



When States Get Excited or a Short Guide to time dependent DFT

Krzysztof Tatarczyk

tatar@fhi-berlin.mpg.de

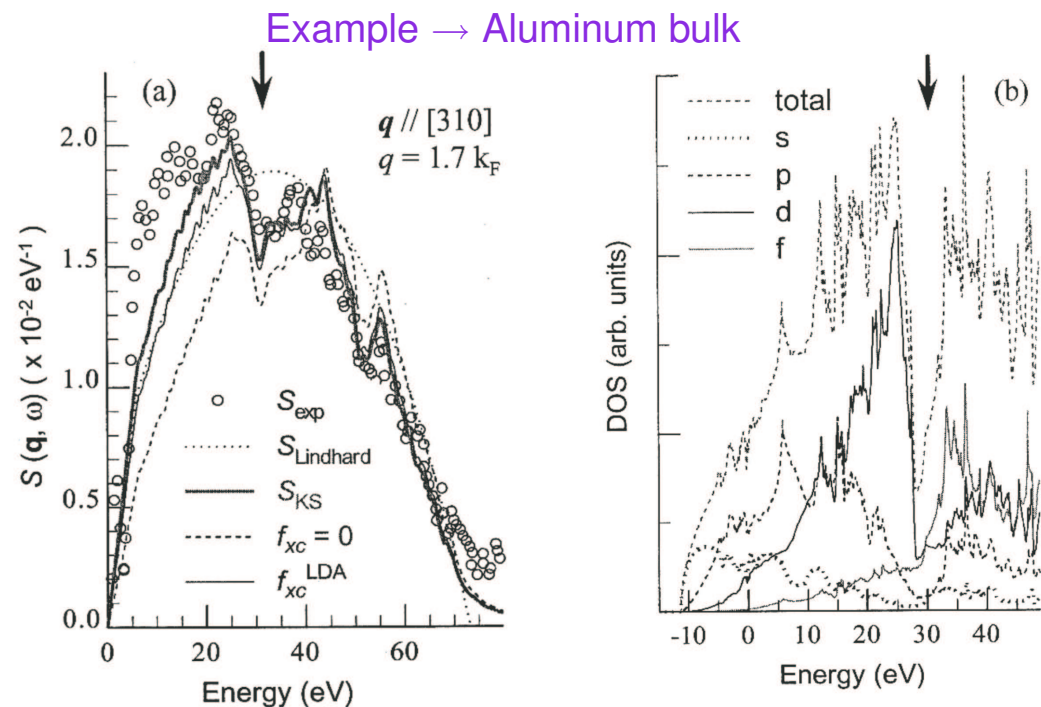
*Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4-6, 14195 Berlin, Germany*



Why study excited states ?

- Because they are there
- Motivation from experiments \Rightarrow progress in spectroscopy methods

- Electron Energy Loss Spectroscopy (EELS)
- Plasmon excitations in bulk systems
- $S(\mathbf{q}, \omega) = -q^2 \Im \epsilon^{-1}(\mathbf{q}, \omega)$
- **Anormalous** behaviour ?
P.M. Platzman *et al.*, PRB 46,12 943(1992)
- **Property** of the material
A. Fleszar *et al.*, PRL, 74, 590(1995)



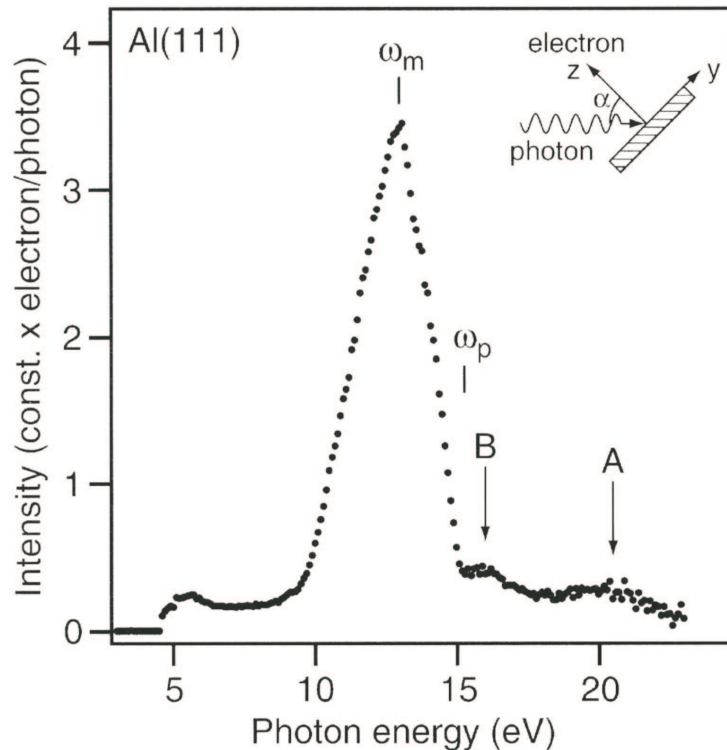
Atomistic studies needed!

- The ultimate gain \rightsquigarrow more realistic description of **exchange** and **correlation** effects



How about surfaces ?

