

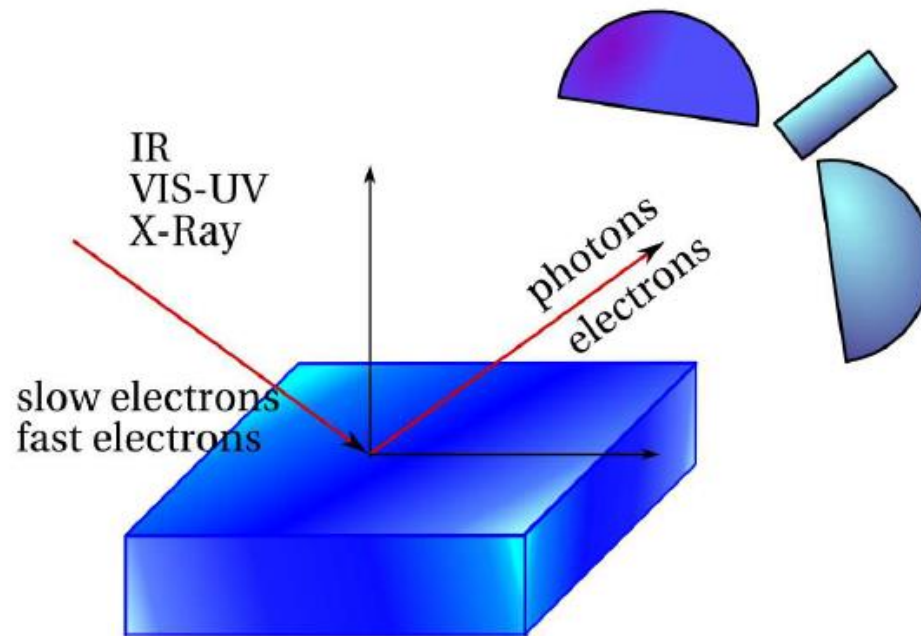
# Density functional theory in solid state physics

## Lecture 13

- Lattice vibrations in solid materials can be well and readily treated within a DFT framework
- Two approaches:
  - Use numerical derivatives of the total energy, forces etc in combination with finite displacements of atoms
  - Calculate derivatives using perturbation theory (DFPT)
- Electron-phonon coupling calculations from DFPT: access to EPC induced band gap renormalizations, superconductivity, Kohn anomalies in metals
- Phonon-phonon interaction from DFPT: phonon self-energy, anharmonic effects, temperature-induced phonon renormalization
- Boltzmann Transport Equation: Electron and phonon dynamics from ab initio, using DFT input data
  - thermal conductivity, electron and hole mobilities, ultrafast relaxation processes

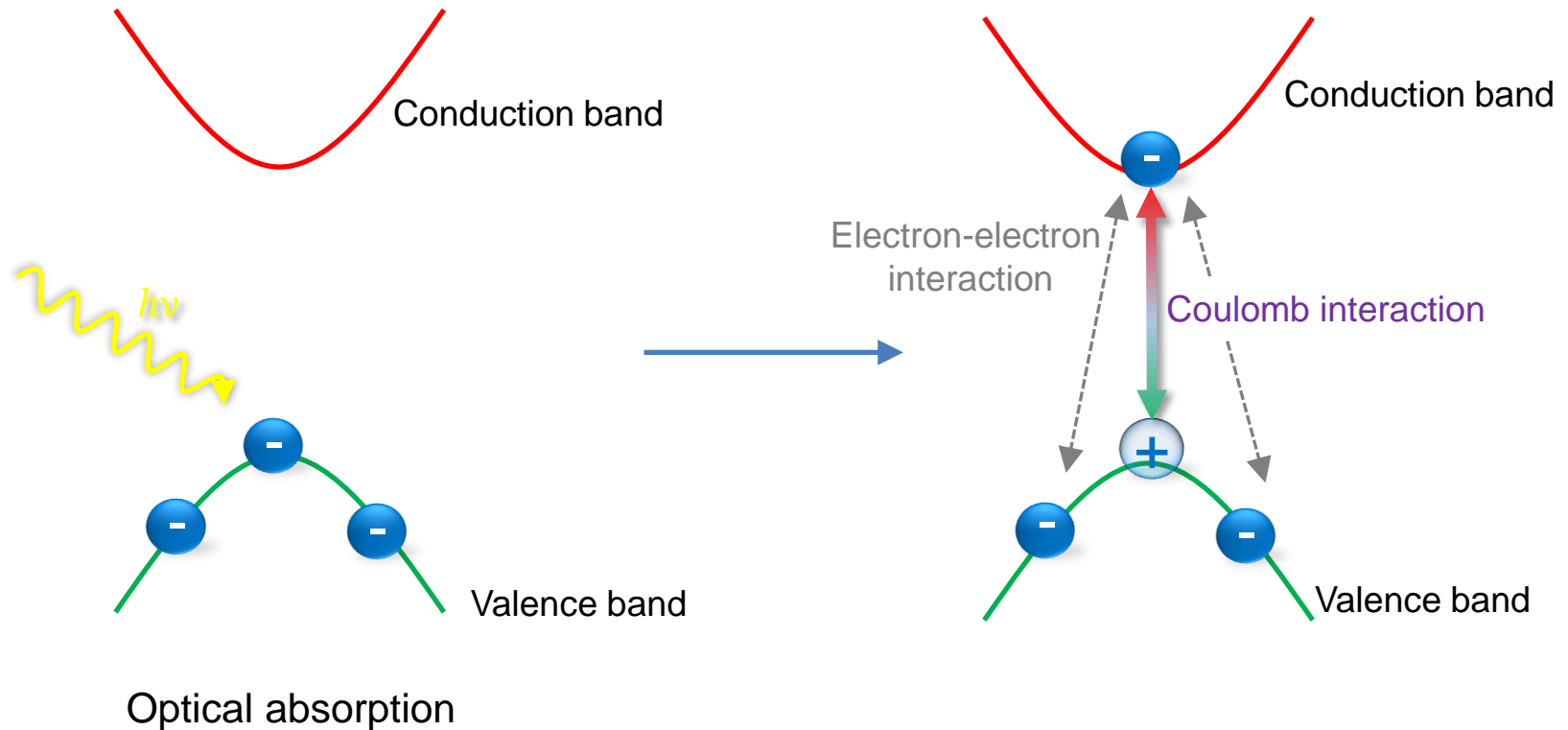
- Molecular dynamics: use Newton's equations of motion to study the temporal evolution of the atomic structure
- Ab initio MD: accurate interatomic forces from DFT
- Introduce temperature through thermostats: system in contact with an external heat bath
- Similarly: Barostats can be used to regulate the pressure acting on the unit cell
- Access to a variety of properties:
  - chemical reactions
  - phase transitions
  - diffusion
  - phonons, dipole moments etc
- Advantage: anharmonic effects, phonon-phonon, electron-phonon interactions are automatically included
- Things to consider:
  - Discrete time-step  $\Delta t$  for propagation, algorithm needs to be stable
  - Thermostats and barostats contain parameters („masses“, „rise time“) that need to be adjusted to well-behaved temperature/pressure control

