Lecture 2

TDCDFT: Linear-response regime

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Benasque, September 2008

Overview

Lecture I: Basic formalism of TDCDFT

Lecture II: Applications of TDCDFT in linear response

- ►Polarizabilities in polymers
- ►Nanoscale transport, stopping power of metals
- ►Linewidths of collective excitations
- ►Excitations in atoms and molecules
- ►Optical properties of bulk metals and insulators
- ►Spin Coulomb drag

Lecture III: TDCDFT in the nonlinear regime

TDCDFT beyond the ALDA: the VK functional

$$\mathbf{A}_{xc,1}(\mathbf{r},\omega) = \mathbf{A}_{xc,1}^{ALDA}(\mathbf{r},\omega) - \frac{c}{i\omega n_0(\mathbf{r})} \nabla \cdot \overleftrightarrow{\sigma}_{xc}(\mathbf{r},\omega)$$

xc viscoelastic stress tensor:

$$\sigma_{xc,jk} = \tilde{\eta}_{xc}\left(\nabla_j \mathrm{v}_{1,k} + \nabla_k \mathrm{v}_{1,j} - \frac{2}{3} \nabla \cdot \mathbf{v}_1 \delta_{jk} \right) + \tilde{\zeta}_{xc} \nabla \cdot \mathbf{v}_1 \delta_{jk}$$

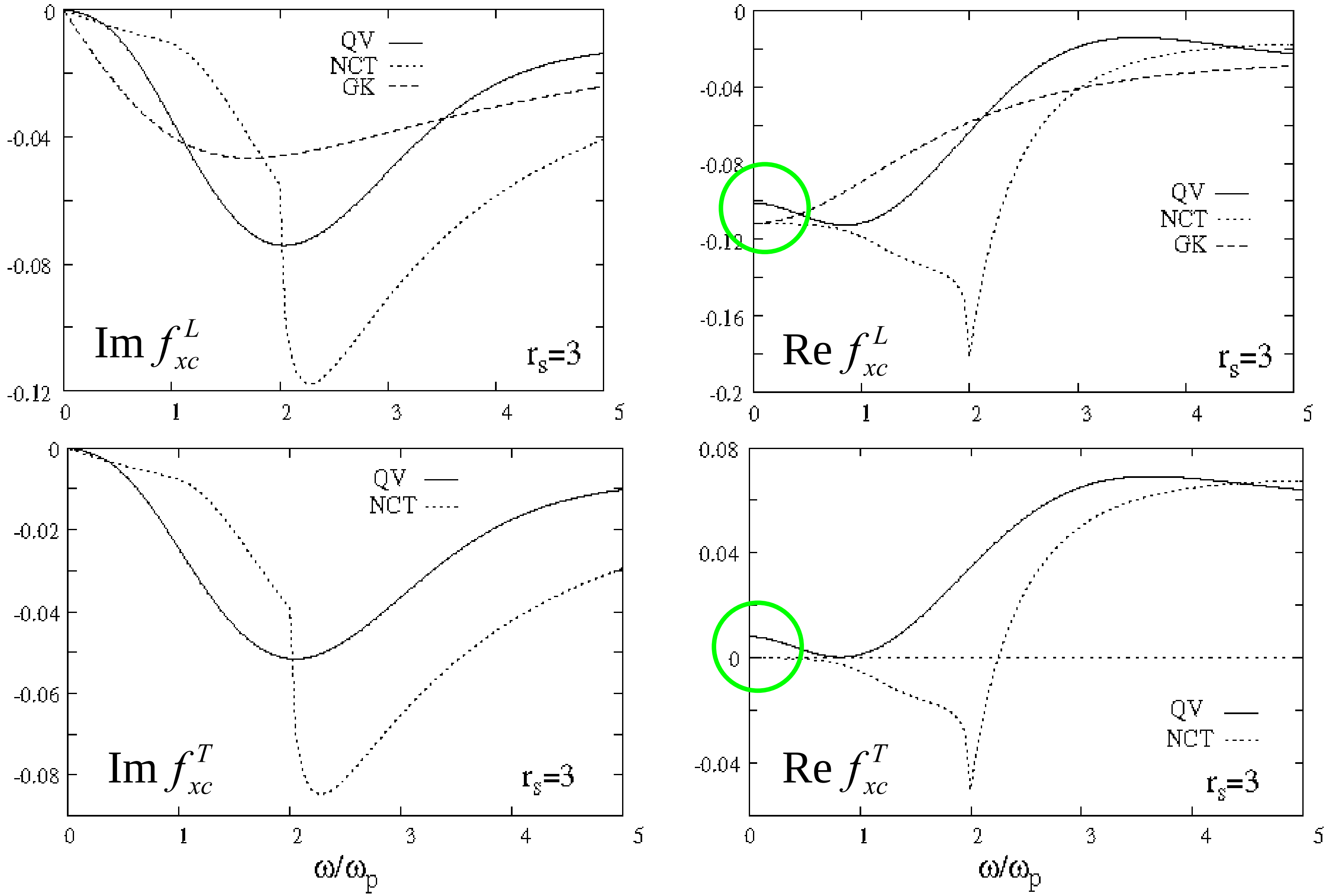
$$\mathbf{v}(\mathbf{r},\omega) = \mathbf{j}(\mathbf{r},\omega) / n_0(\mathbf{r})$$ velocity field

