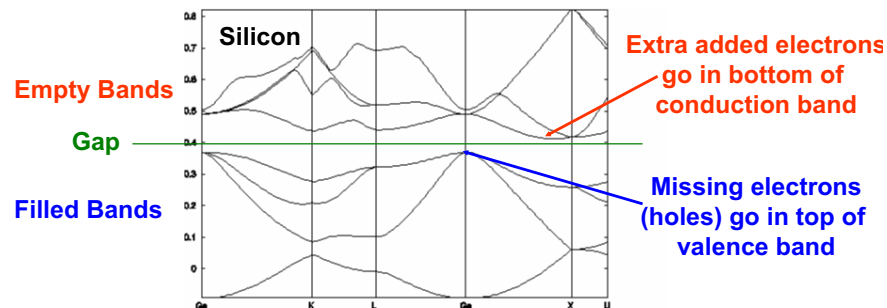


7

Independent Particle Electron Bands

- Understood since the 1920's - independent electron theories predict that electrons form **bands of allowed eigenvalues**, with **forbidden gaps**

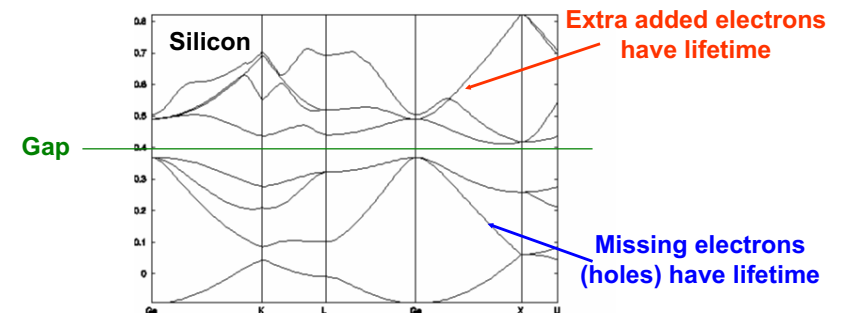
•Eigenvalues of an independent particle hamiltonian



6

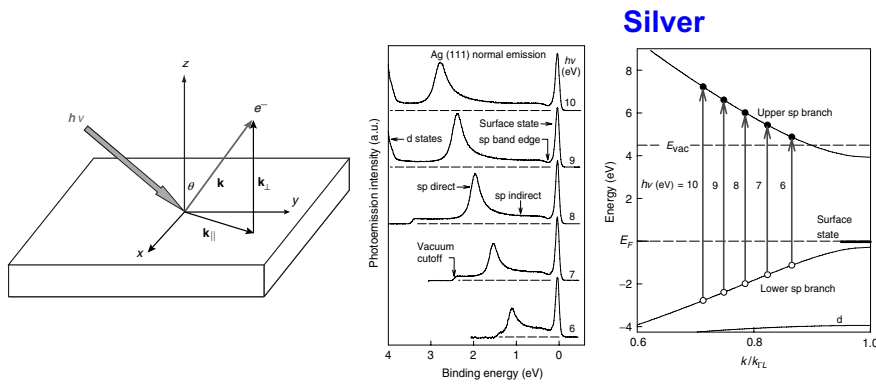
What really happens for removal (addition)

Energies for removing (adding) electrons for high energy states have a lifetime – energies are not well-defined
Called “quasiparticles”



8

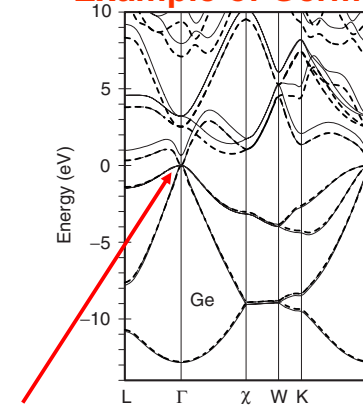
Angle Resolved Photoemission (Inverse Photoemission) Reveals Electronic Removal (Addition) Spectra



Comparison of theory (lines) and experiment (points)

Many-Body “GW” Calculations

• Example of Germanium



A metal in “LDA” calculations!

