

Lecture 13th

# **Time-dependent Density Functional Theory**

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Workshop on  
Application of Density-Functional Theory in Condensed Matter Physics,  
Surface Physics, Chemistry, Engineering and Biology  
Berlin-Dahlem, 23 July - 1 August 2001

Beauty is the first test - there is no permanent  
place in this world for ugly mathematics

Thomas G. Hardy

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# Time-dependent Density Functional Theory

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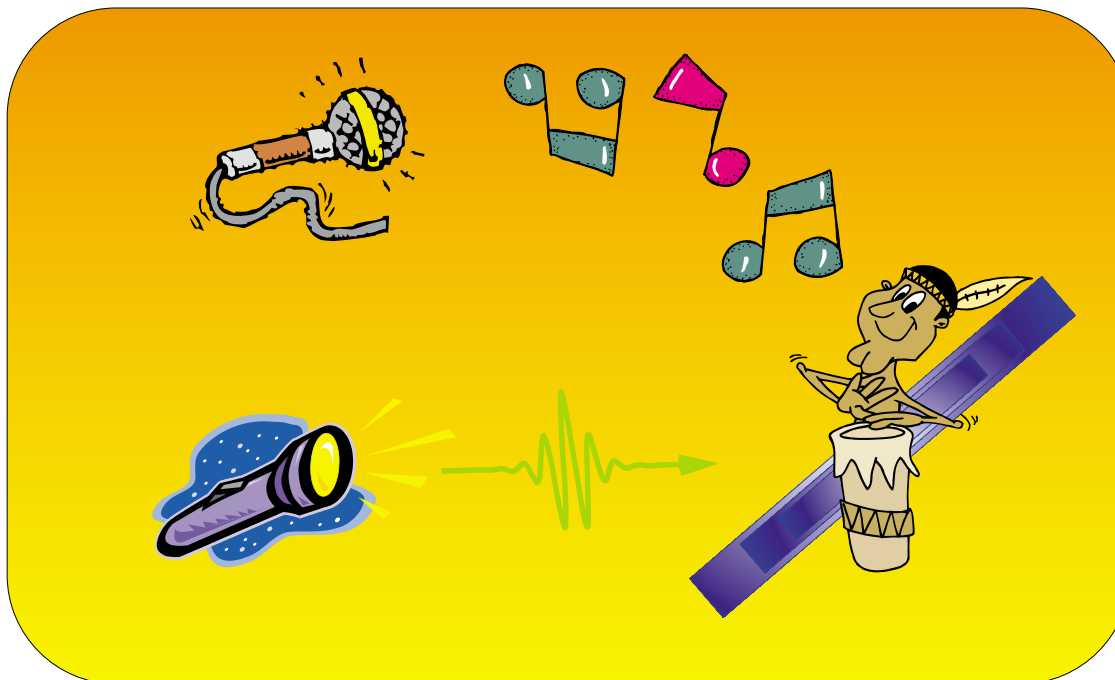
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# Why do states get excited ? And why is this exciting ?



A. H. Zewail

-  Tremendous progress in spectroscopy techniques



-  Emergence of new fields ➤ photochemistry
-  More sophisticated data for theoreticians to study



# Why should we study known things again ?

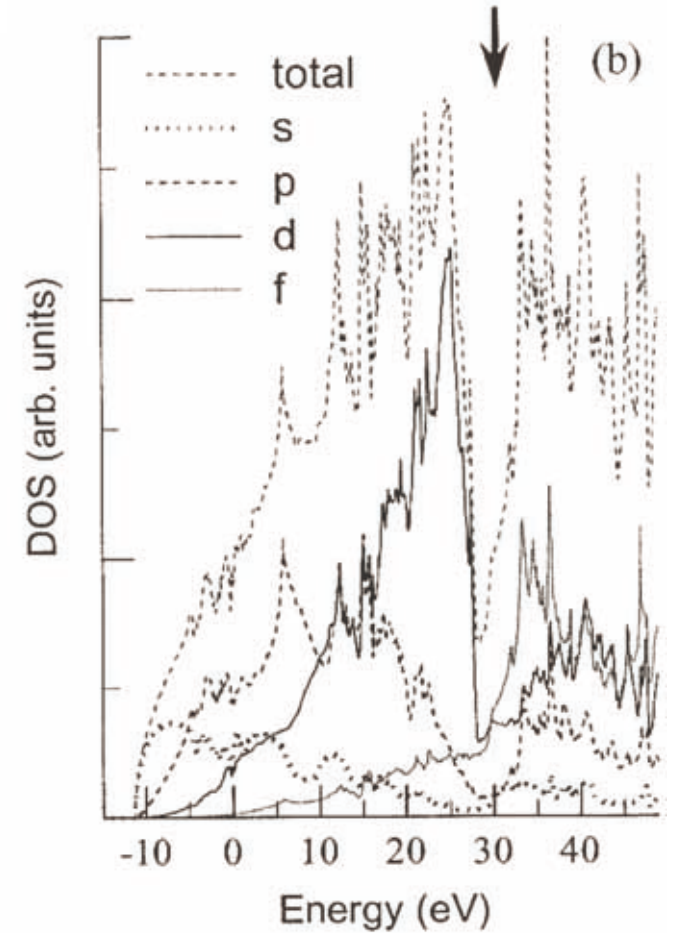
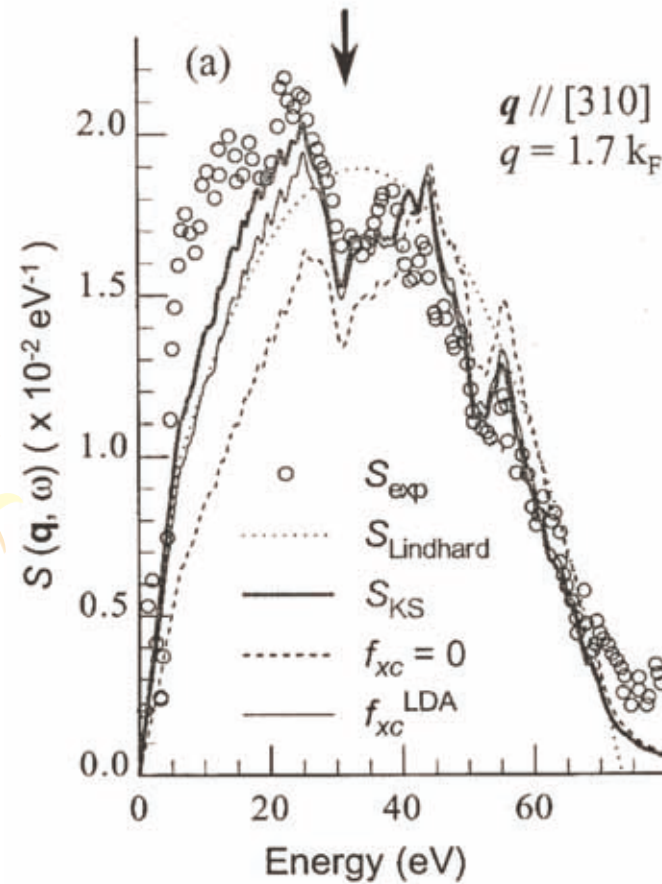


Case of the aluminum bulk

Collective excitations (bulk plasmons)

Plasmon dispersion governed by the dynamical factor  $S$

Dynamical factor can be measured directly!