xc viscosity coefficients:

$$\tilde{\eta}_{xc}(n,\omega) = -\frac{n^2}{i\omega} f_{xc}^T(n,\omega)$$

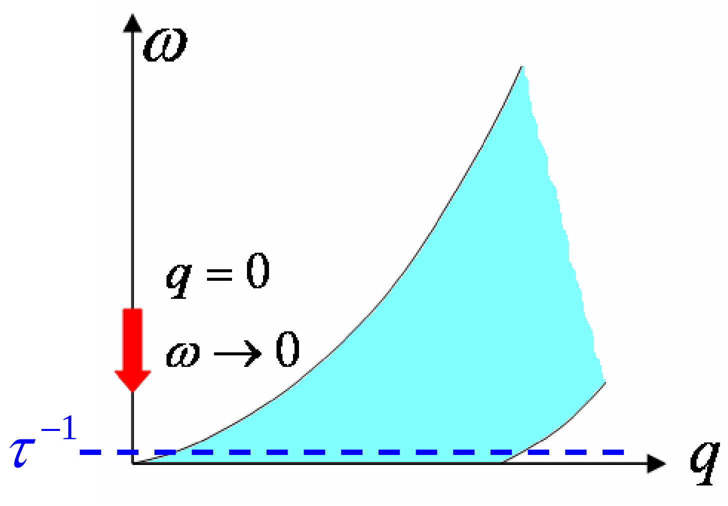
$$\tilde{\zeta}_{xc}(n,\omega) = -\frac{n^2}{i\omega}\left(f_{xc}^L(n,\omega) - \frac{4}{3} f_{xc}^T(n,\omega) - \frac{d^2 e_{xc}^{unif}}{dn^2} \right)$$

xc kernels of the homogeneous electron gas



GK: E.K.U. Gross and W. Kohn, PRL **55**, 2850 (1985)
NCT: R. Nifosi, S. Conti, and M.P. Tosi, PRB **58**, 12758 (1998)
QV: X. Qian and G. Vignale, PRB **65**, 235121 (2002)

static limits of the xc kernels



$$f_{xc}^{L}(0) = \frac{d^2 e_{xc}^{unif}(n)}{dn^2} + \frac{4}{3}\frac{S_{xc}(0)}{n^2}$$

$$f_{xc}^{T}(0) = \frac{S_{xc}(0)}{n^2}$$

The shear modulus of the electron liquid does **not** disappear for $\omega \to 0$, as long as the limit q→0 is taken first.

which is what one should do for a local approximation.