- Theoretical spectroscopy from ab initio



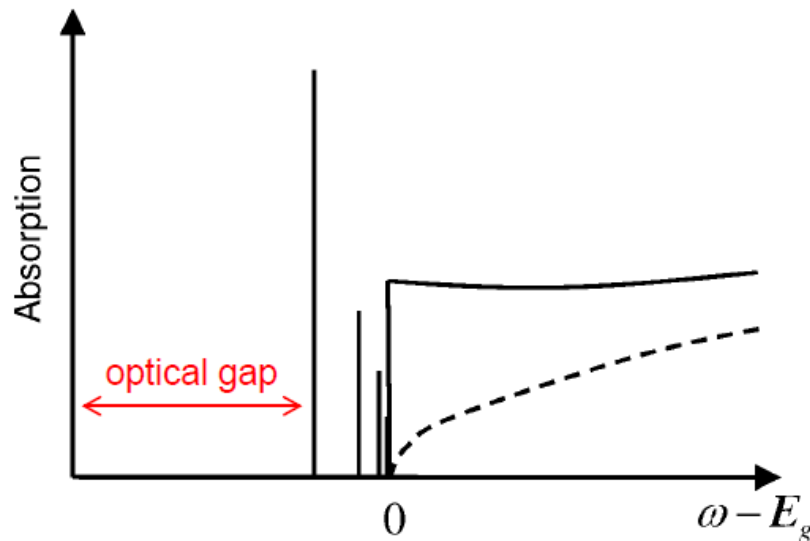
Electronic excitations:

- Optical excitations
- Electron energy loss (EEL)
- Inelastic x-ray scattering
- Photoemission & Inverse photoemission
- ...



- Excited electron and positive „hole“ in the valence band bound by Coulomb interaction. „Exciton“
- Needs proper description of electron-hole and electron-electron interaction effects

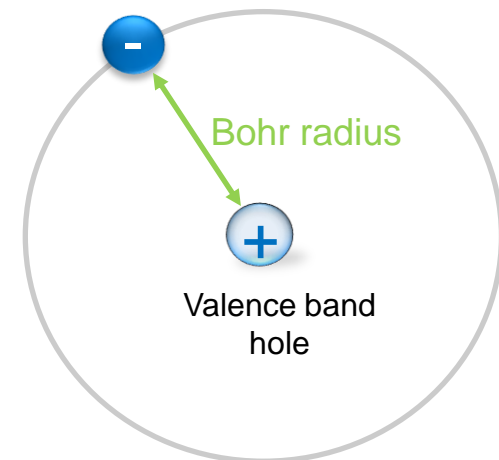
- Sharp features appear below the electronic band gap



S. Koch, „Quantum Theory of the Optical and Electronic Properties of Semiconductors“

### Hydrogen model of excitons

Conduction band electron



Wannier Equation

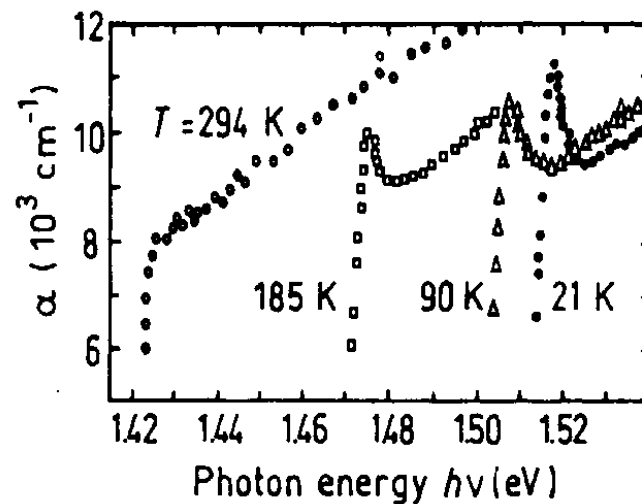
$$\left( -\frac{1}{2} \nabla^2 - \frac{1}{\epsilon r} \right) \phi(r) = E \phi(r)$$

- Reduction of „optical“ band gaps compared to electronic band gaps
- Excitons can often be well described by hydrogen model, excitonic Rydberg series

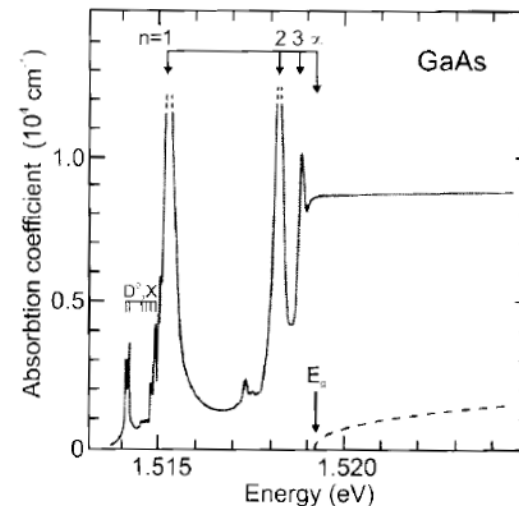
- Example: GaAs

Electronic bandgap at small  $T$ : 1.52 eV

Calculated exciton binding energy: 4 meV, calculated exciton bohr radius: 12 nm



Sturge, Phys. Rev. 127, 768 (1962)



Adv. Solid. State Phys. 25, 299 (1985)

- Absorption coefficient in solids is related to dielectric tensor  $\epsilon_{\alpha\beta}(\omega)$  :

$$A_{\alpha\alpha}(\omega) = \frac{2\omega}{c} \kappa_{\alpha\alpha}$$

- Complex refractive index  $n_{\alpha\beta}^*(\omega) = \underbrace{\sqrt{\frac{|\epsilon_{\alpha\alpha}(\omega)| + \text{Re}\epsilon_{\alpha\alpha}(\omega)}{2}}}_{n_{\alpha\beta}(\omega)} + i \underbrace{\sqrt{\frac{|\epsilon_{\alpha\alpha}(\omega)| - \text{Re}\epsilon_{\alpha\alpha}(\omega)}{2}}}_{\kappa_{\alpha\beta}(\omega)}$