11

Experiment – MgB_2

Recent ARPES experiment on the superconductor MgB_2
Intensity plots show bands very close to those calculated

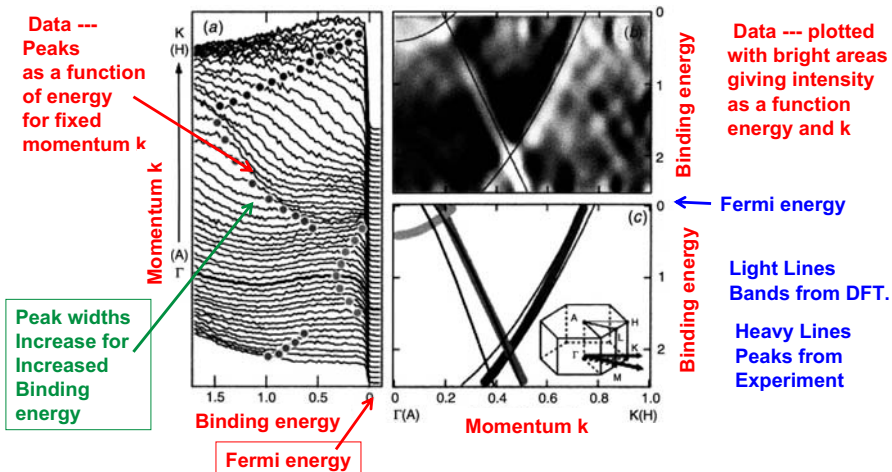
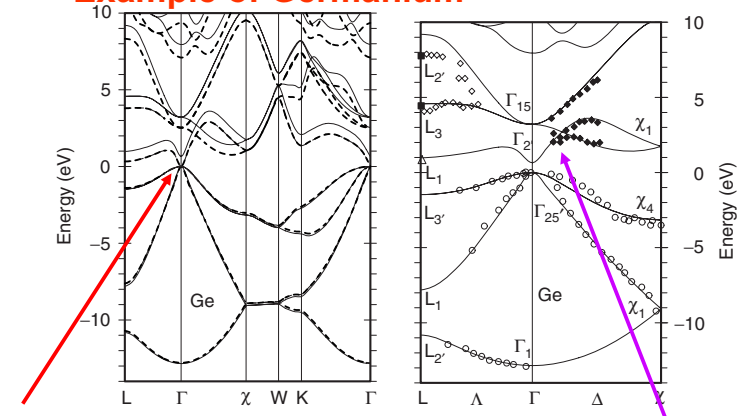


Fig. 2.30 Domasicelli, et al.

Many-Body “GW” Calculations

• Example of Germanium



A metal in “LDA” calculations!

Improved many-body GW calculations

Louie, Hybertsen, . . . 12

What must be accomplished by Many-body methods?

- Accurate values for gaps, energies near edges of bands closes to Fermi energy
- Energies and lifetimes of quasiparticles for higher energy removal (addition)

We will not discuss this here

In most calculations the lifetime is ignored

13

What is $\Phi[G]$

- $\Phi[G]$ is the contribution of exchange and correlation to total energy
 - Analogous to KS functional $E_{xc}[n]$
- What is self-energy?
 - Analogous to KS eigenvalues

15

GW approximation (and history leading up to it)

- 1960 – Luttinger and Ward
 - Showed that the total energy of a many-body system can be written as a functional of the full many-body Green's function G
 - Conceptual advance
 - Standard text-book many-body theory gives expressions in terms of zero order Green's function G_0 – Feynman diagrams
 - Defined functional $\Phi[G]$ Note similarity to DFT – E a functional of density $n(r)$
 - $G(r,r')$ contains the information on the density – the static $G(r,r, \text{frequency} = 0) = n(r)$ and also dynamical spectra
 - Before Hohenberg-Kohn-Sham!
- 1962 Baym
 - Gave conditions on $\Phi[G]$ that approximations are “conserving” momentum, energy, number, . . .
- 1964 Hedin
 - Gave approximations on $\Phi[G]$ that are the GW