Applications of the VK functional

(A) In the (quasi)-static ω→0 limit:

- Polarizabilities of π-conjugated polymers
- Nanoscale transport
- Stopping power of slow ions in metals

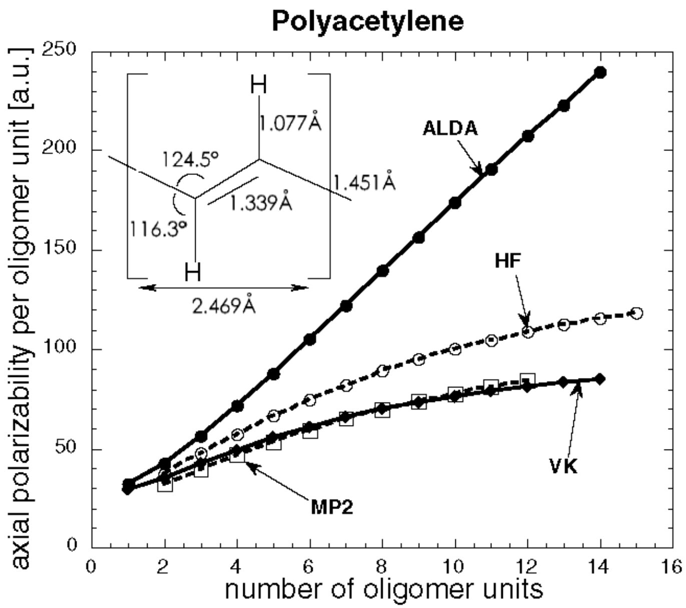
These applications profit from the fact that VK does not reduce to the ALDA in the static limit.

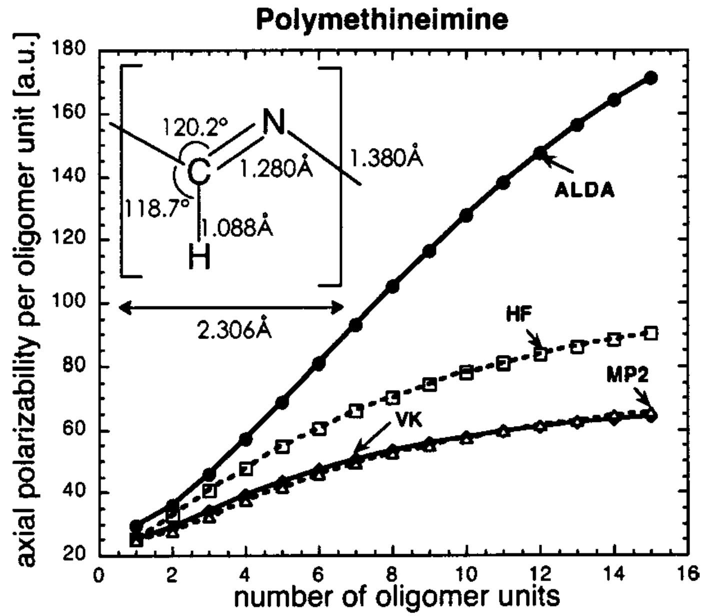
(B) To describe excitations at finite frequencies:

- atomic and molecular excitation energies
- plasmon excitations in doped semiconductor structures
- optical properties of bulk metals and insulators