- In exact QM theory, solve time-dependent Schrödinger Equation

$$\hat{H}(t)\psi(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t)$$

with additional time-dependent external potential (corresponding to the laser field)

- Resonance for particular frequencies  $\omega_I$ , corresponding to electron excitation with many-body wavefunction  $\psi_I$  and excitation energy  $\Delta E_I = E_I - E_{gs}$
- Optical oscillator strength from Fermi's golden rule:  $\Gamma_I \propto |\langle \psi_I | \hat{r} | \psi_{gs} \rangle|^2$

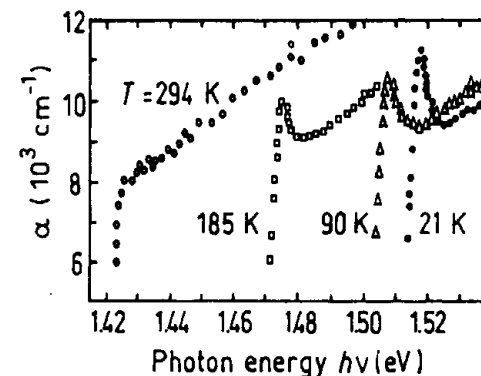
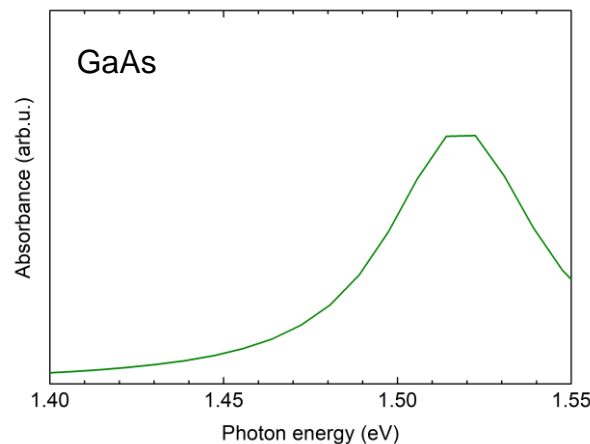


- We can use DFT to derive optical spectra within „independent particle approximation“

$$\text{Dielectric function } \epsilon_{\alpha\beta}(\omega) = \delta_{\alpha\beta} - \frac{1}{V\omega^2} \left[ \sum_i f_{ik} \delta_{\alpha\beta} \sum_j (f_{ik} - f_{jk}) \frac{\langle \varphi_{ik} | \vec{r}_\alpha | \varphi_{jk} \rangle \langle \varphi_{jk} | \vec{r}_\beta | \varphi_{ik} \rangle}{\epsilon_{ik} - \epsilon_{jk} + \omega + i\eta} \right]$$

Fermi occupation

- Effectively sum over transitions between occupied and unoccupied electronic bands, „joint density of states“
- Singularities („poles“) in  $\text{Im}[\epsilon]$  correspond to excitation energies of the system





- But: No coupling between excited electrons and „holes“ in the valence band in DFT  
→ DFT cannot capture excitonic effects in optical spectra, but can work well for systems with small excitonic effects

- Density functional theory is a reformulation of the time-independent Schrödinger Equation
- Is there an equivalent for the time-dependent Schrödinger Equation?
- Yes, time-dependent DFT (TDDFT)
- Formal basis: Runge-Gross theorem *Phys. Rev. Lett. 52, 997 (1984)*

For any system with a Hamiltonian of the form

$$H = T + U + V_{ext},$$

 Electron-electron interaction  
 External potential acting on electrons

there exists a one-to-one mapping

$$n(r, t) \xleftrightarrow{\psi_0} V_{ext}(r, t)$$

at any time  $t$ .

- The electron density determines the potential (and thus the physical properties) of the system at any time  $t$  up to a time-dependent function.

- How to find time-dependent density for given time-dependent potential?
- Use Dirac action  $A[n] = A[\psi[n]] = \int_{t_0}^{t_1} \left\langle \psi(t) \left| i \frac{\partial}{\partial t} - H(t) \right| \psi(t) \right\rangle dt$
- RG II: the true time-dependent density  $n_0$  is the one that makes the action stationary

$$\left. \frac{\delta A[n]}{\delta n(\vec{r}, t)} \right|_{n_0} = 0$$

- Using the variational principle yields the time-dependent Kohn-Sham equations

$$\left[ -\frac{1}{2} \nabla^2 + \underbrace{v_{eff}(\vec{r}, t)}_{v(\vec{r}, t) + v_H(\vec{r}, t) + v_{xc}(\vec{r}, t)} \right] \varphi_j(r, t) = i \frac{\partial}{\partial t} \varphi_j(\vec{r}, t)$$

- The unknowns are pushed into the time-dependent exchange-correlation functional

$$v_{xc}(\vec{r}, t) = \frac{\delta A_{xc}[n]}{\delta n(\vec{r}, t)}$$

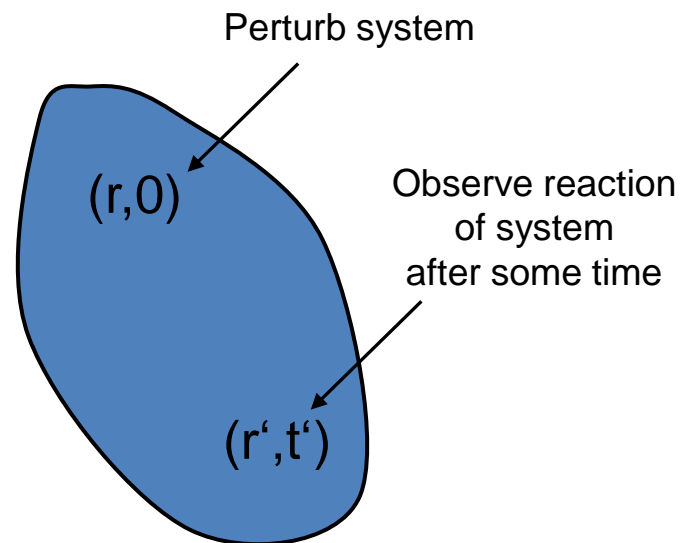
- Careful:  $v_{xc}(r, t)$  contains *retardation* and *memory effects*, i.e. depends on the density on all previous times  $t' \leq t$ .
- In principle exact theory, but  $A_{xc}$  is not known and needs to be approximated
- Adiabatic approximation: we neglect all retardation and memory effects and assume that  $v_{xc}$  changes instantaneously

$$v_{xc}(\vec{r}, t) = \frac{\delta A_{xc}[n]}{\delta n(\vec{r}, t)} \approx \left. \frac{\delta E_{xc}[\tilde{n}]}{\delta \tilde{n}(\vec{r})} \right|_{\tilde{n}(\vec{r})=n(\vec{r}, t)}$$