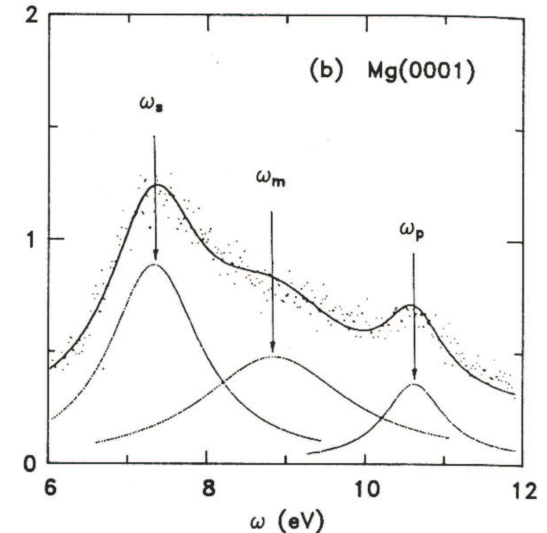
⇒ Photoemission Spectroscopy (PY)



- ✓ The light usually excites only the multipole plasmon
- ✓ features A & B ?

★ Detailed theoretical study desperately wanted ★

⇒ Sample EELS for a surface



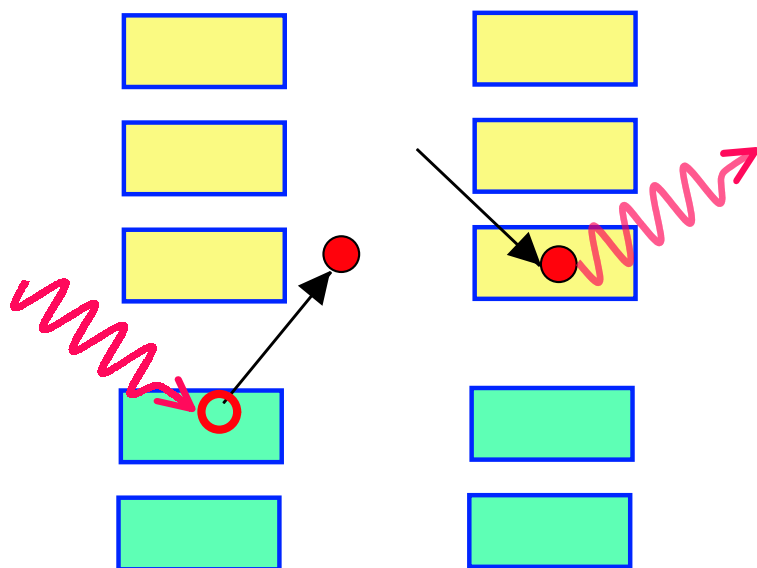
- ✓ Apart from the bulk plasmon there exist two additional
- ✓ The **monopole** surface plasmon ω_s due to the surface
- ✓ The **multipole** surface plasmon ω_m due to diluted density profile



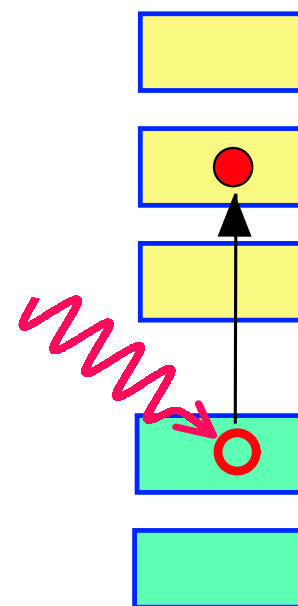
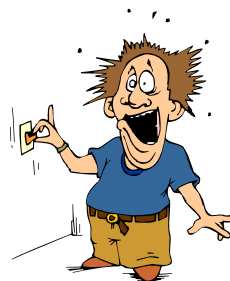
Spectroscopies ?

➡ Prototype Spectroscopy Measurements

☐ Photoemission Spectroscopy (PE)



☐ Absorption



- ★ Electron is removed/added to the system
- ★ **Direct** Photoemission scans **occupied** levels
- ★ **Inverse** Photoemission probes **unoccupied** states

- ★ **Electron-hole** pair is created
- ★ Charge-neutral excitation results
- ★ **Number of electrons unchanged**

★ I can't directly use my ground-state code ★



Kohn-Sham eigenvalues dilemma (?)

□ Description of such measurements is intimately bound to the one-particle/-like energies

□ These can be obtained from DFT, but...

$$\left[-\frac{1}{2}\nabla^2 + V^{\text{ext}}(\mathbf{r}) + V^{\text{H}}(\mathbf{r}) + V^{\text{xc}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_i f_i |\phi_i(\mathbf{r})|^2 \quad E_0 = \min E_{\text{tot}}[n]$$

□ Means ???

■ Static approach to many-body problem

■ By design describes the ground-state properties

■ Kohn-Sham eigenvalues acquire meaning via Janak theorem

$\varepsilon_i = \frac{\delta E_0[n]}{\delta f_i} \rightsquigarrow$ all but the highest occupied one are mathematical artifacts of the method

■ the highest occupied KS eigenvalue corresponds to chemical potential of the system



Can we use DFT for excited states ?

- Kohn-Sham eigenvalues cannot be interpreted directly as excitation energies
 - no formal justification for such action
 - differences of about 10%-50% are observed if the KS excitations energies are compared with experiment
- Janak theorem legitimises use of the ground-state scheme for lowest excited states

$$\begin{aligned} E_0^{DFT}(f_1, \dots, f_i, \dots, f_N) - E_0^{DFT}(f_1, \dots, f_i - 1, \dots, f_N) &= \\ &= \int_0^1 d\zeta \varepsilon_i^{KS}(f_1, \dots, f_i - 1 + \zeta, \dots, f_N) = \varepsilon_i^{KS}(f_i + \frac{1}{2}) \end{aligned}$$

- excitation energy is obtained by two separate, ground-state calculations, Δ SCF
 - problematic in solids
- Band-structure & ... the band-gap ?

$$E^g \equiv I - A = [E_0(N-1) - E_0(N)] - [E_0(N) - E_0(N+1)]$$

$$E^g = \varepsilon_{N+1}(N) - \varepsilon_N(N) + [V_{N+1}^{xc} - V_N^{xc}]$$

HELP ?