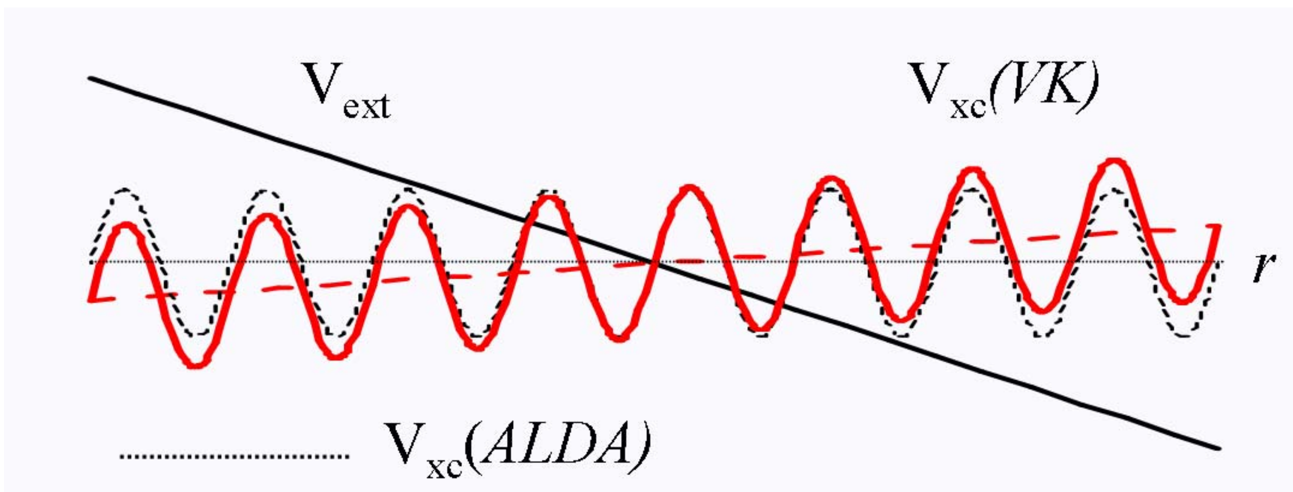
Here the picture is less clear. Some situations are well described, others fail. We'll try to analyze when and why.

TDCDFT for π-conjugated polymers





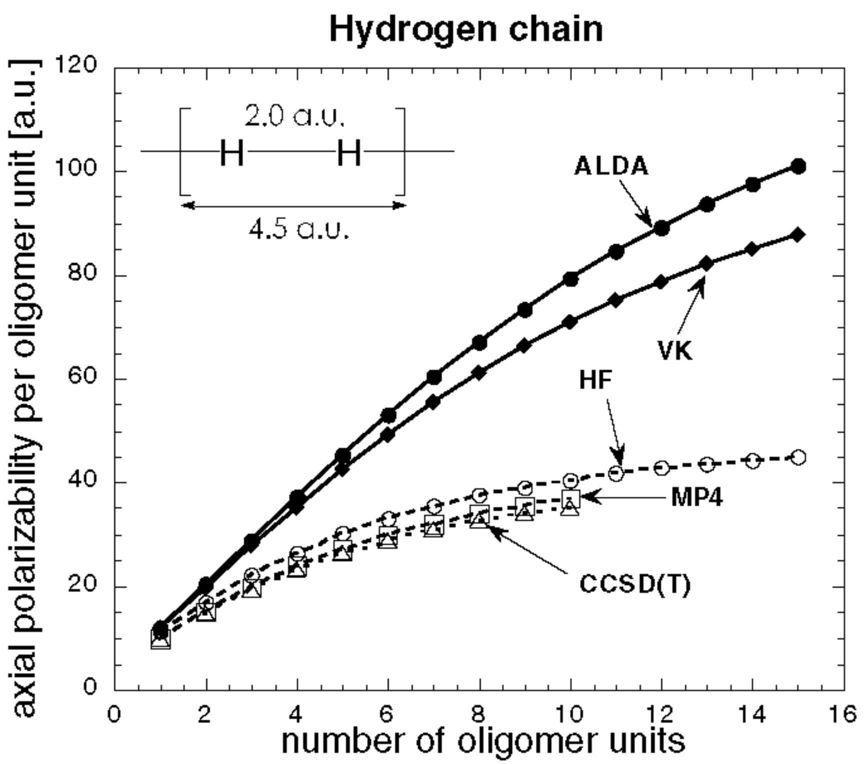
ALDA overestimates polarizabilities of long molecular chains. The long-range VK functional produces a counteracting field, due to the finite shear modulus at $\omega \to 0$.



M. van Faassen et al., PRL **88**, 186401 (2002) and JCP **118**, 1044 (2003)

Other long-chain molecules

VK works extremely well for π-conjugated polymers,
but not so well for other types of long-chain molecules.