- We can then use all XC functionals from time-independent DFT, e.g. adiabatic LDA (ALDA):

$$v_{xc}^{ALDA}(\vec{r}, t) = v_{xc}^{ALDA}(n(\vec{r}, t))$$

- Typical use: Time evolution of the electron density/orbitals/energies as a reaction to an external perturbation, for example under the effect of an external time-dependent field



- We can do this by „propagating“ the TD-KS equations to calculate the time evolution of the electron density

1. Prepare the initial state, usually the ground state, by a time-independent calculation

This yields the initial electron density  $n(\vec{r}, t = 0)$  and orbitals  $\varphi_i^0(\vec{r})$

2. Solve the TDKS equations  $\left[-\frac{1}{2}\nabla^2 + v_{eff}(\vec{r}, t)\right] \varphi_j(\vec{r}, t) = i \frac{\partial}{\partial t} \varphi_j(\vec{r}, t)$

selfconsistently for the time range  $t \in [0, T]$  through updating the potential  $v_{eff}(\vec{r}, t)$ .

This gives the TDKS orbitals  $\varphi_j(\vec{r}, t)$  and the electron density  $n(\vec{r}, t) = \sum_i |\varphi_j(\vec{r}, t)|^2$ .

Conveniently express the orbitals through  $\varphi_j(\vec{r}, t) = \sum_i a_{ij}(t) \varphi_i^0(\vec{r})$

3. Calculate observables of interest using the results.

- Like for molecular dynamics, we use a discrete time step  $\Delta t$  to propagate

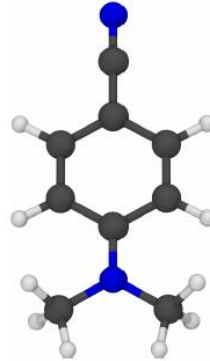
$$\varphi_j(\vec{r}, t + \Delta t) = T \exp \left( -i \int_0^t \hat{H}(t') dt' \right) \varphi_j(\vec{r}, t)$$

- Several algorithms exist for the propagation. We want to keep choose  $\Delta t$  as large as possible but keep the algorithm stable
- Propagator should be unitary, have a systematically improvable error and be stable
- Example: Crank-Nicolson algorithm:

$$\varphi_j(\vec{r}, t + \Delta t) \approx \frac{1 - i \frac{\Delta t}{2} \hat{H}}{1 + i \frac{\Delta t}{2} \hat{H}} \varphi_j(\vec{r}, t) \quad \rightarrow \quad \left[ I + i \frac{\Delta t}{2} \hat{H} \right] \varphi_j(\vec{r}, t + \Delta t) = \left[ I - i \frac{\Delta t}{2} \hat{H} \right] \varphi_j(\vec{r}, t)$$

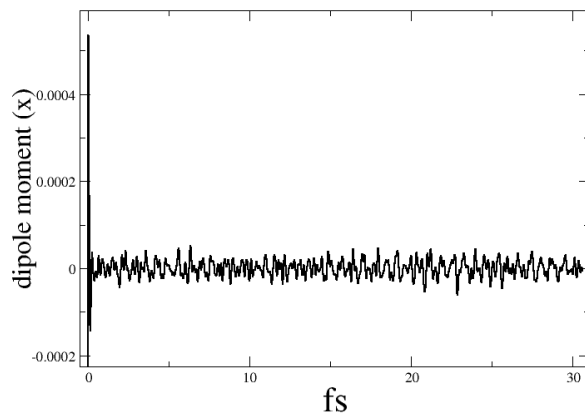
- More accuracy:
  1. Solve equation to estimate  $\varphi_j(\vec{r}, t + \Delta t)$
  2. Estimate  $\hat{H}(t + \Delta t)$  („predictor“)
  3. Build „corrected“  $\hat{H}(t + \frac{\Delta t}{2}) = \frac{1}{2} [\hat{H}(t + \Delta t) + \hat{H}(t)]$  and use that to obtain better  $\varphi_j(\vec{r}, t + \Delta t)$

- For example: Apply a short perturbative field representing a pulsed laser

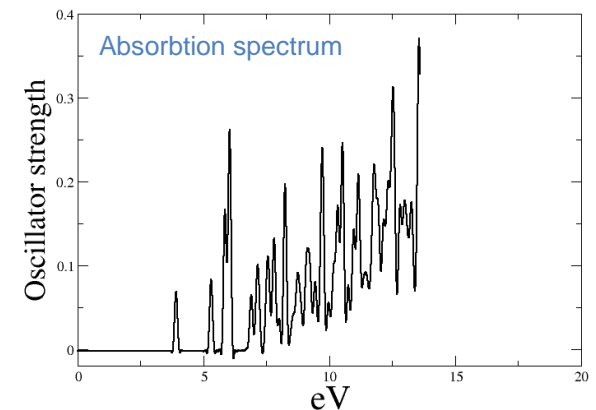


N,N-dimethylaminobenzonitrile  
(DMABN)

TD-KS calculation for  $t \in [0, 30 \text{ fs}]$



Fourier transformation,  
obtain dynamical  
polarizability  $\alpha(\omega) \propto FT[\vec{\mu}]$



[http://benasque.org/2012tddft/talks\\_contr/071\\_Benasque\\_1-2.pdf](http://benasque.org/2012tddft/talks_contr/071_Benasque_1-2.pdf)

- The longer the simulation time  $T$ , the better the energy resolution



- Previous approach does not work for solids, because of periodic boundary conditions and bad computational scaling
- Alternative for optical spectra: Linear response
- Approach: Assume that perturbation of external potential,  $\delta v(\vec{r}, t)$ , is small, so that

$$n(\vec{r}, t) = n_0(\vec{r}) + \delta n(\vec{r}, t)$$



First-order density response

- Standard response theory:  $\delta n(\vec{r}, t) = \int_0^\infty \int \chi(\vec{r}, \vec{r}'; t, t') \delta v(\vec{r}', t') dr' dt'$
- Interested in the density-density response function  $\chi(\vec{r}, \vec{r}'; t, t') = \left. \frac{\delta n(\vec{r}, t)}{\delta v(\vec{r}, t')} \right|_{v_0}$
- $\chi(\vec{r}, \vec{r}'; \omega)$  is directly related to the dielectric function of a system → access to optical properties