Ways to go...

In order to obtain excitation energies:

□ Improve description of the bandstructure

- in a way that it yields electron addition/removal energies seen in spectroscopy experiments
- Means ? Solve the band-gap problem!

◆ Employ the Many-Body Perturbation Theory (MBPT)

$$\left[-\frac{1}{2}\nabla^2 + V^H(\mathbf{r}) \right] \phi_i(\mathbf{r}) + \int d^3r' \Sigma(\mathbf{r}, \mathbf{r}', \varepsilon_i^{QP}) \phi_i(\mathbf{r}') = \varepsilon_i^{QP} \phi_i(\mathbf{r})$$

↪ Effective quasiparticle Hamiltonian with the optical mass (self-energy) operator → the GW method

◆ Stay within the DFT and improve the XC potential

$$V^x = \left. \frac{\delta E^x}{\delta n} \right|_{n=n_0}, \quad E^x = -\frac{1}{2} \sum_{i,j} \int d^3r d^3r' \phi_i^*(\mathbf{r}) \phi_j^*(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') \phi_i(\mathbf{r}) \phi_j(\mathbf{r}')$$

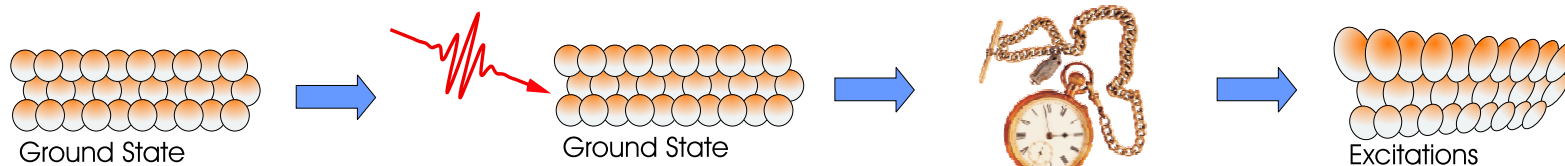
the EXX method → it works (!)



How about charge-neutral excitations ?

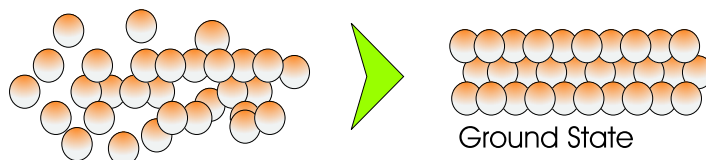


Hint from experiments



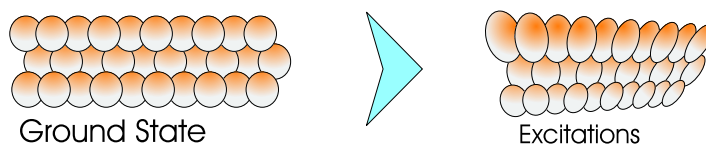
□ Perturbed system is studied

■ Obtain the ground-state



~> HK theorem, KS equations

■ Study the time-evolution



~> ??? ??? ???

□ I need to generalise DFT to time-dependent phenomena!





Starting point

- Consider two separate systems of N electrons

$$\textcircled{1} \hat{H}^{\textcircled{1}} = \hat{T} + \hat{V}(t) + \hat{W}$$

$$\textcircled{2} \hat{H}^{\textcircled{2}} = \hat{T} + \hat{V}'(t) + \hat{W}'$$

- and two continuity equations

- for the electron density $\partial_t n(\mathbf{r}, t) = -\nabla \cdot \mathbf{j}(\mathbf{r}, t)$

- for the current density $\partial_t \mathbf{j}(\mathbf{r}, t) = -i \langle \Psi | [\hat{\mathbf{j}}(\mathbf{r}, t), \hat{H}^{\textcircled{1}, \textcircled{2}}(t)] | \Psi \rangle$

- Ask the question \rightarrow

Could it be that $n^{\textcircled{1}}(\mathbf{r}, t) \equiv n^{\textcircled{2}}(\mathbf{r}, t)$?

- Always true, if

- $n^{\textcircled{1}}(\mathbf{r}, t_0) \equiv n^{\textcircled{2}}(\mathbf{r}, t_0)$ and $\mathbf{P}^{\textcircled{1}}(t_0) = \mathbf{P}^{\textcircled{2}}(t_0)$

- ☆ currents and densities vanish at infinity ☆

 R. van Leeuwen, PRL, 82, 3863 (1999).



Conclusions ???