Exp.: P.M.Platzman et al, PRB 46, 12943 (1992)

W. Ku and A. Eguiluz, Proceedings from International workshop on Electron Correlations and Material Properties, Crete, Greece '98, edited by A.Gonis and N. Kioussis (Plenum, NY, '99)



Detailed theoretical study desperately needed

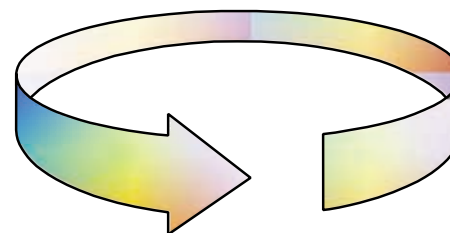
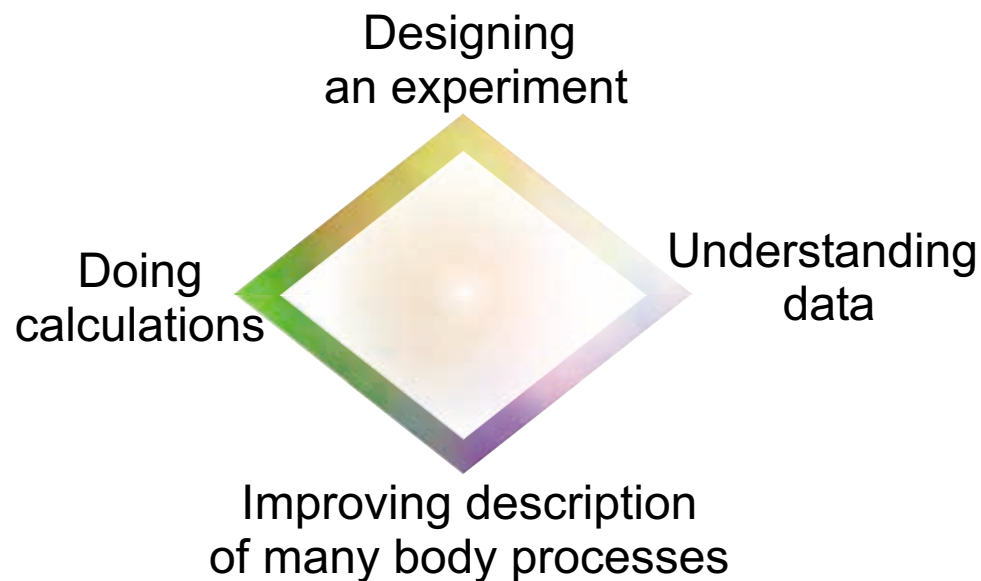
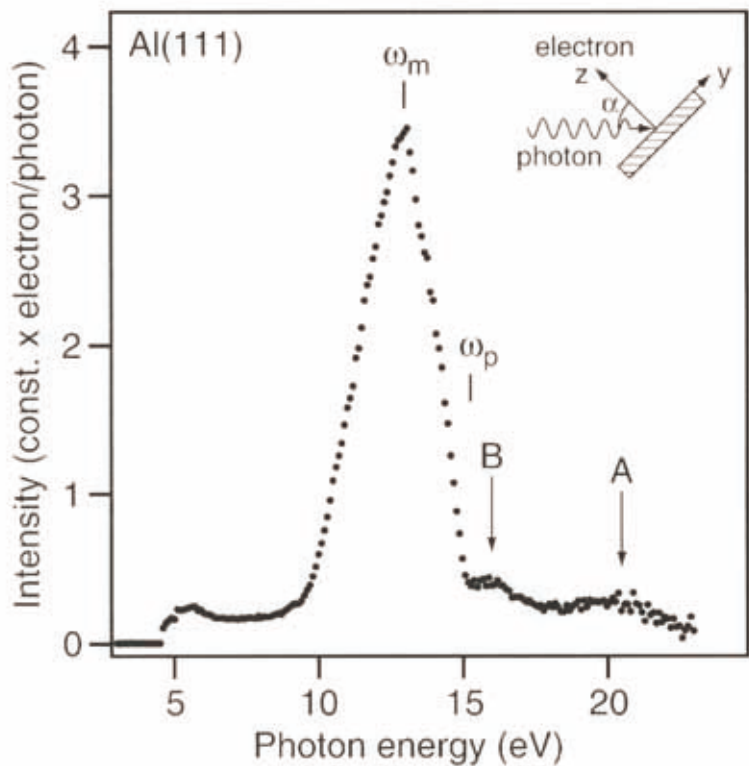
# Why should we study known things again ?



## Case of the aluminum (111) surface



How does it go ?



S.R.Barman & K.Horn  
Appl.Phys. A 69, 519 (1999)



Theoretician desperately wanted ?

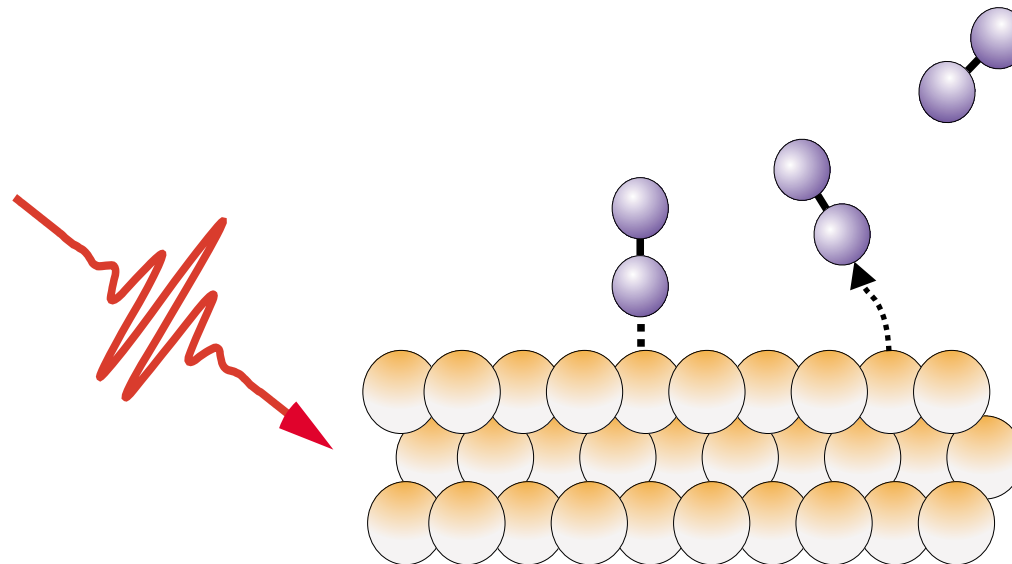
How  
about  
theory ?



# What is the problem ?



What kind of processes do these experimentalists study ?



Photoinduced **excitations**

Results of **dynamic** many body processes



Ooooooppppssss... I can't (directly) use my fhi98md code !!!!!

# Omnipotent 'ab initio' ?



In DFT electron density plays crucial role

Treat electrons as noninteracting particles moving in an effective potential

$$\left[ -\frac{1}{2}\nabla^2 + V_{ext} + V_H + V_{xc} \right] \phi_i(\vec{r}) = \epsilon_i \phi(\vec{r})$$



Rayleigh-Ritz variational principle to find the 'exact' ground state density

$$E_{tot} = E[n] \mapsto E_0 = \min E[n]$$

$$n(\vec{r}) = \sum f_i |\phi_i(\vec{r})|^2$$



Can we still use DFT to study excitations ?



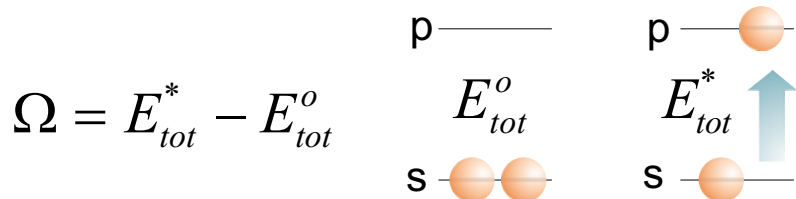
What does **it mean** in practice ?



Configuration Interaction (CI) approach



Static approach to many body problem



By definition the method is designed to describe ground state properties



Kohn-Sham energy differences are only very raw approximation to their real system counterparts (differences of about 10-50%)



Looks a bit unnatural especially for big systems

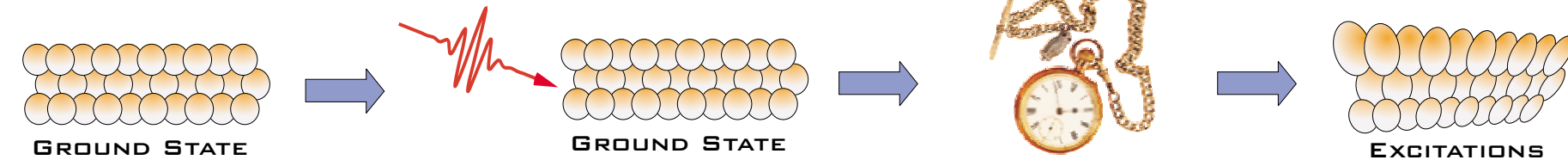
# So what now ?