14

GW approximation - I

- Approximation to Φ and Σ --- Cannot give details – but really it is very intuitive

Writing expressions as a functional of G and the full screened interaction W

Picture equivalent to original Baym paper:

$$\begin{aligned} \Phi^{GW} &= -\frac{1}{2} \text{ (diagram)} - \frac{1}{4} \text{ (diagram)} - \frac{1}{6} \text{ (diagram)} + \dots \\ \text{a) } \Sigma^{GW} &= \text{ (diagram)} + \text{ (diagram)} + \text{ (diagram)} + \dots \\ \Phi^{(2)} &= -\frac{1}{2} \text{ (diagram)} - \frac{1}{4} \text{ (diagram)} - \frac{1}{4} \text{ (diagram)} \\ \text{b) } \Sigma^{(2)} &= \text{ (diagram)} + \text{ (diagram)} + \text{ (diagram)} \end{aligned}$$

GW --
Developed by
the Hedin

The Φ diagrams and self-energies $\Sigma = \delta\Phi / \delta G$

GW approximation - II

- Approximation to Φ and Σ --- Cannot give details – but really it is very intuitive

Writing expressions as a functional of G and the full screened interaction W

Finally we have the very simple pictorial representation:

$$\Sigma(r, r', \omega) = \frac{W(r, r', \omega)}{G(r, r', \omega)}$$

GW --
Developed by
the Hedin

Simple interpretation – electron propagates scattered by the potential that is screened by all the other electrons

GW approximation - III

- What is typically done in actual calculations
- The screened interaction is simply Coulomb divided by the frequency dependent dielectric function
Can be found by various methods and approximations
- Many methods: 1. Using the form from KS --- called W_0
2. Detailed calculations

$$\Sigma(r, r', \omega) = \frac{W(r, r', \omega)}{G(r, r', \omega)}$$

- The electron Green's function – not so easy to give simple form
- The G_0 – approximation using the form from KS --- called G_0

MUCH DEBATE – Is this OK – Is the very simplest lowest order approximation OK?
Seems to be very good ---- Why?

GW approximation - II

- What needs to be calculated in the GW approximation
- The screened interaction is simply Coulomb divided by the frequency dependent dielectric function

Can be found by various methods and approximations

$$\Sigma(r, r', \omega) = \frac{W(r, r', \omega)}{G(r, r', \omega)}$$

GW --
Developed by
the Hedin

- The electron Green's function – not so easy to give simple form

Many-body methods applied in practice to materials

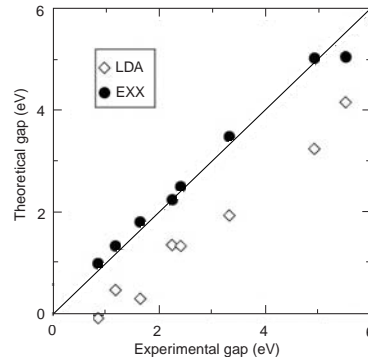
- Present approximate DFT calculations can be the starting point for explicit many-body calculations
 - “GW” - Green's function for excitations
 - Use DFT wavefunctions as basis for many-body perturbation expansion
 - QMC – quantum Monte Carlo for improved treatment of correlations
 - Use DFT wavefunctions as trial functions
 - DMFT – dynamical mean field theory
 - Use DFT wavefunctions and estimates of parameters
- Why is DFT a reasonable starting point for explicit many-body calculations?
 - KS eigenvalues not so far from the actual G eigenvalues for many system
 - Perturbation is not too large for many systems, e.g. Silicon

Comparison of experiment: GW and Kohn-Sham

The lowest gap in the set of covalent semiconductors

LDA (also GGAs) give gaps that are too small – the “band gap problem”

GW is much better!