□ Let $\star \hat{W}^{\textcircled{1}} = \hat{W}^{\textcircled{2}} \quad \star \Phi_0^{\textcircled{1}} = \Phi_0^{\textcircled{2}}$

□ \rightsquigarrow Runge-Groß theorem

■ $V^{\text{ext}}(t) = V^{\text{ext}}[n] + C(t)$

■ $\frac{\delta A[n]}{\delta n} = 0$

$$A[n] = \int_{t_0}^{t_1} dt \int d^3N r \psi^*({\mathbf{r}}, t) \left\{ i\partial_t + \frac{1}{2}\nabla^2 - V^{\text{ee}}({\mathbf{r}}, t) - V^{\text{ext}}({\mathbf{r}}, t) \right\} \psi({\mathbf{r}}, t)$$

■ time-dependent Kohn-Sham system

$$n({\mathbf{r}}, t) = \sum_i f_i \phi_i^*({\mathbf{r}}, t) \phi_i({\mathbf{r}}, t)$$
$$\left\{ i\partial_t + \frac{1}{2}\nabla^2 \right\} \phi_i({\mathbf{r}}, t) = \left\{ V^{\text{ext}}({\mathbf{r}}, t) + \int d^3r' \frac{n({\mathbf{r}}, t)}{|{\mathbf{r}} - {\mathbf{r}}'|} + \frac{\delta A^{\text{xc}}[n]}{\delta n} \Big|_{n=n({\mathbf{r}}, t)} \right\} \phi_i({\mathbf{r}}, t)$$

□ Questions :

■ What do I do with A^{xc} ?

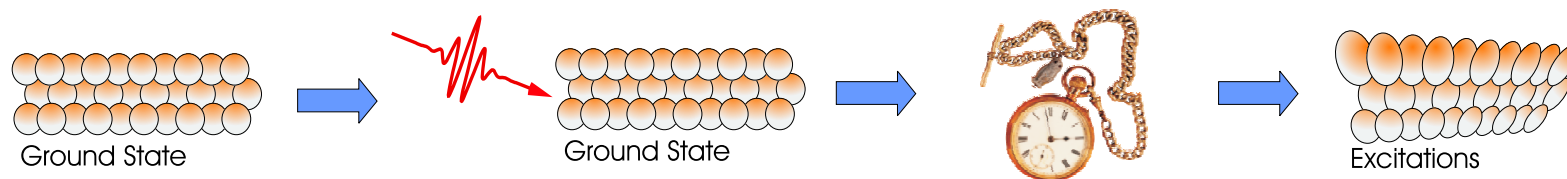
■ Can I calculate things efficiently with this scheme ?

📎 E. Runge and E.K.U. Gross, PRL, 52, 997(1984).



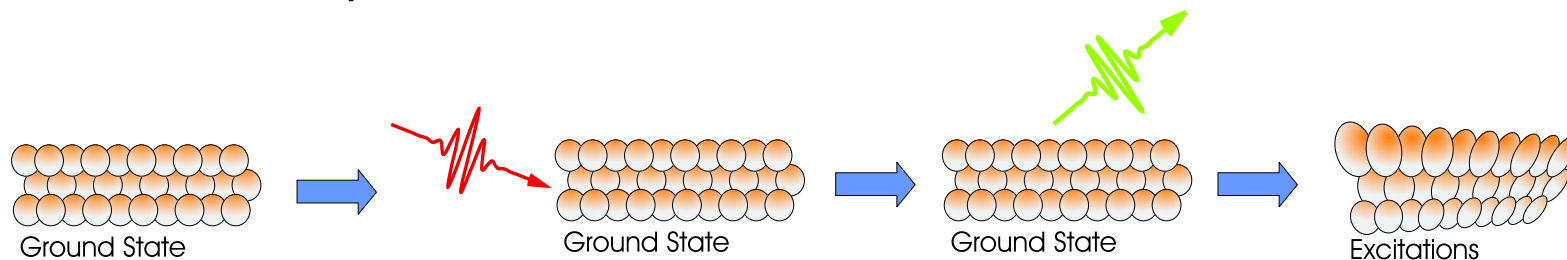
Take a look at experiments again

- Time-evolution of a system under perturbation



~> quite demanding task

- situation in experiments



~> the linear response → a shortcut

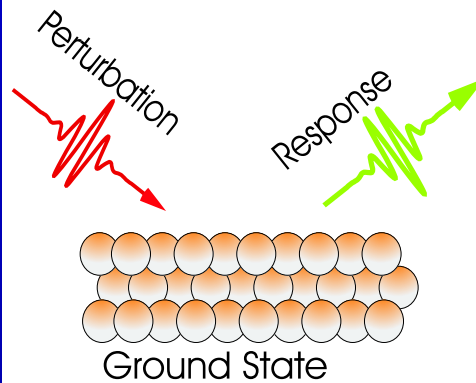
- The response function \equiv density-density correlation function

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \sum_{i,j} (f_i - f_j) \frac{\phi_i(\mathbf{r}) \phi_j^*(\mathbf{r}') \phi_j(\mathbf{r}') \phi_i^*(\mathbf{r})}{\varepsilon_j - \varepsilon_i + \omega + i\eta}$$

for noninteracting particles



Here we go again



Assume external potential of the form

$$v^{\text{ext}}(\mathbf{r}, t) = v_0^{\text{ext}}(\mathbf{r}) + v_1^{\text{ext}}(\mathbf{r}, t)\Theta(t - t_0)$$

Expand electron density into Taylor series

$$n(\mathbf{r}, t) = n_0(\mathbf{r}) + n_1(\mathbf{r}, t) + \dots$$

The first-order term is :