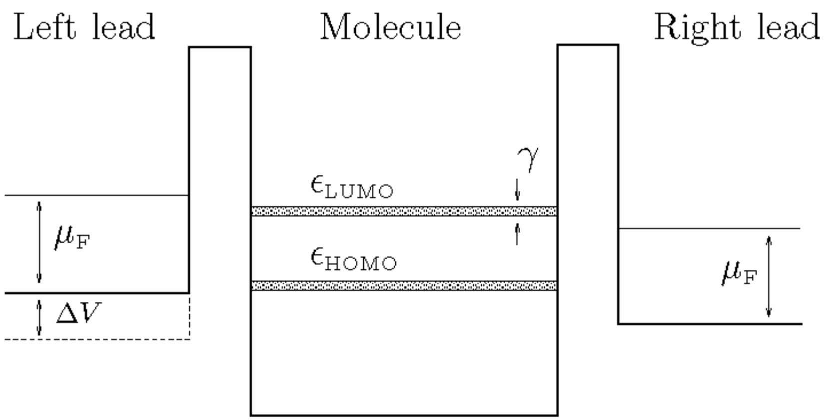


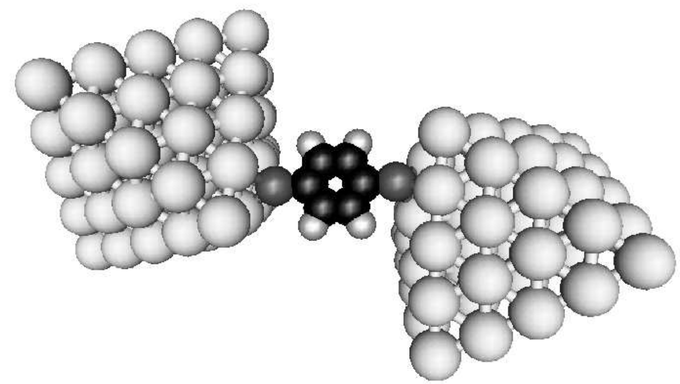
H-chain: localized σ-bonds dominate, and we probe density regions with $r_s<1$
→ XC viscosities not well known in these regions!

M. van Faassen et al., PRL **88**, 186401 (2002) and JCP **118**, 1044 (2003)

Nanoscale transport

Koentopp, Chang, Burke, and Car, J. Phys. Condens. Mat. **20**, 083203 (2008)





Simple approach: two-terminal Landauer formula:

$$I = \frac{2}{\pi} \int_{-\infty}^{\infty} dE\, T(E) \left[f_L(E) - f_R(E) \right]$$

Transmission coefficient, usually obtained from DFT-nonequilibrium Green's function; often gives quite wrong results – need TDDFT!

Nanoscale transport in the weak-bias regime

Current response: $$\vec{j}(\vec{r},\omega)=\int d^3r'\,\overleftrightarrow{\sigma}_0(\vec{r},\vec{r}',\omega)\vec{E}_{eff}(\vec{r}',\omega)$$

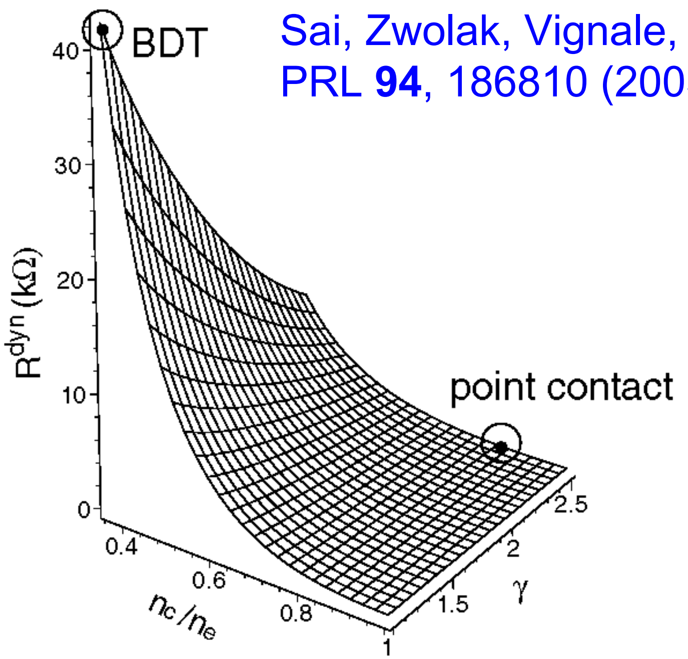
$$\delta I(\omega\to 0)=\frac{T_0(\varepsilon_F)}{\pi}\int d^3r'\left[\delta E_{ext}(\omega)+\delta E_H(\vec{r}',\omega)+\delta E_{xc}(\vec{r}',\omega)\right]$$