- Dyson-like equation

$$\chi(\vec{r}, \vec{r}', \omega) = \chi^0(\vec{r}, \vec{r}', \omega) + \chi^0(\vec{r}, \vec{r}', \omega) * \left( \frac{1}{|\vec{r} - \vec{r}'|} + f_{xc}(\vec{r}, \vec{r}'; \omega) \right) * \chi(\vec{r}, \vec{r}', \omega)$$

„XC kernel“

For ALDA:  $f_{xc}^{ALDA}(\vec{r}, \vec{r}'; t) = \delta(\vec{r} - \vec{r}') \frac{dv_{xc}^{LDA}[n]}{dn} \Big|_{n=n(\vec{r}, t)}$

- $\chi^0$  is the non-interacting susceptibility from time-independent KS:

Orbitals from time-independent  
Kohn-Sham calculation

$$\chi^0(\vec{r}, \vec{r}', \omega) = \sum_{i,j} (f_i - f_j) \frac{\varphi_i^*(\vec{r}) \varphi_j(\vec{r}) \varphi_j(\vec{r}') \varphi_i^*(\vec{r}')}{\varepsilon_i - \varepsilon_j + \omega + i\eta}$$

- Poles of  $\chi$  correspond to the excitation energies of the system, shifted compared to  $\chi^0$  through effect of electron-electron interaction
- We can get the optical properties from the results of time-independent KS without explicit propagation of the TD-KS equations

- Often used for solids: Dyson Equation in reciprocal space

$$\chi_{G,G'}(\vec{q}, \omega) = \chi_{G,G'}^0(\vec{q}, \omega) + \sum_{G''} \chi_{G,G'}^0(\vec{q}, \omega) \left[ \frac{4\pi}{|\vec{q} + \vec{G}''|^2} + f_{xc}(\vec{q}, \vec{G}, \vec{G}'') \right] \chi_{G'',G'}(\vec{q}, \omega)$$

- Simple form for the microscopic inverse dielectric function in this case:

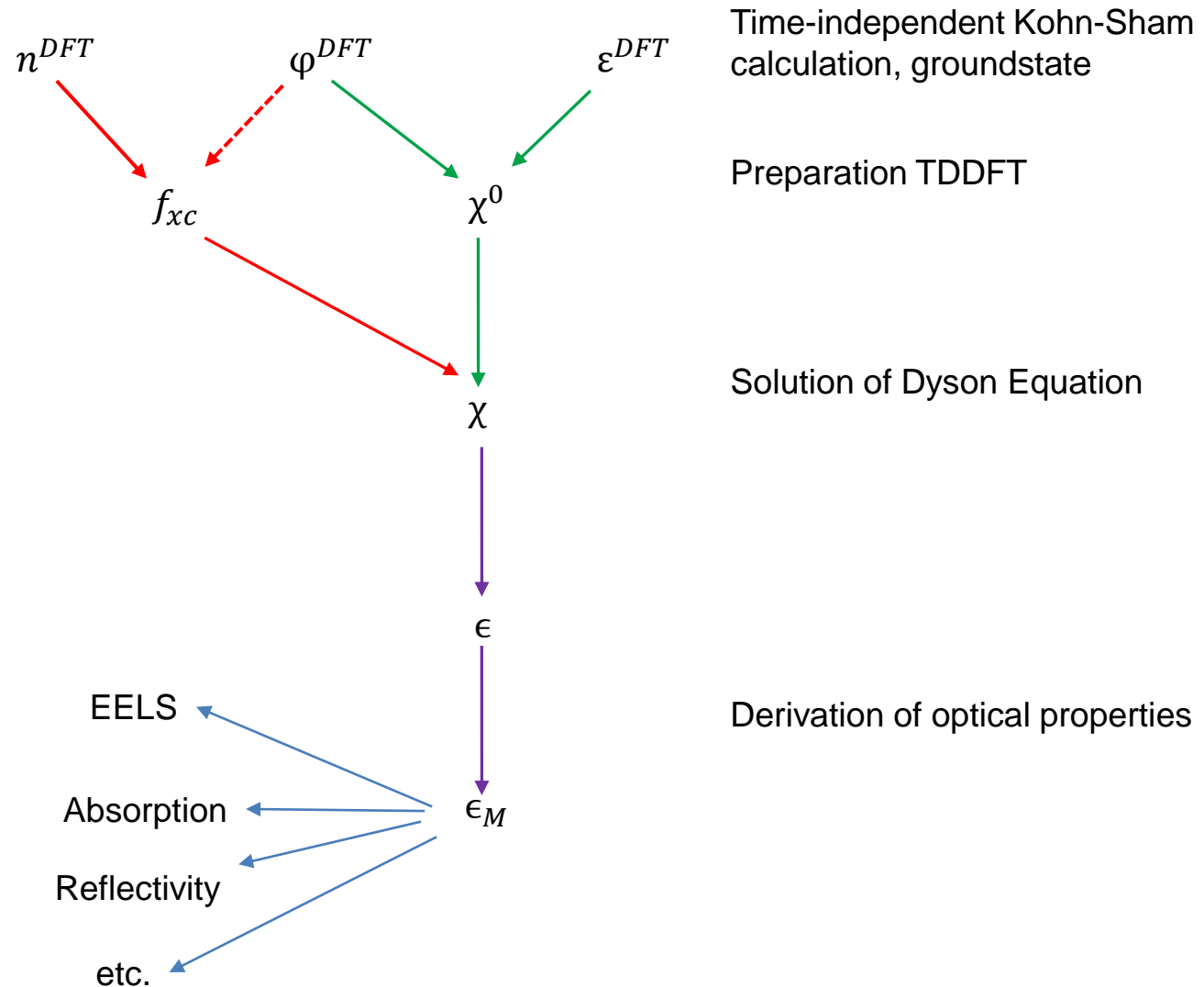
$$\epsilon_{G,G'}^{-1}(\vec{q}, \omega) = \delta_{G,G'} + \frac{4\pi}{|\vec{q} + \vec{G}|^2} \chi_{G,G'}(\vec{q}, \omega)$$

- Macroscopic dielectric function:  $\epsilon_M(\omega) = \lim_{\vec{q} \rightarrow 0} \frac{1}{[\epsilon_{G,G'}^{-1}(\vec{q}, \omega)]_{G,G'=0}}$

This includes local field effects due to  
Interaction of light with the electronic charge