Failure of the DFT ? - a consequence of the foundation



Bright idea needed



Explicit time dependence grants direct access to dynamic processes

Excitations result from the time evolution



I should then generalize DFT to time dependent phenomena



Hohenberg-Kohn theorem


Kohn-Sham scheme





# Foundation of TD-DFT

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

 Starting point  $i\partial_t\Psi(t)=\hat{H}(t)\Psi(t)$  With  $\Psi(t=0)=\Psi_0$

 We need to show the HK theorem holds for the time dependent case as well

$$V(\vec{r},t) \Leftrightarrow n(\vec{r},t)$$

$$V(\vec{r},t) \neq V'(\vec{r},t) + c(t)$$

$$V(\vec{r},t) \Rightarrow n(\vec{r},t), V'(\vec{r},t) \Rightarrow n'(\vec{r},t)$$

Potentials expandable in Taylor series

 Prove that the current densities are different for each of the potentials

$$\vec{j}(\vec{r},t) = \langle \Psi(t) | \hat{j}_p(\vec{r},t) | \Psi(t) \rangle \quad \partial_t \vec{j}(\vec{r},t) = -i \langle \Psi | [\hat{j}_p, \hat{H}] | \Psi \rangle$$

$$\vec{j}(\vec{r},t) \neq \vec{j}'(\vec{r},t)$$

$$\partial_t^{k+1} (\vec{j}(\vec{r},t) - \vec{j}'(\vec{r},t)) = -n_o(\vec{r}) \nabla (\partial_t^k (V(\vec{r},t) - V'(\vec{r},t))) \neq 0$$

 Play a little bit with the continuity equation

$$\partial_t [n(\vec{r},t) - n'(\vec{r},t)] = -\nabla [\vec{j}(\vec{r},t) - \vec{j}'(\vec{r},t)] \quad \partial_t^{k+2} [n(\vec{r},t) - n'(\vec{r},t)] = -\nabla [n_o(\vec{r}) \nabla \partial_t^k (V(\vec{r},t) - V'(\vec{r},t))]$$

$$\nabla [n_o(\vec{r}) \nabla \partial_t^k (V(\vec{r},t) - V'(\vec{r},t))] \equiv 0 \quad \int d^3r n_o(\vec{r}) [\nabla \partial_t^k (V(\vec{r},t) - V'(\vec{r},t))]^2 = \dots \quad n_o(\vec{r}) [\nabla \partial_t^k (V(\vec{r},t) - V'(\vec{r},t))]^2 \equiv 0$$

$$n(\vec{r},t) \neq n'(\vec{r},t)$$

# Foundation of TD-DFT (2)



Where do I get the density from ?

$$E_{tot} = E[n] \mapsto E_0 = \min E[n]$$

not  
useful  
now



Define the action functional



Solutions of the time-dependent Schrödinger equation correspond to a stationary point in the quantum mechanical action

$$A[n] = \int_{t_0}^{t_1} dt \langle \Psi(t) | i\partial_t - \hat{H}(t) | \Psi(t) \rangle$$

$$\frac{\delta A[n]}{\delta n(\vec{r}, t)} = 0$$



Time dependent Kohn-Sham scheme



Dynamics not necessarily on the Born-Oppenheimer surface

$$n(\vec{r}, t) = \sum_j |\varphi_j(\vec{r}, t)|^2 \quad i\partial_t \varphi_j(\vec{r}, t) = \left( -\frac{1}{2} \nabla^2 + v(\vec{r}, t) + v^H(\vec{r}, t) + v^{xc}(\vec{r}, t) \right) \varphi_j(\vec{r}, t)$$



Time dependent Kohn-Sham scheme is EXTREMELY time consuming



Problem - will the parameterizations for XC interactions work for non-ground states?

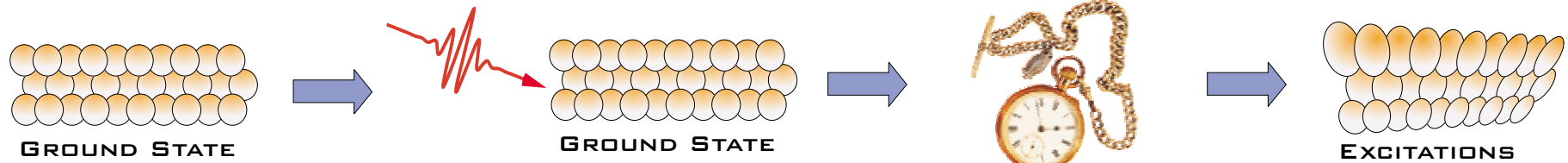



J. Theilhaber, PRB 46, 12990 (1992), G.F.Bertsch et al, PRB 62, 7998 (2000)

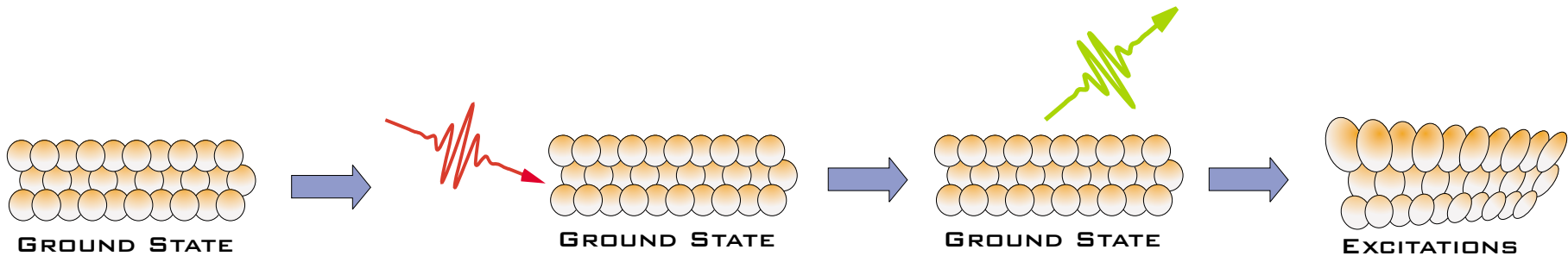
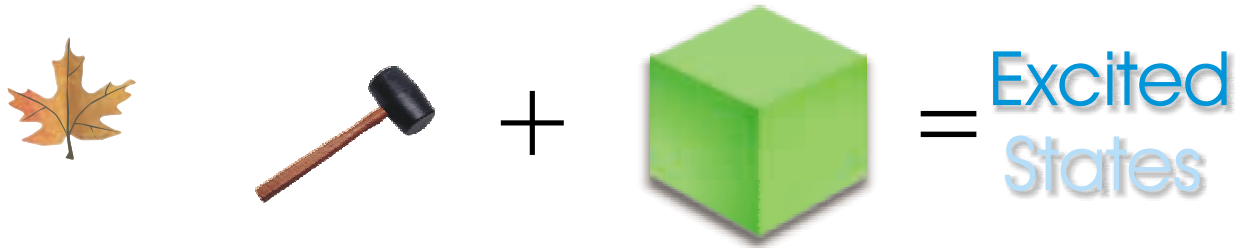


# A dilemma ?

 We employed directly

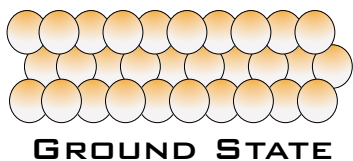


 Demanding conceptually and numerically



 Linear response ..... a shortcut

# Linear response - basics



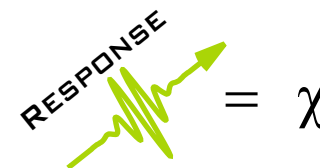
Assume perturbation of the form

$$V^{ext}(\vec{r}, t) = \begin{cases} v_o(\vec{r}) & t \leq t_o \\ v_o(\vec{r}) + v_1(\vec{r}, t) & t > t_o \end{cases}$$



Expand density into the Taylor series

$$n(\vec{r}, t) = n_o(\vec{r}) + n_1(\vec{r}, t) + \dots$$



The induced density is given by

$$n_1(\vec{r}, t) = \int dt' \int d^3r' \chi(\vec{r}, \vec{r}', t, t') v_1(\vec{r}', t')$$



$$\chi(\vec{r}, \vec{r}', t, t') = \left. \frac{\delta n(\vec{r}, t)}{\delta V_{ext}(\vec{r}', t')} \right|_{v_o}$$



Why should anyone be interested in the response function ?