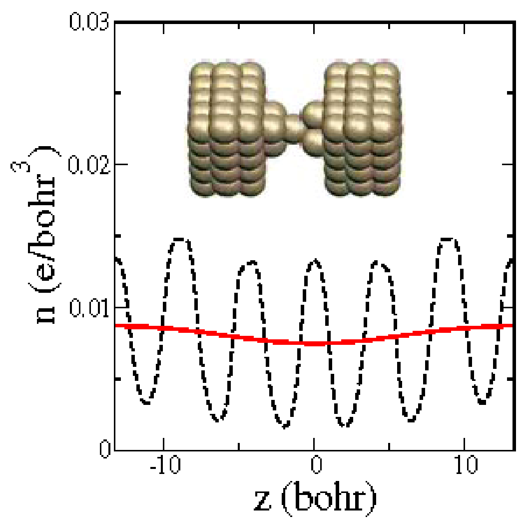
XC piece of voltage drop: shear viscosity

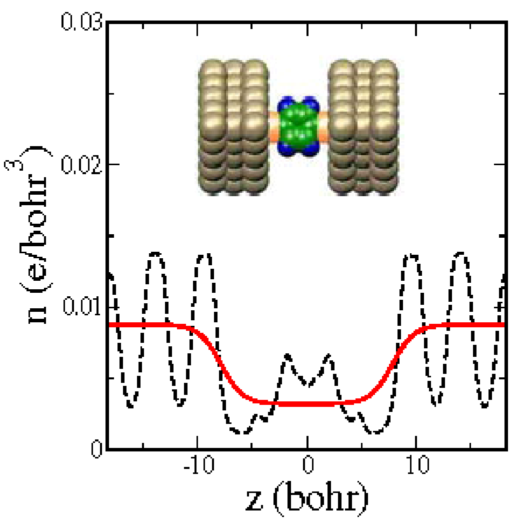
$$R^{dyn}=\frac{4}{3e^2A_c}\int \eta\,\frac{(\partial_z n)^2}{n^4}\,dz$$

Sai, Zwolak, Vignale, Di Ventra, PRL **94**, 186810 (2005)