- Need to iteratively solve the Dyson equation, with  $\chi_{G,G'}^0$  as starting guess

- LR-TDDFT calculation scheme



- In finite systems: excitation energies are discrete
- In this case, one can use the Casida equations

$$\begin{bmatrix} \vec{A} & \vec{B} \\ \vec{B}^* & \vec{A}^* \end{bmatrix} \begin{bmatrix} \vec{X}_j \\ \vec{Y}_j \end{bmatrix} = \omega_j \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} \vec{X}_j \\ \vec{Y}_j \end{bmatrix}$$

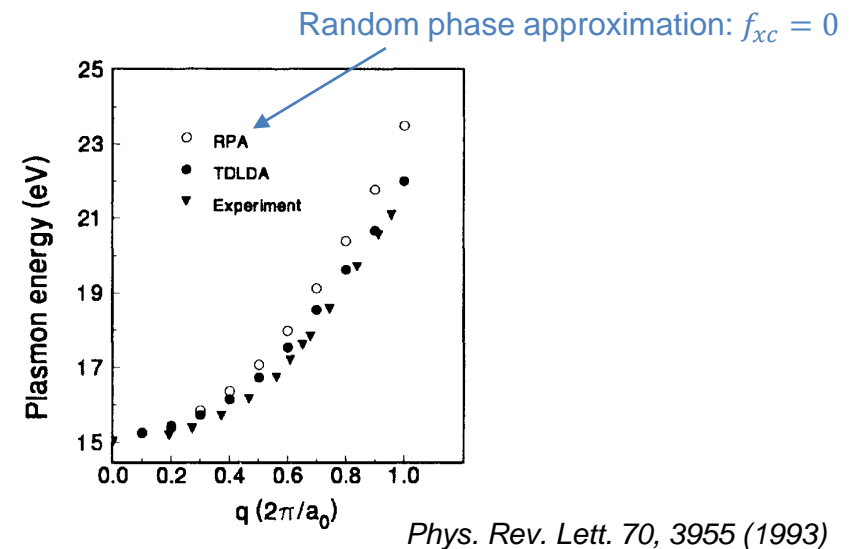
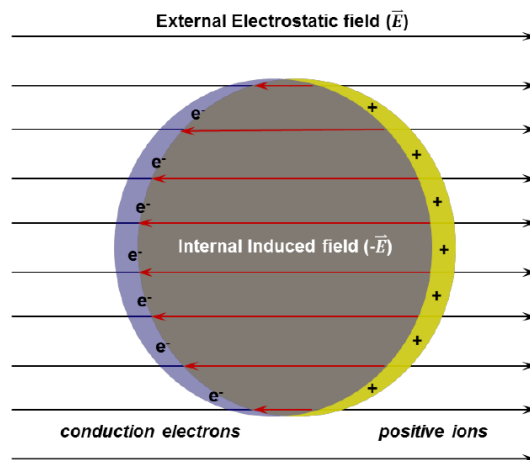
to obtain the excitation energies  $\omega_j$  (i.e. the poles of  $\chi$ ) of the system of interest.

- Under the adiabatic approximation:  $B_{ik,jl} = \int \varphi_i^*(r) \varphi_k(r) \varphi_l(r') \varphi_j^*(r') \left( \frac{1}{|r-r'|} + f_{xc} \right) dr dr'$

$$A_{ik,jl} = \delta_{ij,kl}(\varepsilon_i - \varepsilon_k) + B_{ik,lj}$$

- Tamm-Dancoff approximation (TDA): neglect de-excitation effects, i.e.  $\vec{B} = 0$
- $\vec{X}_j$  and  $\vec{Y}_j$  contain information about the excited states, can be used to derive optical oscillator strengths of excitations using Fermi's Golden rule

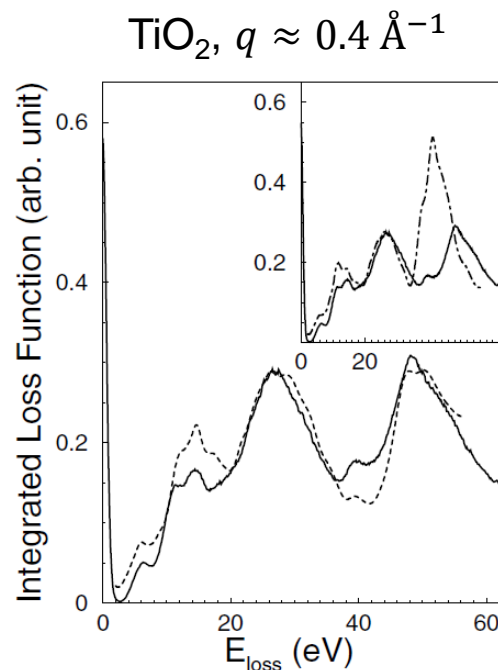
- TDDFT-based approaches are quite popular in chemistry due to computational simplicity, relative accuracy and the possibility of combining TDDFT with molecular dynamics
- How does TDDFT perform in solid state physics?
- ALDA+TDDFT is good for simple metals, e.g. plasmon dispersion in Al



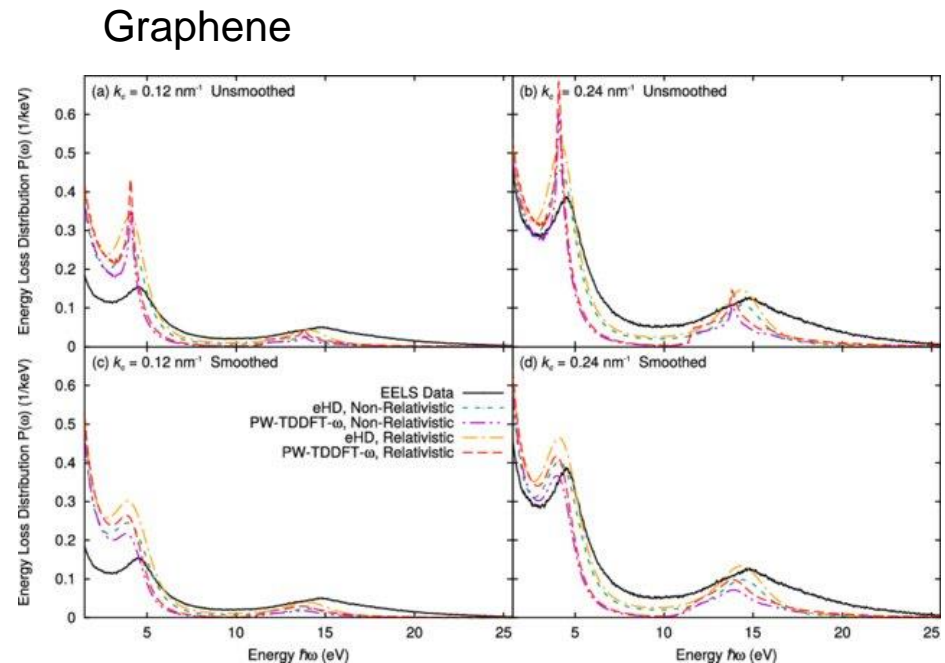
- For such systems, ALDA is a correction to the RPA case