Poles of the response function

$$\chi^{-1}(\omega) = 0$$

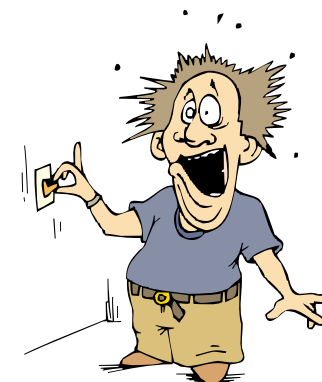
define excitation energies of a system



So the procedure...

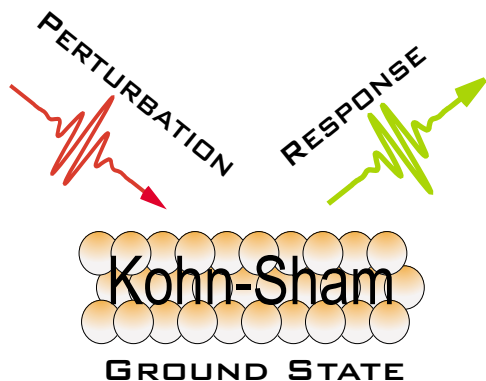


$$\chi^{-1}(\omega) = 0$$



Not so fast please

# Linear response - the Dyson equation



We work on the Kohn-Sham system

$$\chi^o(\vec{r}, \vec{r}', \omega) = \left. \frac{\delta n(\vec{r}, \omega)}{\delta V_{eff}(\vec{r}', \omega)} \right|_{v_o[n_o]}$$



The Kohn-Sham response function

$$\chi^o(\vec{r}, \vec{r}', \omega) = \sum_{m,n} (f_m - f_n) \frac{\varphi_m(\vec{r}) \varphi_n^*(\vec{r}) \varphi_m^*(\vec{r}') \varphi_n(\vec{r}')}{\varepsilon_m - \varepsilon_n + \omega + i\eta}$$

has poles at the KS energy differences



Let's play a bit with the definitions...

$$\chi(\vec{r}, \vec{r}', \omega) = \left. \frac{\delta n}{\delta V_{ext}} \right|_{v_o} = \left. \frac{\delta n}{\delta V_{eff}} \frac{\delta V_{eff}}{\delta V_{ext}} \right|_{v_o[n_o]} = \frac{\delta n}{\delta V_{eff}} \frac{\delta V_{eff}}{\delta n} \frac{\delta n}{\delta V_{ext}}$$



The Dyson equation

$$\chi = \chi^o + \chi^o (V_c + f^{xc}) \chi$$

with the XC kernel

$$f^{xc} = \left. \frac{\delta V_{xc}}{\delta n} \right|_{n_o}$$



Describes dynamic XC interactions arising due to a perturbation

# Linear response - excitations

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

How do I search for the poles ?

$$\chi = \chi^o + \chi^o (V_c + f^{xc}) \chi$$

$$f_{GG}^{xc}(\vec{q}, \omega) = \frac{\delta V_G^{xc}(q, \omega)}{\delta n_G(q, \omega)}$$



$$\chi^{-1}(\omega) = 0$$



Play a little bit with the Dyson equation

$$\chi = \chi^o + \chi^o (V_c + f^{xc}) \chi$$



$$\chi = [1 - \chi^o (V_c + f^{xc})]^{-1} \chi^o$$

Search for the frequencies for which the R operator cannot be inverted

$$R(\omega) = 1 - \chi^o (V_c + f^{xc})$$

Search for the frequencies for which the eigenvalues of

$$\chi^o (V_c + f^{xc}) |\xi\rangle = \lambda(\omega) |\xi\rangle$$

$$\lambda(\Omega) \equiv 1$$

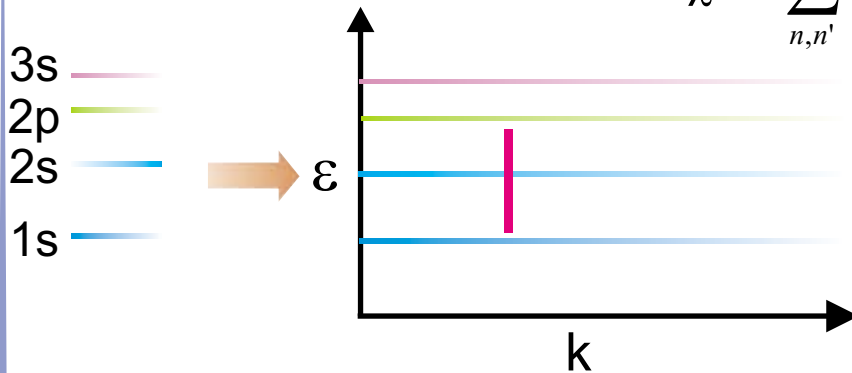
are equal to 1

# Linear response - excitations (2)

Unfortunately the formalism works differently for localized and extended systems

Acorn icon: **Atoms&Molecules**

$$\chi^o = \sum_{n,n'} F[\varphi, \varepsilon]$$



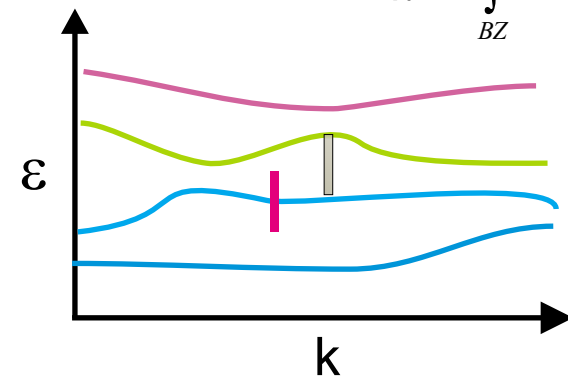
Leaf icon: Laurent expansion of the PGG eigenvalue problem gives an explicit formula for excitation energies

$$\Omega_{jk} = \varepsilon_j - \varepsilon_k + K[\varphi_j, \varphi_k, V_c, f^{xc}]$$

Leaf icon: Xchange processes more pronounced

Acorn icon: **Bulk crystals, surfaces...**

$$\chi^o = \int_{BZ} d^3k \sum_{n,n'} F_k[\varphi, \varepsilon]$$



Leaf icon: Laurent expansion meaningless

Leaf icon: Xchange and correlation processes important, spatial nonlocality crucial !





How  
does  
it  
work ?