dynamical resistance: ~10% correction

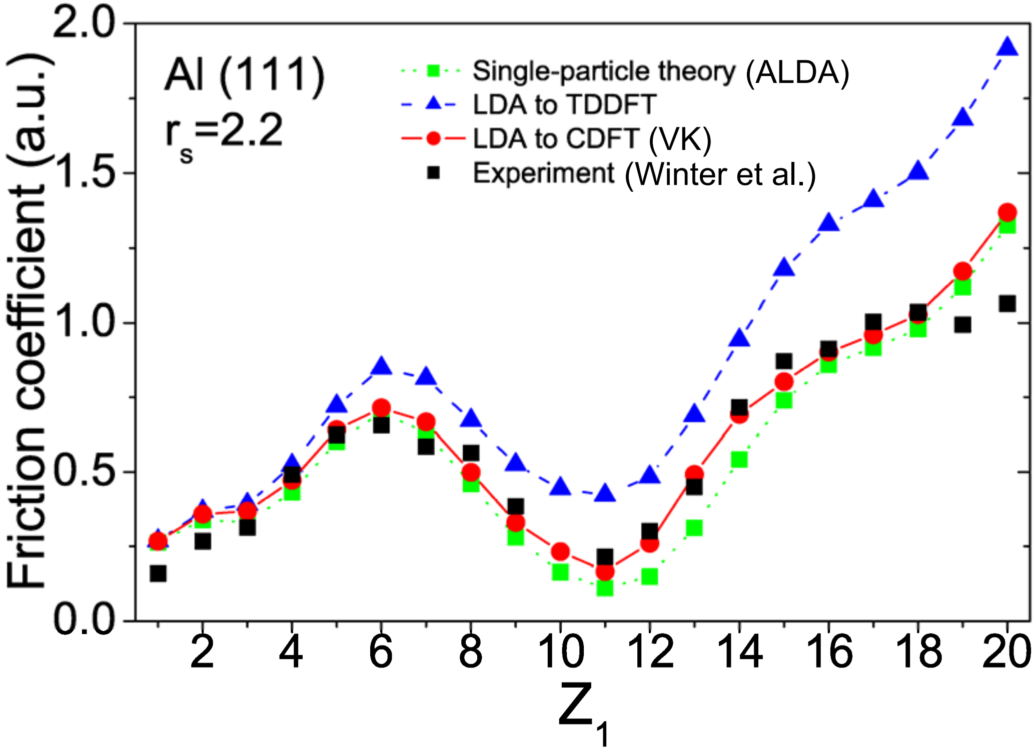






Stopping power of electron liquids

Nazarov, Pitarke, Takada, Vignale, and Chang, PRB **76**, 205103 (2007)



friction coefficient:

$$Q = Q_{\substack{single\\particle}} + Q_{xc}$$

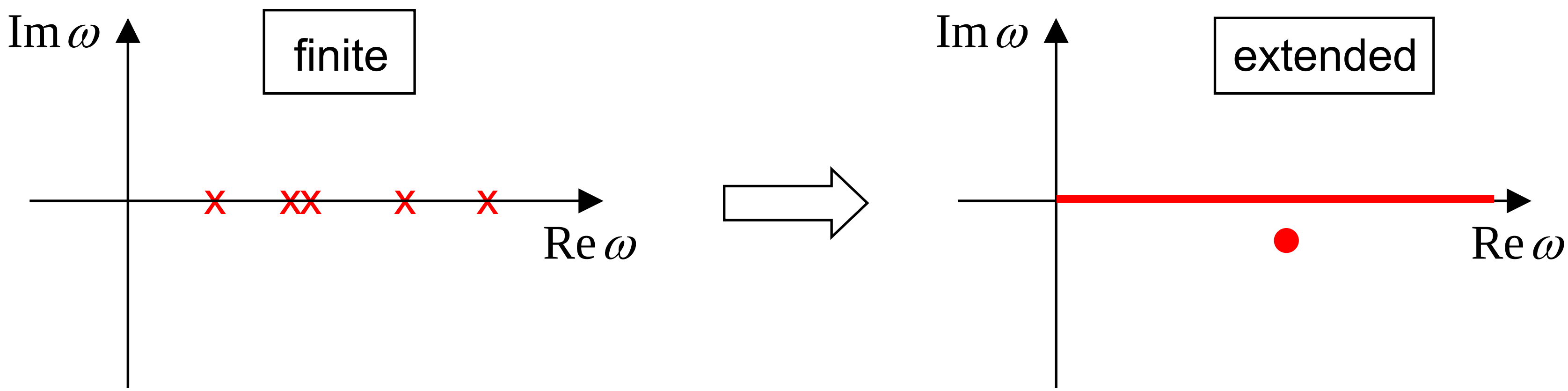
$$Q_{xc} = -\iint \left[\nabla n_0(\mathbf{r})\cdot\hat{\mathbf{v}}\right]\left[\nabla' n_0(\mathbf{r}')\cdot\hat{\mathbf{v}}\right] \times \left.\frac{\partial\,\mathrm{Im}\, f_{xc}(\mathbf{r},\mathbf{r}',\omega)}{\partial\omega}\right|_{\omega=0} d^3r\, d^3r'$$

- ► Stopping power measures friction experienced by a slow ion moving in a metal due to interaction with conduction electrons
- ► ALDA underestimates friction (only single-particle excitations)
- ► TDCDFT gives better agreement with experiment: additional contribution due to viscosity