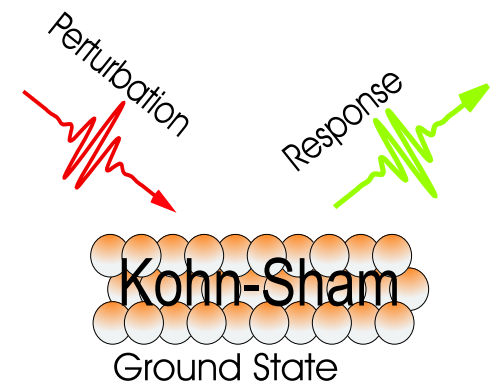
$$n_1(\mathbf{r}, t) = \int dt' \int d^3r' \chi(\mathbf{r}, t, \mathbf{r}', t') v_1^{\text{ext}}(\mathbf{r}', t'), \quad \chi(\mathbf{r}, t, \mathbf{r}', t') = \frac{\delta n(\mathbf{r}, t)}{\delta v^{\text{ext}}(\mathbf{r}', t')}$$

Due to utilising the Kohn-Sham system

$$\chi_0(\mathbf{r}, t, \mathbf{r}', t') = \frac{\delta n(\mathbf{r}, t)}{\delta v^{\text{eff}}(\mathbf{r}', t')}$$

$$\chi_0(\mathbf{r}, \mathbf{r}', \omega) = \sum_{i,j} (f_i - f_j) \frac{\phi_i(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r}')\phi_i^*(\mathbf{r})}{\epsilon_j^{\text{KS}} - \epsilon_i^{\text{KS}} + \omega + i\eta}$$

☆ poles at KS excitation energies ☆





Getting excited

- Play a little bit with definitions

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \frac{\delta n(\mathbf{r}, \omega)}{\delta v^{\text{ext}}(\mathbf{r}, \omega)}, \quad \chi_0(\mathbf{r}, \mathbf{r}', \omega) = \frac{\delta n(\mathbf{r}, \omega)}{\delta v^{\text{eff}}(\mathbf{r}, \omega)}$$

- functional chain rule

$$\frac{\delta n}{\delta v^{\text{ext}}} = \frac{\delta n}{\delta v^{\text{eff}}} \frac{\delta v^{\text{eff}}}{\delta v^{\text{ext}}} = \frac{\delta n}{\delta v^{\text{eff}}} \frac{\delta v^{\text{eff}}}{\delta n} \frac{\delta n}{\delta v^{\text{ext}}}$$

- The Dyson equation

$$\chi = \chi_0 + \chi_0(v_C + f^{\text{xc}})\chi, \quad f^{\text{xc}}[n] = \left. \frac{\delta v^{\text{xc}}}{\delta n} \right|_{n=n_0}$$

- shifts the poles

- dynamic XC effects

- How do I search for the poles ?

$$\chi = [1 - \chi_0(v_C + f^{\text{xc}})]^{-1} \chi_0 \rightsquigarrow R(\omega) = 1 - \chi_0(v_C + f^{\text{xc}})$$
$$\chi_0(v_C + f^{\text{xc}})|\zeta\rangle = \lambda(\omega)|\zeta\rangle \quad \lambda(\Omega) \equiv 1$$

✉ M. Petersilka, U.J. Gossmann, and E.K.U. Gross, PRL, 76, 1212(1996).



Mysterious kernel

- What is it ?

$$f^{\text{xc}}[n](\mathbf{r}, \mathbf{r}', \omega) = \frac{\delta v^{\text{xc}}[n](\mathbf{r})}{\delta n(\mathbf{r}', \omega)}$$

nonlocal and dynamic response of the exchange-correlation potential

- Why is it important ?

$$\chi = \chi_0 + \chi_0(v_C + f^{\text{xc}})\chi$$

f^{xc} introduces electron-hole attraction

- Where does it come from ?

$$f^{\text{xc}} = \chi^{-1} - \chi_0^{-1} - v_C$$

χ has to be known first

- How do we use it ?

$$f_{\text{ALDA}}^{\text{xc}}(\mathbf{r}, \mathbf{r}', 0) = \delta(\mathbf{r} - \mathbf{r}') \frac{\delta v_{\text{LDA}}^{\text{xc}}}{\delta n} \quad f_{\text{RPA}}^{\text{xc}} \equiv 0$$

parameterisations are based on electron gas $f_{\text{gas}}^{\text{xc}}(q, \omega) = -v_C(q)G_{\text{gas}}(q, \omega)$



Stiring the states

Recipe for excitation energies

To obtain excitation energies :

- ❑ perform the ground-state calculation to acquire $\phi_i(\mathbf{r}), \varepsilon_i$
- ❑ build up the KS response function χ_0
- ❑ solve the Dyson equation to access χ
- ❑ find the poles of χ



☆ How does it work in practice ? ☆



The grey reality

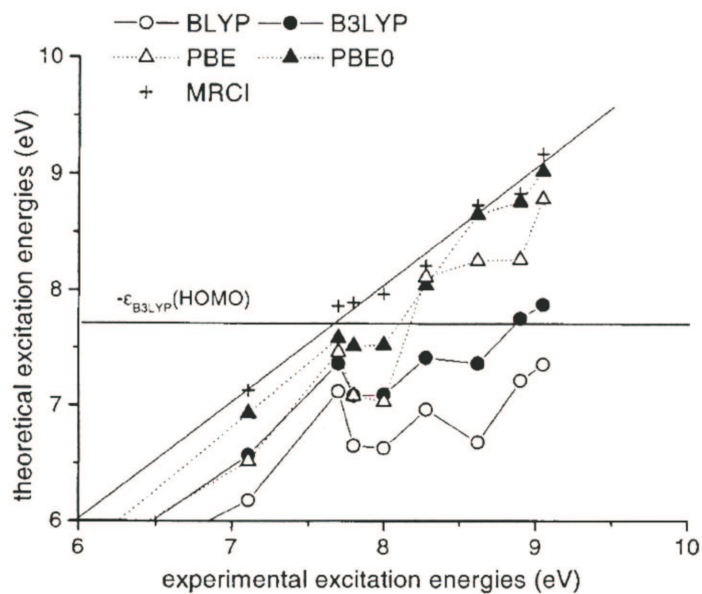
✌ Theory gets a little bit schizophrenic ✌