- ALDA+TDDFT works rather well for electron energy loss (EELS) spectra

$$EEL[\vec{q} + \vec{G}, \omega] = -\frac{4\pi}{|\vec{q} + \vec{G}|^2} \text{Im}[\chi_{G,G'}]$$



*Phys. Rev. Lett.* 88, 037601 (2002)

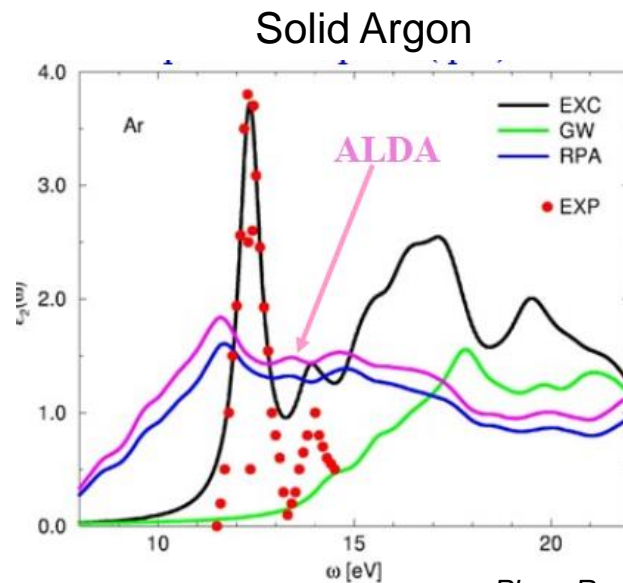


*Rad. Eff. Def. Sol.* 173, 8 (2018)

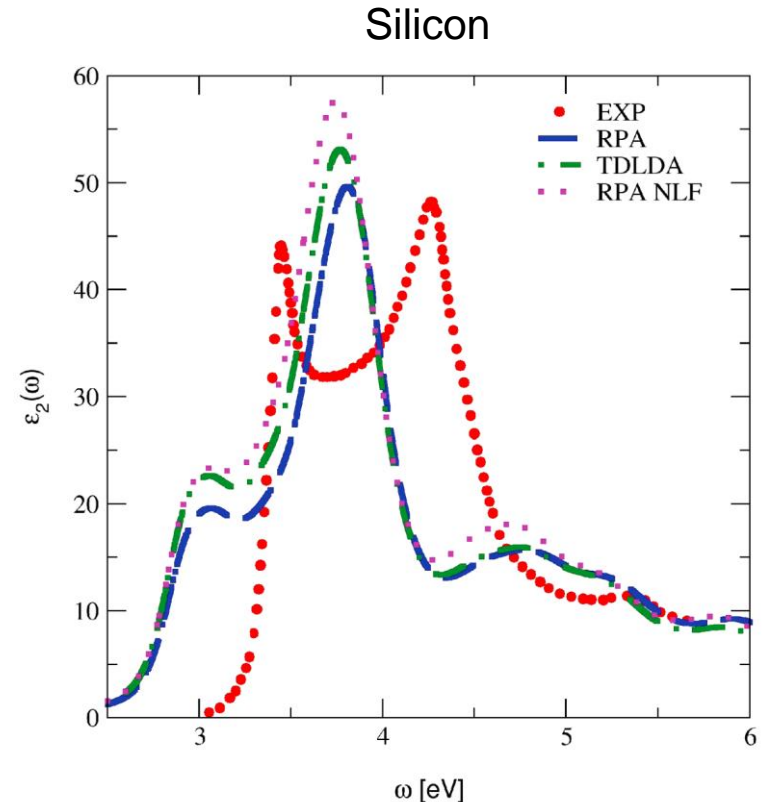
- Peak positions and relative intensities ok, small difference to using the RPA

- ALDA does not work well for absorption spectra (or excitons in general):

- Absorption edge red-shifted (band gap underestimation, missing electron-electron interaction)
- Intensity of excitonic first peak strongly underestimated compared to experiment



*Phys. Rev. Lett. 88, 066404 (2002)*



*Rep. Prog. Phys. 70, 357 (2007)*



- Absorption corresponds to  $Im[\epsilon_M] = - \lim_{\vec{q} \rightarrow 0} \frac{4\pi}{|\vec{q} + \vec{G}|^2} Im[\bar{\chi}_{G,G}]$

with the modified response function

$$\bar{\chi} = \chi^0 + \chi^0 * (\bar{V} + f_{xc}) * \chi$$

$\bar{V} = 0$  for  $G = 0$ ,  
 $\frac{4\pi}{|q + G|^2}$  otherwise

- ALDA behaves like constant for  $q \rightarrow 0$ , hence small effect on optical properties, lack of *long-range* interactions
- ALDA cannot describe excitonic neutral excitations or Rydberg series thereof
- Problem smaller for finite systems, as influence of long-range interactions is less important there

- Several corrections available

- Long-range corrected TDDFT:  $f_{xc,G,G'}^{LRC}(\vec{q}, \vec{G}, \vec{G}') = \frac{\alpha}{|\vec{q} + \vec{G}|^2}$  *Phys. Rev. Lett. 88, 066404 (2002)*

Empirical parameter

- Bootstrap kernel:  $f_{xc}^{boot}(\vec{q}, \vec{G}, \vec{G}', \omega) = \frac{\epsilon_{G,G'}^{-1}(\vec{q}, 0)}{\chi_{0,0}^0(\vec{q}, 0)}$  *Phys. Rev. Lett. 89, 096402 (2002)*