This is not the right figure!
The correct figure is similar!

New Idea – a form of self-consistency

- The G_0W_0 approximation show be best if the perturbation due to many-body effects is small
 - Works well for Si,
 - However, often the difference from KS is large
- Idea from Faleev, Van Schilfgaarde, Kotani:
 - Do NOT use KS as starting point
 - Define an independent particle problem with eigenvalues close to the final G_0W_0 eigenvalues
 - Make self-consistent –
 - Start with some guess like KS and interate until the difference with G_0W_0 is small
- Works better for large gaps

Electron excitation at fixed number N

Electron excitation at fixed number N

$$\Delta E^* = E^*(N) - E_0(N)$$

Can be considered as:

1. Removing an electron leaving a hole (N-1 particles)
2. Adding an electron (Total of N particles)
3. Since both are present, there is an electron-hole interaction

Since electron-hole interaction is attractive

$$\Delta E^* < E_{\text{gap}}$$

In independent particle approaches, there is no electron-hole interaction ---- thus excitations are simply combination of addition and removal

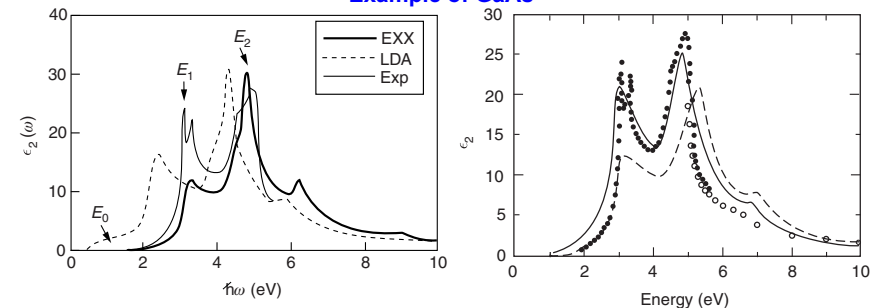
Electron excitation at fixed number N

Example of optical excitation

Optical excitation is the spectra for absorption of photons with the energy going into electron excitations

$$\Delta E^* = E^*(N) - E_0(N)$$

Example of GaAs

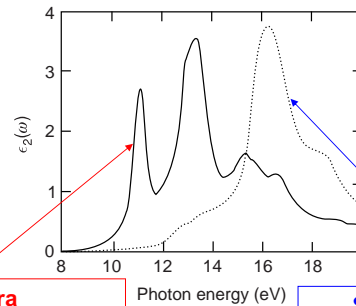


Experiment shows electron-hole interaction directly – spectra is NOT the simple combination of non-interacting electrons and holes

Electron excitation at fixed number N

Example of optical excitation

Example of CaF_2 – complete change of spectra due to electron-hole interaction



Observed spectra changed by electron-hole interaction

Excitons are the elementary excitations

Spectra for non-interacting electrons and holes

The end

Solve Bethe-Salpeter Equation

Problem for two particles

Excitons, shifts in spectral weight at higher energy

Dynamic Response Function χ^0

Recall the static response function for independent particles, for example the density response function:

The response to a variation of the *total potential* $V_{\text{eff}}(\mathbf{r})$ at point $\mathbf{r} = \mathbf{r}'$ (see App. A for definition of functional derivatives) defines the density response function

$$\chi_n^0(\mathbf{r}, \mathbf{r}') = \frac{\delta n(\mathbf{r})}{\delta V_{\text{eff}}(\mathbf{r}')} = 2 \sum_{i=1}^{\text{occ}} \sum_{j=1}^{\text{empty}} \frac{\psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) \psi_j^*(\mathbf{r}') \psi_i(\mathbf{r}')}{\varepsilon_i - \varepsilon_j}, \quad (\text{D.3})$$