□ Excitation energies contain two different approximations

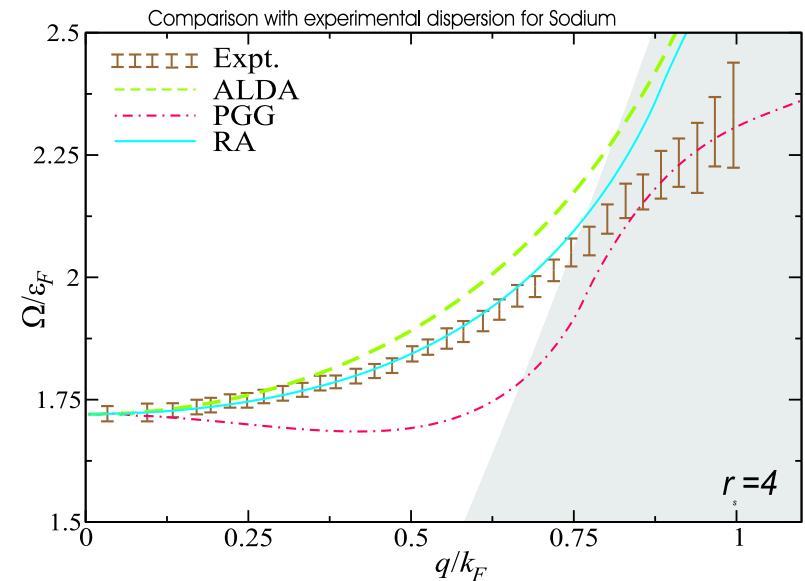
■ to XC potential

■ to XC kernel

☞ Localised systems



☞ Extended systems



★ TD-DFT works well only for finite systems ★

✉ C. Adamo, G.E. Scuseria, and V. Barone, J.Chem.Phys, 111(7), 2889(1999).

✉ K. Tatarczyk, A. Schindlmayr, and M. Scheffler, PRB, 63, 235106(2001).



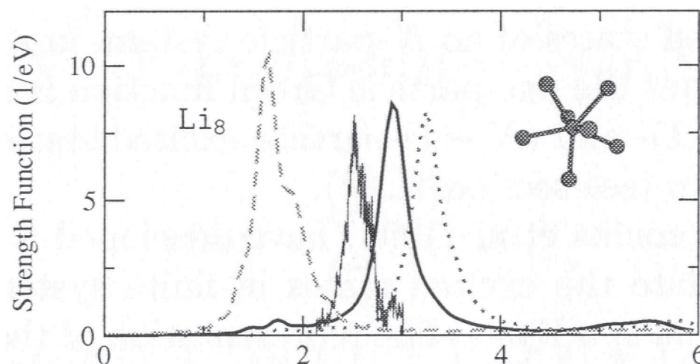
The Dyson equation at work

- Renormalization of the KS response function

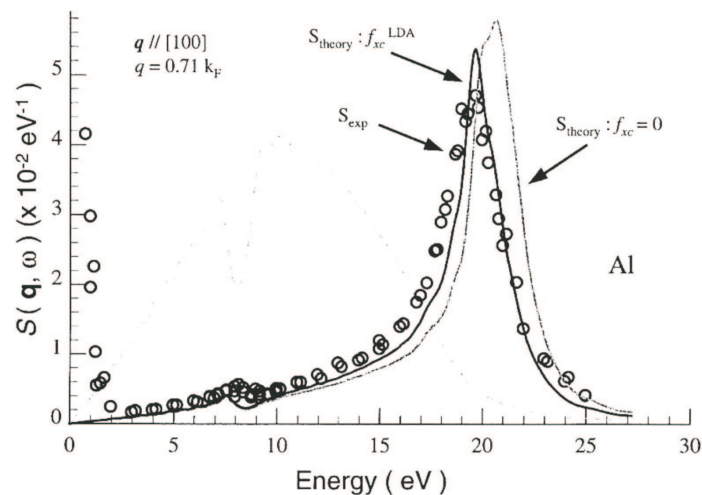
$$\chi = \chi_0 + \chi_0(v_C + f^{xc})\chi$$

Do we really need this kernel ?

- ☞ Localised systems



- ☞ Extended systems



☆ The kernel is necessary for quantitative results ☆

✎ M.A.L. Marques, A. Castro, and A. Rubio,
J.Chem.Phys, 115, 3006(2001).