# The Dyson equation again



The Kohn-Sham response function

$$\text{bubble} = \sum_{m,n} (f_m - f_n) \frac{\varphi_m(\vec{r}) \varphi_n^*(\vec{r}) \varphi_m^*(\vec{r}') \varphi_n(\vec{r}')}{\varepsilon_m - \varepsilon_n + \omega + i\eta}$$

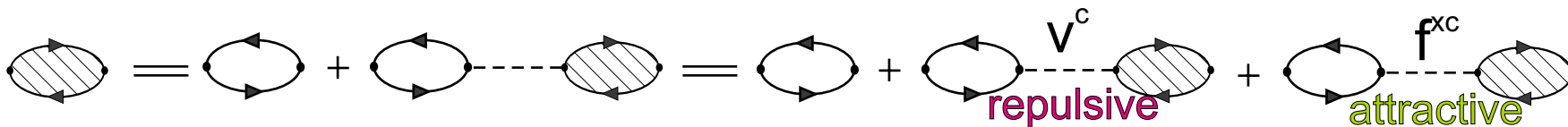


Sum over noninteracting electrons and holes

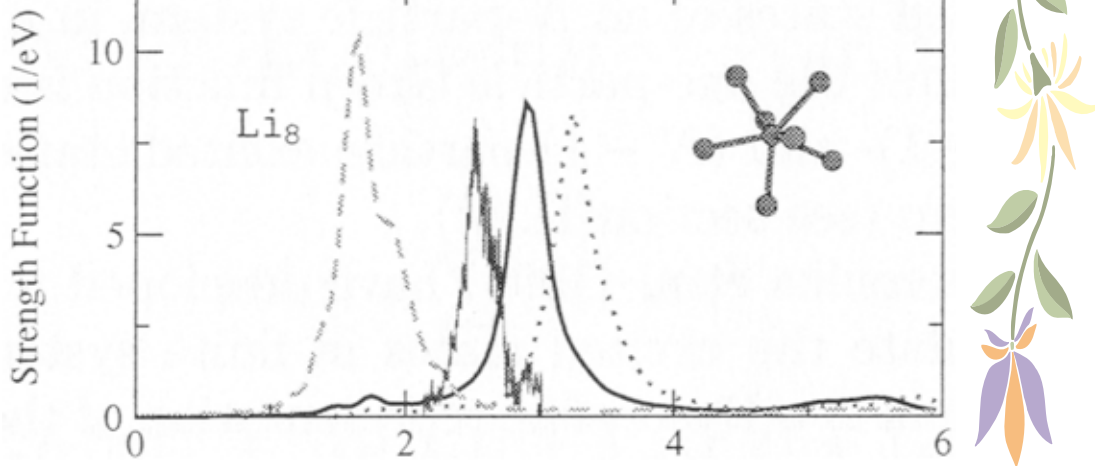


'Tunning' the Kohn-Sham response function

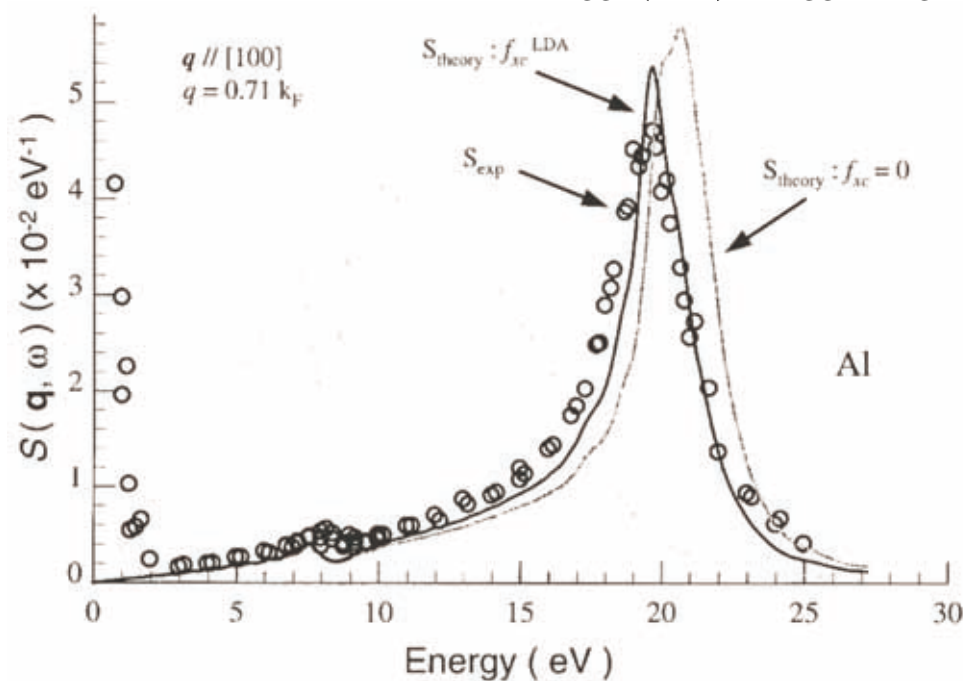
$$\chi = \chi^o + \chi^o (V_c + f^{xc}) \chi$$



$$S(\omega) = \omega \text{Im}\alpha(\omega) \quad \alpha(\omega) = -\int d^3r \delta n(\vec{r}, \omega)$$



$$S(\mathbf{q}, \omega) = -\text{Im}\varepsilon_{GG}^{-1}(\mathbf{q}, \omega) \quad \varepsilon_{GG}^{-1}(\mathbf{q}, \omega) = \delta_{GG} + V_G^c \chi_{GG}$$



M.A.L.Marques et al, submitted to J.Chem.Phys.(2001)

A. Eguiluz et al, J.Phys.Chem.Solids 61, 383(2000)



# The mysterious kernels



The kernel is still a mystery

$$f^{xc}(\vec{q}, \omega) = ?$$



In practice the XC kernel has to be approximated

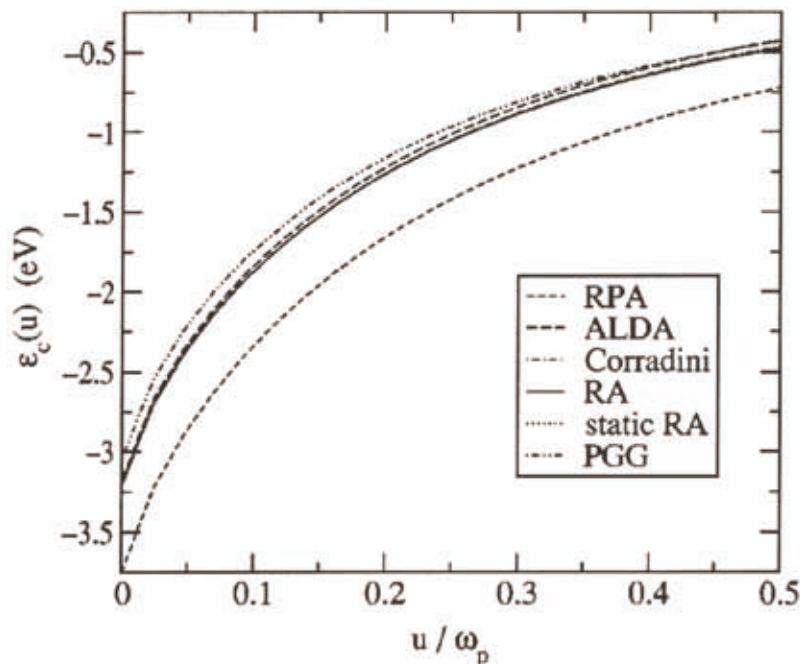


The approximations are based on the properties of the homogeneous electron gas and....the most common approximation is... ALDA!