The dynamic response function for independent particles at frequency ω is:

a complex function, with a small imaginary damping factor $\eta > 0$,

$$\chi_{a,b}^0(\omega) = 2 \sum_{i=1}^{\text{occ}} \sum_{j=1}^{\text{empty}} \frac{[M_{ij}^a]^* M_{ij}^b}{\varepsilon_i - \varepsilon_j + \omega + i\eta}, \quad (\text{D.16})$$

or

$$\begin{aligned} \text{Re} \chi^0(\omega)_{a,b} &= \sum_{i=1}^{\text{occ}} \sum_{j=1}^{\text{empty}} \frac{[M_{ij}^a]^* M_{ij}^b}{(\varepsilon_i - \varepsilon_j)^2 - \omega^2}, \\ \text{Im} \chi^0(\omega)_{a,b} &= \sum_{i=1}^{\text{occ}} \sum_{j=1}^{\text{empty}} |[M_{ij}^a]|^2 M_{ij}^b \delta(\varepsilon_j - \varepsilon_i - \omega). \end{aligned} \quad (\text{D.17})$$

Dynamic Response Function χ

Recall the static form:

(Can be expressed in real or reciprocal space)

$$\chi = \frac{\delta n}{\delta V_{\text{eff}}} \frac{\delta V_{\text{eff}}}{\delta V_{\text{ext}}} = \chi^0 \left[1 + \frac{\delta V_{\text{int}}}{\delta n} \frac{\delta n}{\delta V_{\text{ext}}} \right] = \chi^0 [1 + K\chi],$$

where the kernel K given in \mathbf{r} space in (9.12) or in \mathbf{q} space as

$$K(\mathbf{q}, \mathbf{q}') = \frac{\delta V_{\text{int}}(\mathbf{q})}{\delta n(\mathbf{q}')} = \frac{4\pi}{q^2} \delta_{\mathbf{q}, \mathbf{q}'} + \frac{\delta^2 E_{\text{xc}}[n]}{\delta n(\mathbf{q}) \delta n(\mathbf{q}')} \equiv V_C(q) \delta_{\mathbf{q}, \mathbf{q}'} + f_{\text{xc}}(\mathbf{q}, \mathbf{q}').$$

Solving (D.9) (Exercise D.2), leads to the ubiquitous form [96, 284, 865]

$$\chi = \chi^0 [1 - \chi^0 K]^{-1} \quad \text{or} \quad \chi^{-1} = [\chi^0]^{-1} - K.$$

At frequency ω this is simply:

$$K(\mathbf{q}, \mathbf{q}', \omega) = V_C(q) \delta_{\mathbf{q}, \mathbf{q}'} + f_{\text{xc}}(\mathbf{q}, \mathbf{q}', \omega), \quad (\text{D.19})$$

and a similar expression in \mathbf{r} space. Thus the dynamical generalization of (D.11) can be written in compact form as

$$\chi(\omega) = \chi^0(\omega) [1 - \chi^0(\omega) K(\omega)]^{-1}. \quad (\text{D.20})$$

Dynamic Response Function χ

What is the meaning of frequency dependence?

Written as a function of time:

$$\begin{aligned} K(\mathbf{q}, \mathbf{q}', t - t') &= \frac{\delta V_{\text{int}}(\mathbf{q}, t)}{\delta n(\mathbf{q}', t')} \\ &= \frac{4\pi}{q^2} \delta_{\mathbf{q}, \mathbf{q}'} \delta(t - t') + \frac{\delta^2 E_{\text{xc}}[n]}{\delta n(\mathbf{q}, t) \delta n(\mathbf{q}', t')}, \end{aligned} \quad (\text{D.18})$$

Coulomb interaction – instantaneous in non-relativistic theory

Density response at different times

Time Dependent DFT -- TDDFT

Exact formulation of TDDFT – Gross and coworkers

Extends the Hohenberg-Kohn Theorems (section 6.4)

Exact theorems that time evolution of system is fully determined by the initial state (wave function) and the time dependent density!

But no hint of how to accomplish this!