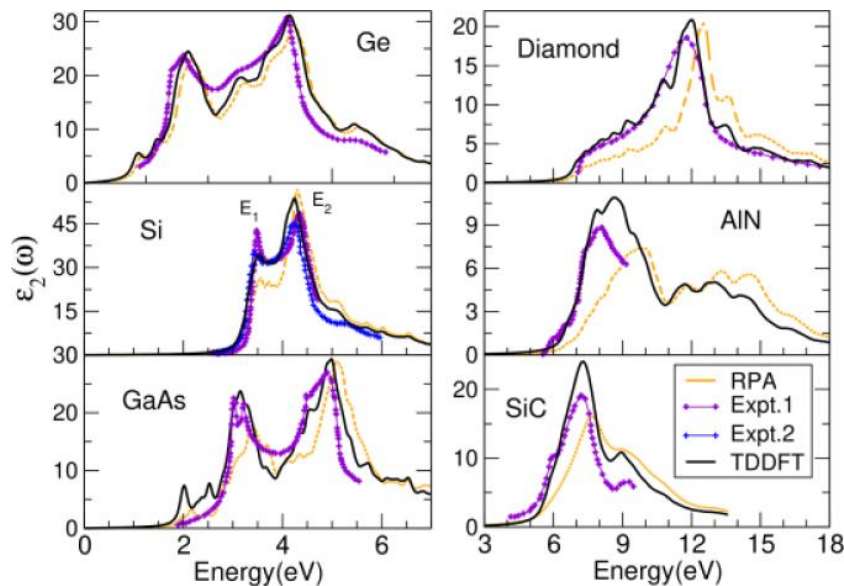
- „Jellium-with-gap“ model:  $f_{xc}^{JGM}(\vec{q}; n, E_g) \propto \frac{4\pi}{q^2}$  *Phys. Rev. B 87, 205143 (2013)*

- ...

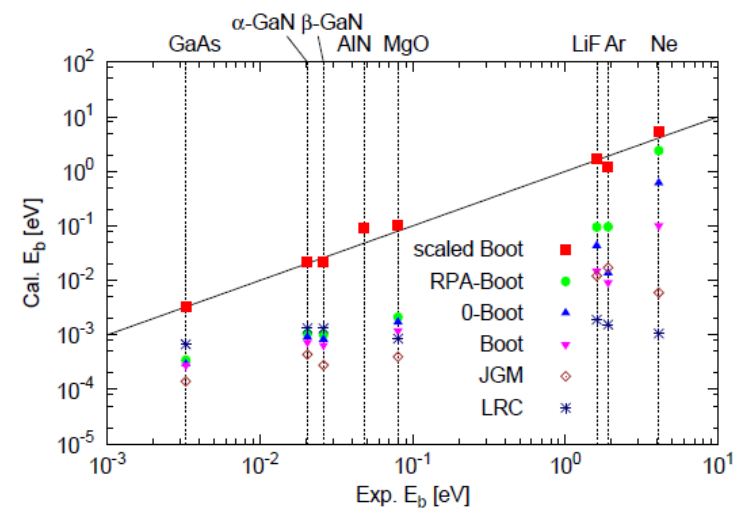
- Qualitative shape of optical spectra can be very good (at least for selected materials)
- Despite recent progress, accuracy for exciton binding energies is still not consistently satisfactory

→ more work necessary

Optical spectra from bootstrap kernel

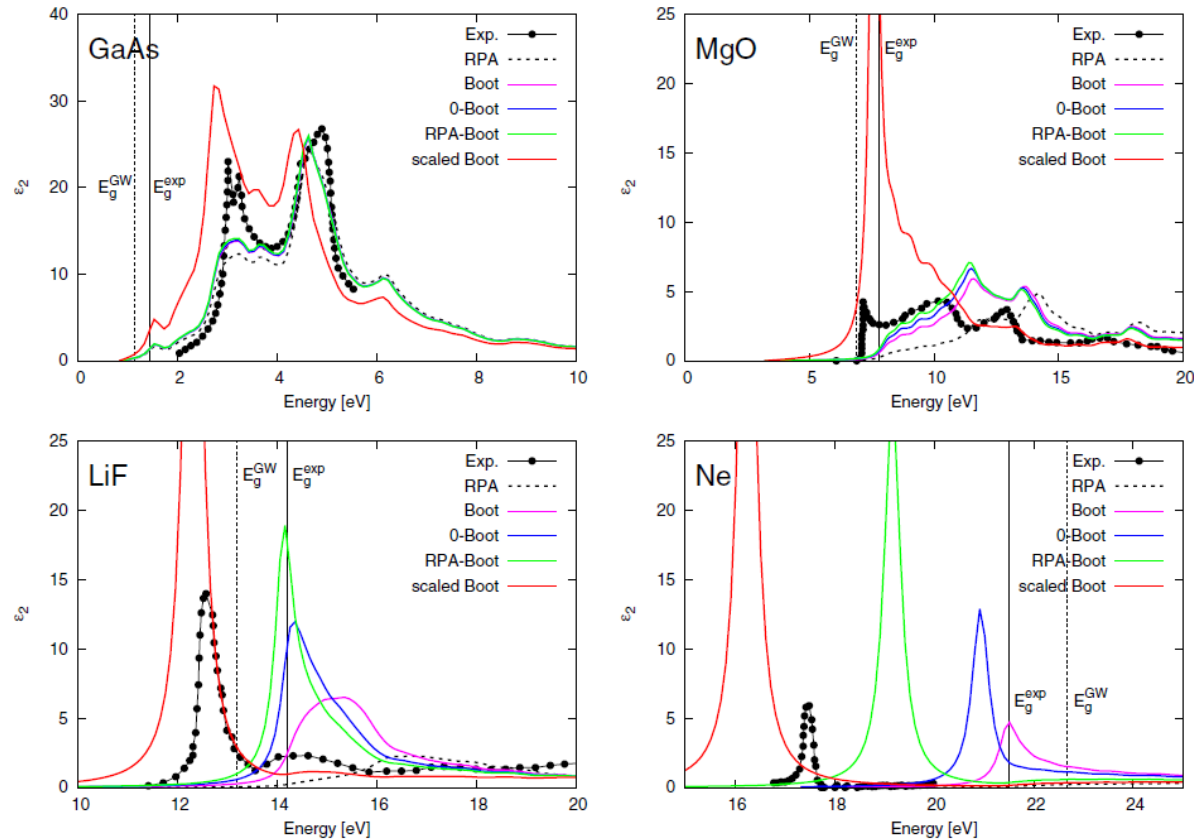


Phys. Rev. Lett. 107, 186401 (2011)



Phys. Rev. B 95, 205136 (2017)

- The scaled bootstrap kernel  $f_{xc}^{scaledB} = A(x)f_{xc}^{boot}$  was fitted to give good exciton binding energies, but in exchange, it overestimates optical oscillator strengths



- The band gap problem is not solved

*Phys. Rev. B 95, 205136 (2017)*