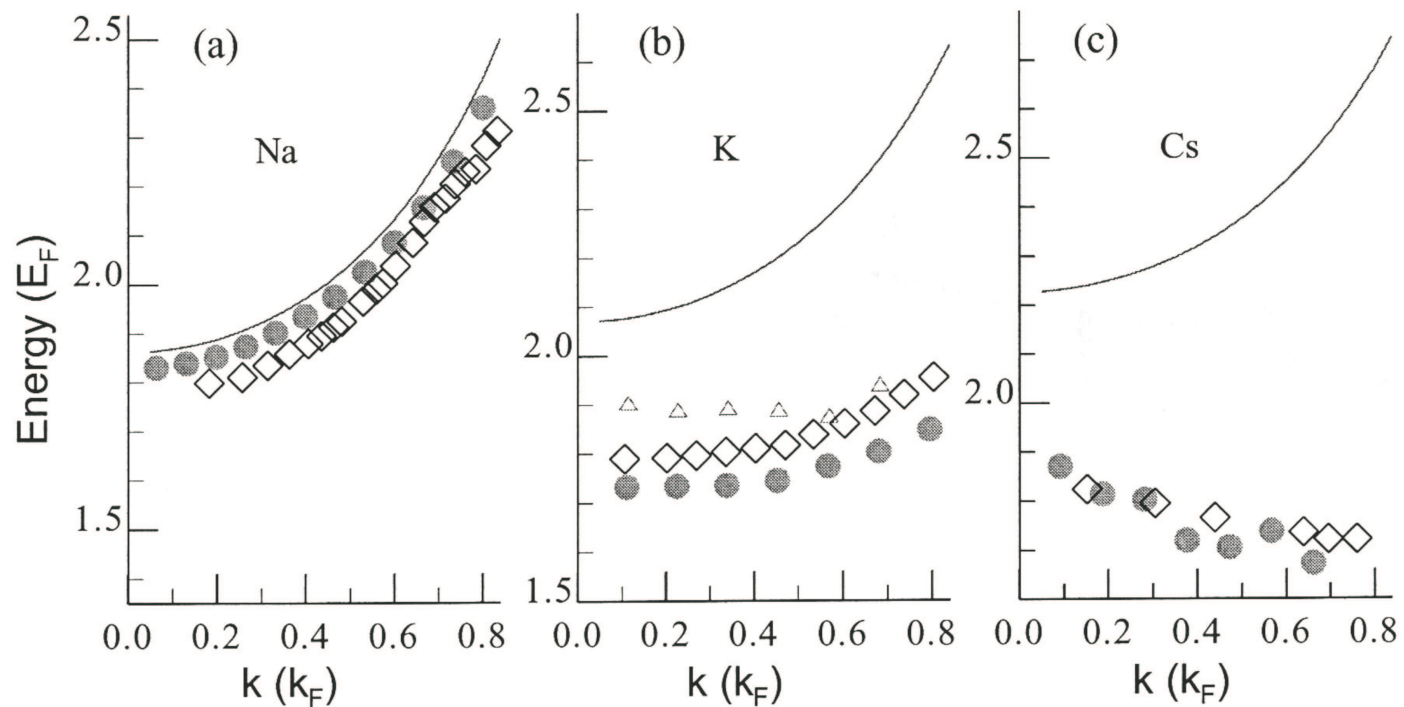
✎ A.G. Eguiluz, W. Ku, and J.M. Sullivan,
J.Phys.Chem.Solids, 61, 383(2000).



Plasmon dispersion in bulk

□ How do I calculate plasmons ? $\rightarrow S(\mathbf{q}, \omega) \approx -\Im\chi(\mathbf{q}, \omega)$

- Alkali metals are free-electron systems



★ The RPA catastrophe resolved

✎ W. Ku and A.G. Eguiluz in Proceedings edited by A.Gonis and N. Kioussis (Plenum, NY'99).



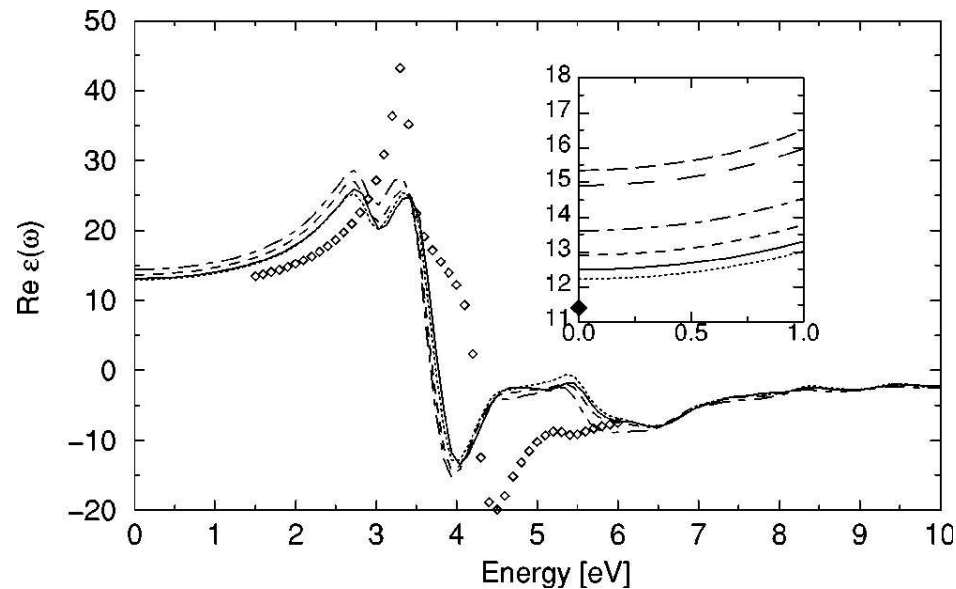
Dielectric function of Silicon

□ In terms of response function

$$\epsilon_M(\omega) = \lim_{|q| \rightarrow 0} \frac{1}{\epsilon_{0,0}^{-1}(\mathbf{q}, \omega)}, \quad \epsilon_{\mathbf{G},\mathbf{G}'}^{-1}(\mathbf{q}, \omega) = \delta_{\mathbf{G},\mathbf{G}'} + v_C^{\mathbf{G},\mathbf{G}'}(\mathbf{q}) \chi_{\mathbf{G},\mathbf{G}'}(\mathbf{q}, \omega)$$

- Easily accessed if the response function is at hand

□ Let's see it :



★ $\epsilon_M^{\text{exp}} = 11.4$ while $\epsilon_M^{\text{TDDFT}} = 12.2 + \rightsquigarrow \text{Oooppsssss} :-)$

✉ V. Olevano, M. Palumbo, G. Onida, and R.D. Sole, PRB 60, 14224(1999).