Time Dependent Kohn-Sham (section 7.6)

Replace interacting-electron problem with a soluble non-interacting particle problem in a time dependent potential

Time evolution of the density of Kohn-Sham system is the same as the density of the interacting system!

TDDFT - Kohn-Sham approach

Exact formulation of TDDFT – in principle

If one adds the Kohn-Sham idea of replacing the density with the density of independent particles, this leads to time-dependent Kohn-Sham density functional theory (TDDFT), in which there is a time-dependent Schrödinger-like equation

$$i\hbar \frac{d\psi_i(t)}{dt} = \hat{H}(t) \psi_i(t), \quad (7.22)$$

with an effective hamiltonian that depends upon time t

$$\hat{H}_{\text{eff}}(t) = -\frac{1}{2} \nabla^2 + V_{\text{ext}}(\mathbf{r}, t) + \int \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{\text{xc}}[n](\mathbf{r}, t), \quad (7.23)$$

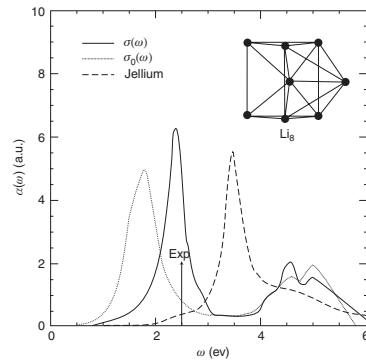
where $V_{\text{xc}}[n](\mathbf{r}, t)$ is a function of \mathbf{r} and t and a *functional* of $n(\mathbf{r}', t')$. Note that in the formally exact theory, $V_{\text{xc}}[n](\mathbf{r}, t)$ is a functional of t' for all earlier times $t' < t$. This is the Achilles' heel of the present theory of TDDFT: it is not known how to create a useful universal functional of time. Essentially all work to date (see Ch. 20) uses the *adiabatic approximation* in which the exchange–correlation potential is the usual time-independent functional of the density $V_{\text{xc}}[n(t)](\mathbf{r})$, e.g. in the adiabatic LDA (ALDA), it is simply $V_{\text{xc}}(\mathbf{r}, t) = V_{\text{xc}}(n(\mathbf{r}, t))$.

TDDFT - Adiabatic Approximation I

The simplest approximation – adiabatic assumption – $f_{xc}(t-t') \sim \delta(t-t')$

That is $V_{xc}(t)$ is assumed to be a function of the density **at the same time**

When is this useful? Low frequencies, localized systems, ...
Now widely used in molecules, clusters,



TDDFT - Beyond the Adiabatic Approximation

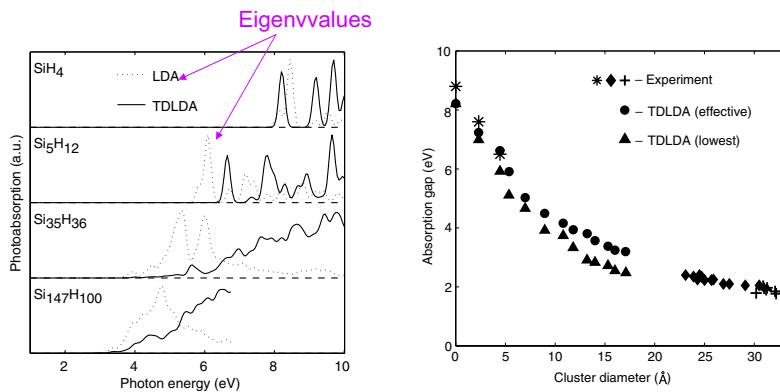
Crucial in extended systems – much current research

Leads methods that explicitly treat interacting particles!

Lectures by Lucia Reining – Nov. 8, 10

TDDFT - Adiabatic Approximation II

Calculations on semiconductor clusters – from small to hundreds of atoms



Real-time method developed by us and others – can treat non-linear effects, etc. Not shown here -- See text