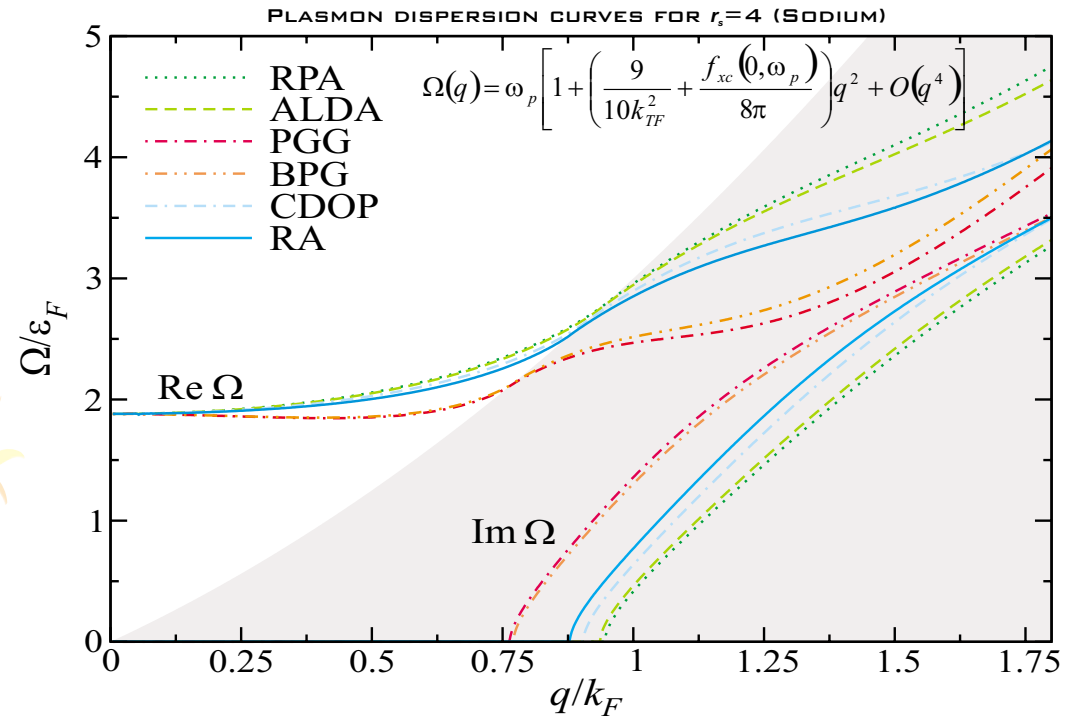


What is crucial ?

$$f^{xc}(\vec{q}=0, \omega=0) = \frac{\delta V_{LDA}^{xc}}{\delta n}$$



M. Lein et al, PRB 61, 13 431 (2000)



$\text{Im } f^{xc} \approx \text{Im } \chi^{mp}$  Frequency dependence important !



# Excitation energies and LR in practice

Calculation of excitation energies contain **two different** approximations:

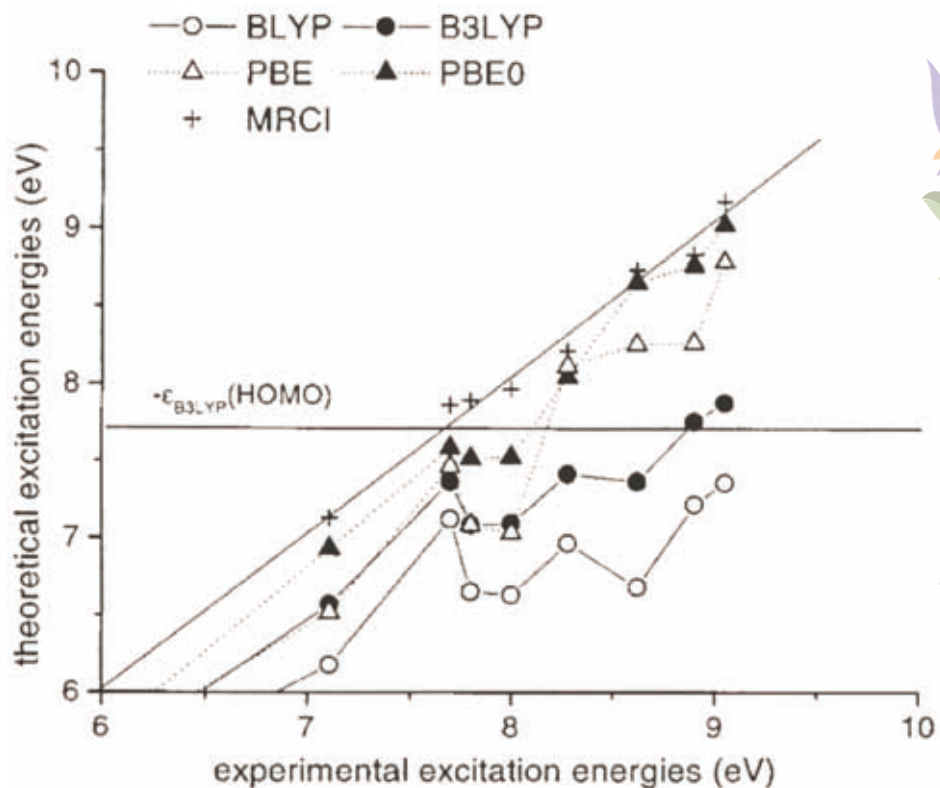
- \* approximation for **XC potential** in  $\chi^0$
- \* approximation for **XC kernel**



Which of the parameterizations is crucial ?



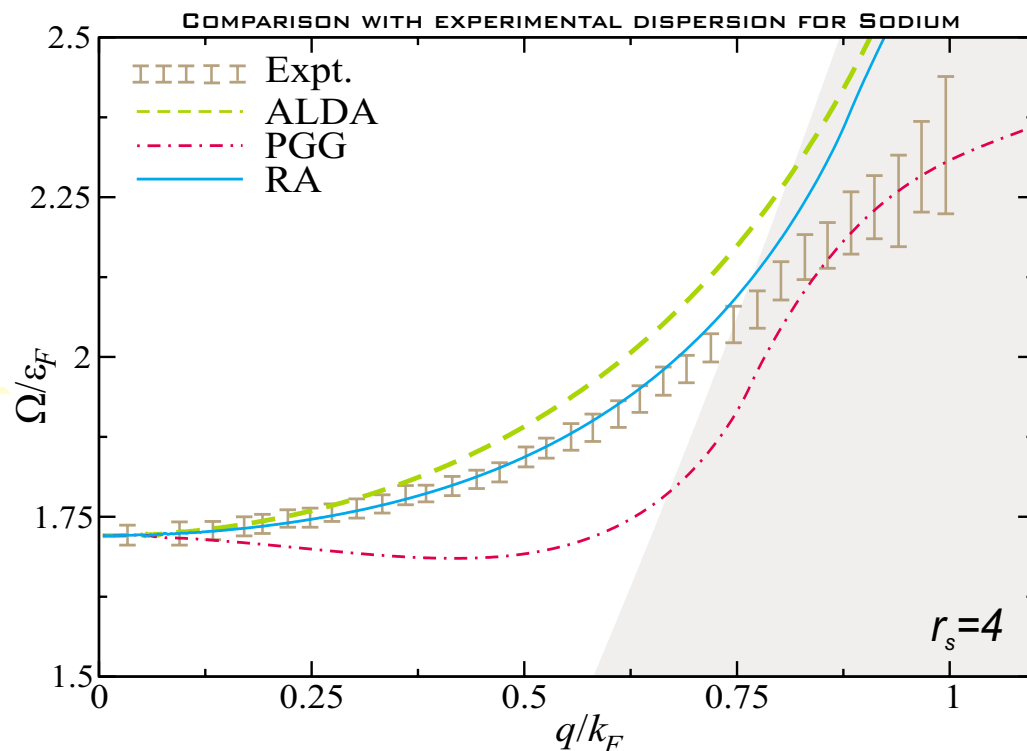
## Localized systems



Adamo et al, J.Chem.Phys, 111(7), 2889 (1999)



## Extended systems



Tatarczyk, Schindlmayr, Scheffler, PRB 63, 235106 (2001)

# TD-DFT and LR in practice



Different behaviour for localized and extended systems is observed

$$E^{xc}[n]$$

$$V^{xc}[n] = \frac{\delta E^{xc}}{\delta n}$$

$$f^{xc} = \frac{\delta V^{xc}}{\delta n}$$



In both cases the XC kernel is needed to obtain quantitative results. However without the kernel the results are already in qualitative agreement with the experimental spectra



In case of the kernel spatial nonlocality is more important than the frequency dependence



Established method of the quantum chemistry  
**MORE DETAILED STUDY OF EXTENDED SYSTEMS WITHIN  
 THE TD-DFT NEEDED**



# Examples (1)



Alkali metals are 'jellium-like'