What is wrong ?

- The formulation strictly valid for localised systems only
 - we requested that the density & currents vanish at ∞
 - RG theorem holds, provided that $\oint n(\mathbf{r}, t_0) [\nabla u^2(\mathbf{r})] \cdot d\mathbf{f} \equiv 0$
- The correspondence $v(\mathbf{r}, t) \rightleftharpoons n(\mathbf{r}, t)$ is proven by $v(\mathbf{r}, t) \rightleftharpoons \mathbf{j}(\mathbf{r}, t)$ and then $\mathbf{j}(\mathbf{r}, t) \rightleftharpoons \mathbf{n}(\mathbf{r}, t)$
- What happens if we choose the current density as a basic variable ?

$$\left\{ \frac{1}{2} \left[\mathbf{p} + \frac{1}{c} \mathbf{A}^{\text{eff}}[\mathbf{j}](\mathbf{r}, t) \right]^2 + v^{\text{eff}}(\mathbf{r}, t) \right\} \phi(\mathbf{r}, t) = i\partial_t \phi(\mathbf{r}, t)$$

$$\mathbf{j}(\mathbf{r}, t) = \Im \sum_{i_{\text{occ}}} \phi_i^*(\mathbf{r}, t) \nabla \phi_i(\mathbf{r}, t) - \frac{1}{c} n(\mathbf{r}, t) \mathbf{A}^{\text{eff}}(\mathbf{r}, t)$$

- TD-Current-DFT $\mathbf{A}^{\text{eff}} = \mathbf{A}^{\text{ext}} + \mathbf{A}^{\text{H}} + \mathbf{A}^{\text{T}} + \mathbf{A}^{\text{xc}}$

- $\mathbf{E}^{\text{xc}} = \frac{i\omega}{c} \mathbf{A}^{\text{xc}} = \alpha \mathbf{P}^{\text{mac}} + \omega \beta \mathbf{j}^{\text{T}}$

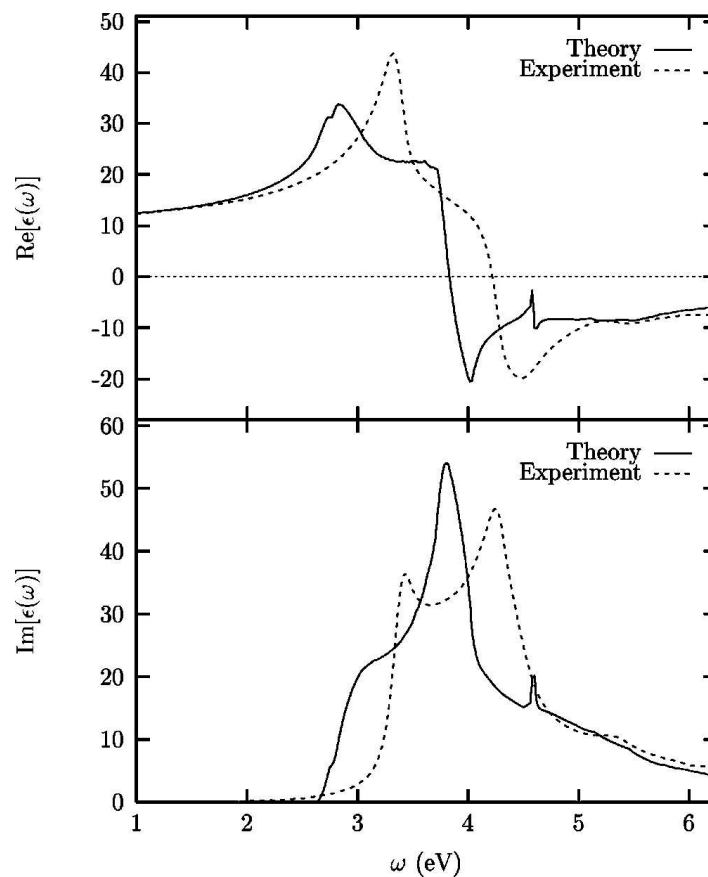
✍ G. Vignale and W.Kohn, PRL, 77, 2037(1996).

✍ N.T. Maitra, I. Souza, and K. Burke, to appear in PRB.



Dielectric function of Silicon...again

□ Does it work now ?



$$\star \epsilon_M^{\text{exp}} = 11.4 \approx \epsilon_M^{\text{ALDA}} = 11.6$$

✎ F. Koostra, P.L. de Boeij, and J.G. Snijders, J.Chem.Phys. 112, 6517(2000).





Summary

- ❑ Charge-neutral (optical) excitations can be conveniently accessed via time-generalisation of DFT
- ❑ The excitations can be studied through :
 - time-evolution of a system under perturbation
 - linear-response approach
- ❑ Due to early stage of development, the results usually are in qualitative/quantitative agreement with experiment
- ❑ Better description of XC effects desperately needed
- ❑ Many open questions await to be answered