Jellium plasmon dispersion curve in a good agreement with experimental one

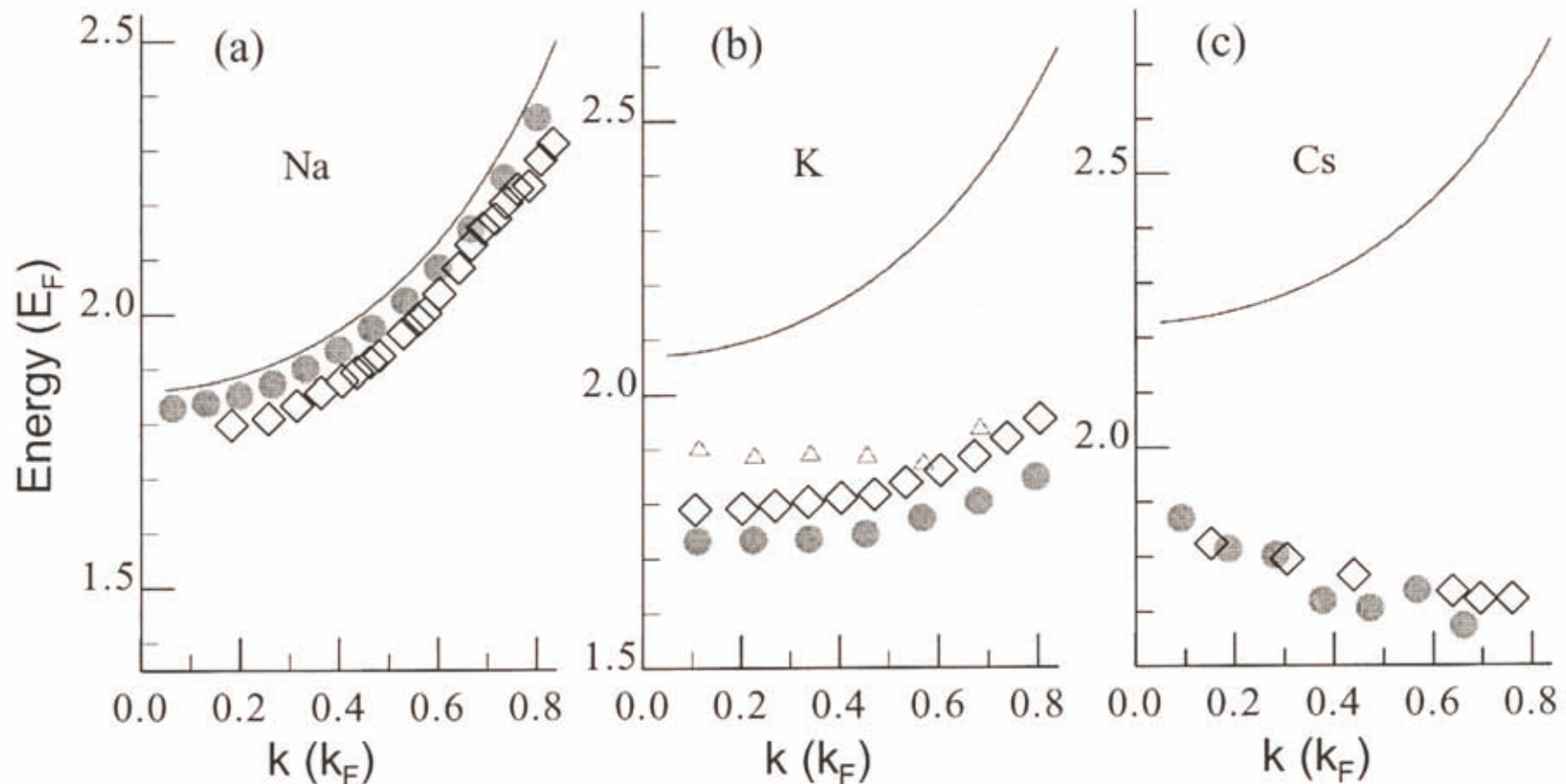
$$S(q, \omega) = -\text{Im} \varepsilon_{GG'}^{-1}(q, \omega)$$



$$\varepsilon = 1 - V_c \chi^L$$



RPA catastrophe



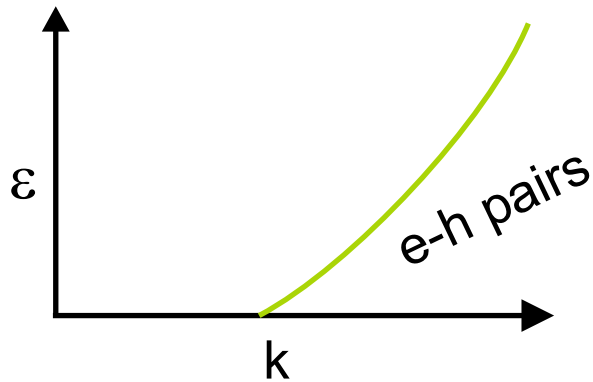
# Examples (2)



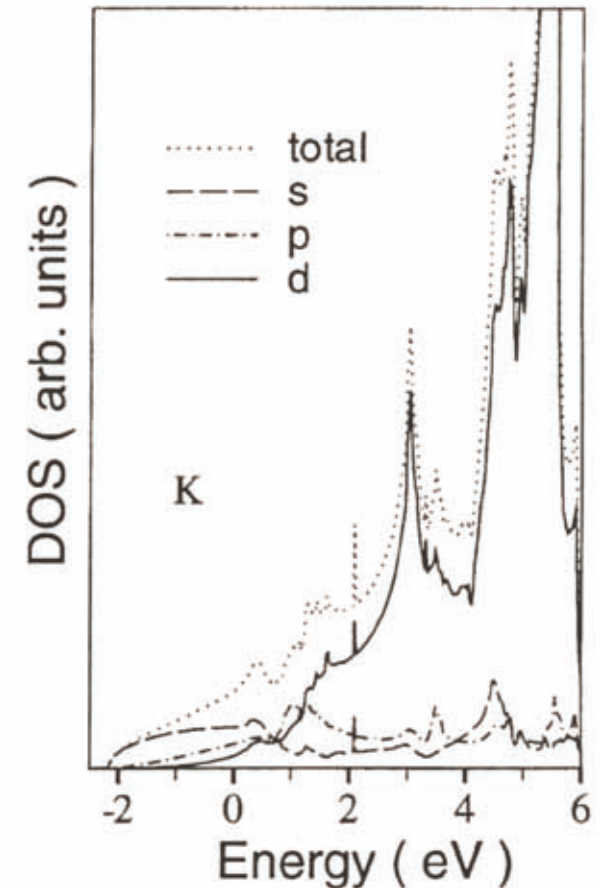
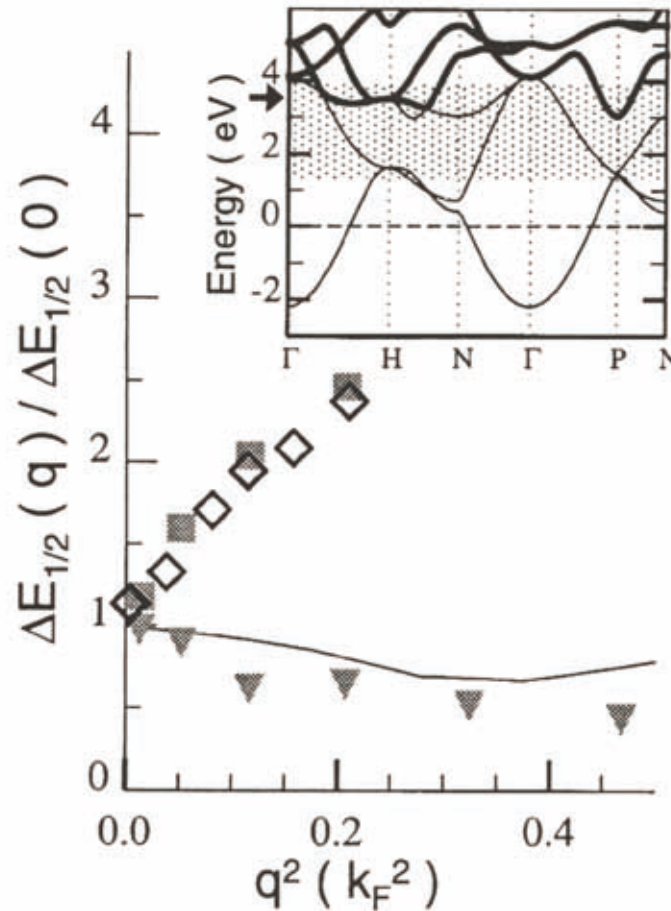
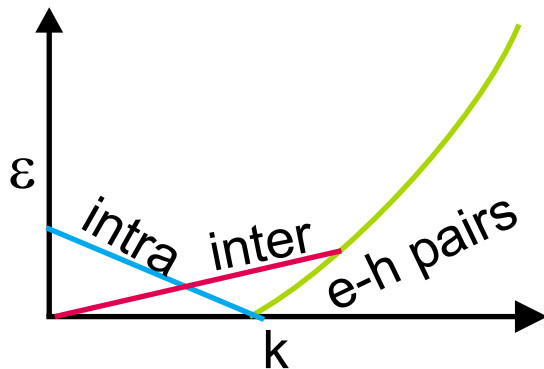
## Life-time of plasmonic excitations



Jellium



Real systems



A. Eguiluz and W. Ku, PRL 82, 2350 (1999)



How to  
make  
it work

# Setting up the KS response

## Ground state calculations


### For extended systems

$$\chi_{G,G'}^o(\vec{q}, \omega) = \frac{2}{\Omega} \sum_{n,n',k} \frac{f(\epsilon_{n',k}) - f(\epsilon_{n,k+q})}{\epsilon_{n',\vec{k}} - \epsilon_{n,\vec{k}+\vec{q}} + \omega + i\eta} \langle n', \vec{k} | e^{-i(\vec{q}+\vec{G})\vec{r}} | n, \vec{k} + \vec{q} \rangle \langle n, \vec{k} + \vec{q} | e^{i(\vec{q}+\vec{G}')\vec{r}'} | n', \vec{k} \rangle$$

 Slow convergence

 Denser MP mesh needed

 Around 200 unoccupied, well converged states required

 Time consuming !!!  
Problems with implementation

### Escape from the summation over unoccupied states

 By introducing the projector operator

Baroni et al, PRL 68, 1861 (1987).

 By analytically summing up one sum in the above expression

A.A.Quong and A.Eguiluz, PRL 70, 3955 (1993)

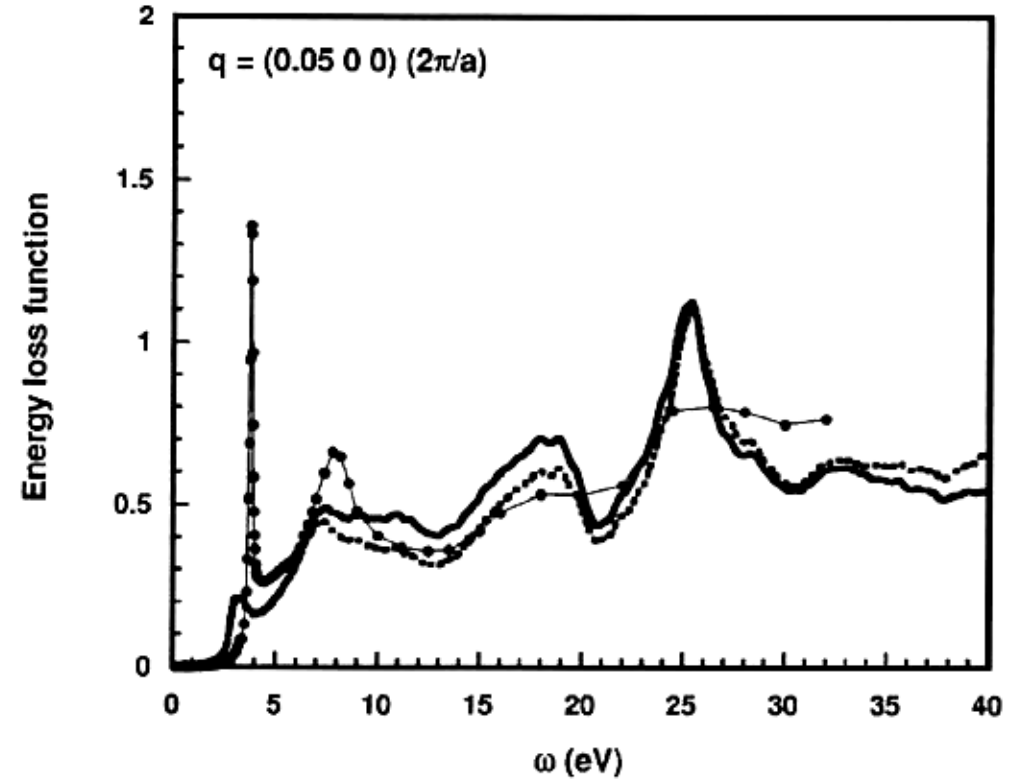
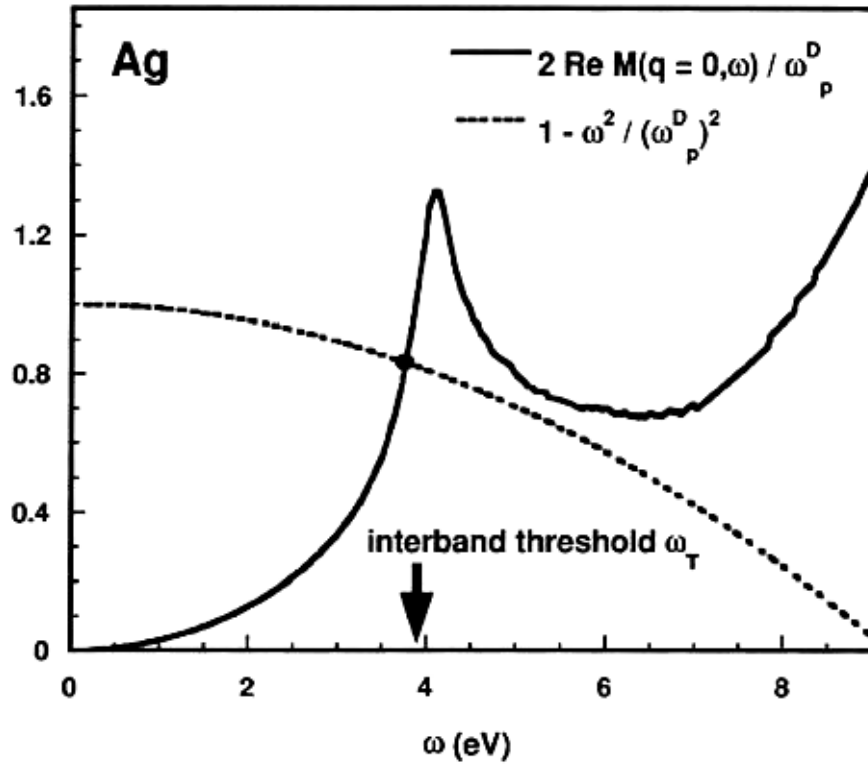
### Use iterative methods when dealing with matrices

 Lots of tricks



# Warning Case of Ag

 TD-DFT is a post ground-state scheme !



M.A.Cazalilla et al, PRB 61, 8033 (2000)

 Be careful with the ground-state calculations





# Summary



The DFT can be generalized and applied to excited states as well



Through study of a time evolution of a system



Through the linear response approach



Despite its early stage of development the theory can explain many of the 'anomalous' phenomena. Usually calculated results are in a good qualitative agreement with experiments.



Different behaviour of the theory is observed, when it is applied to localized and extended systems. The need for more sophisticated description of the XC interactions is revealed.



TD-DFT is a post-ground state scheme. Be careful when providing the ground-state input data!