Excitations in finite and extended systems

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \lim_{\eta\to 0^+}\left[\sum_j \frac{\langle\Psi_0|\hat{n}(\mathbf{r})|\Psi_j\rangle\langle\Psi_j|\hat{n}(\mathbf{r}')|\Psi_0\rangle}{\omega - \underbrace{E_j + E_0}_{\Omega_j} + i\eta} + c.c.(\omega\to-\omega)\right]$$

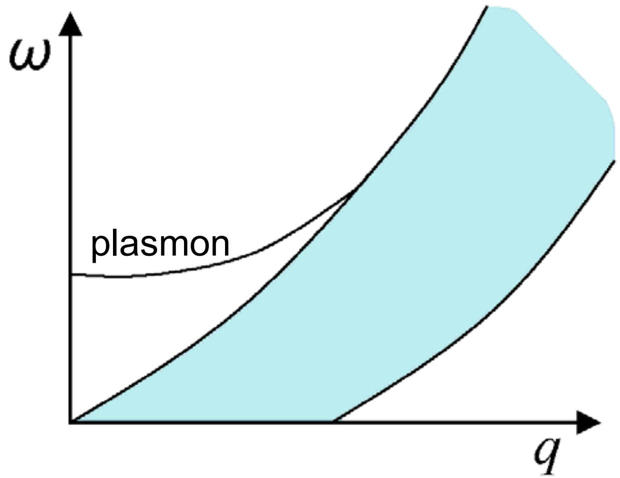
The full many-body response function has poles at the exact excitation energies



► Discrete single-particle excitations merge into a continuum (branch cut in frequency plane)

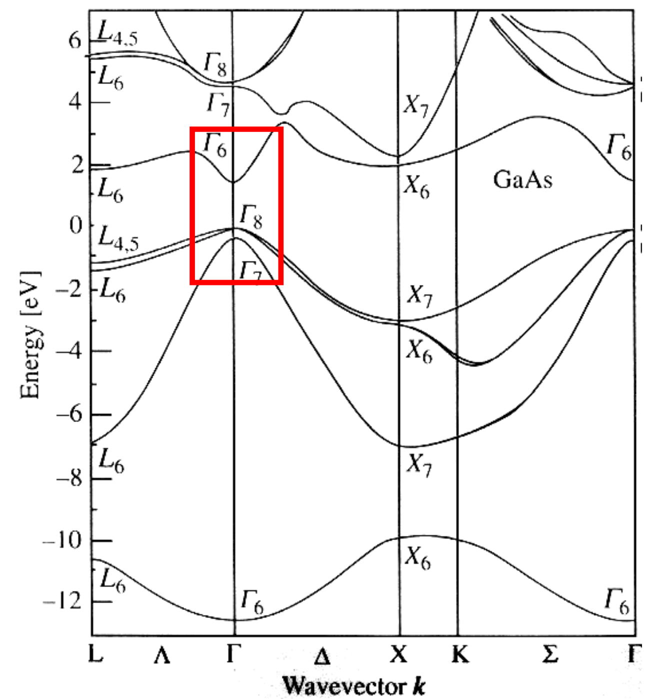
► New types of <u>collective excitations</u> appear off the real axis (finite lifetimes)

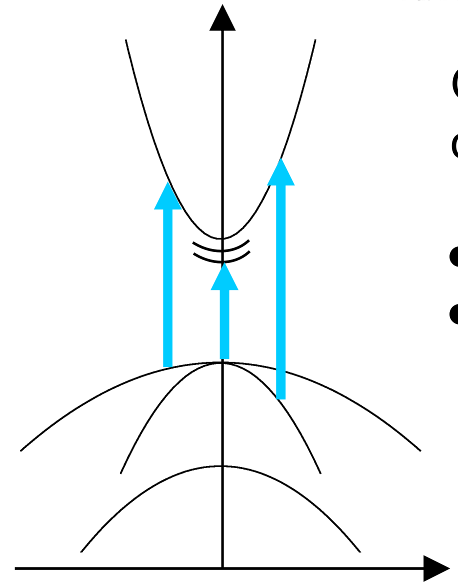
Metallic systems vs. insulators



Excitation spectrum of simple metals:

- single particle-hole continuum (incoherent)
- collective plasmon mode

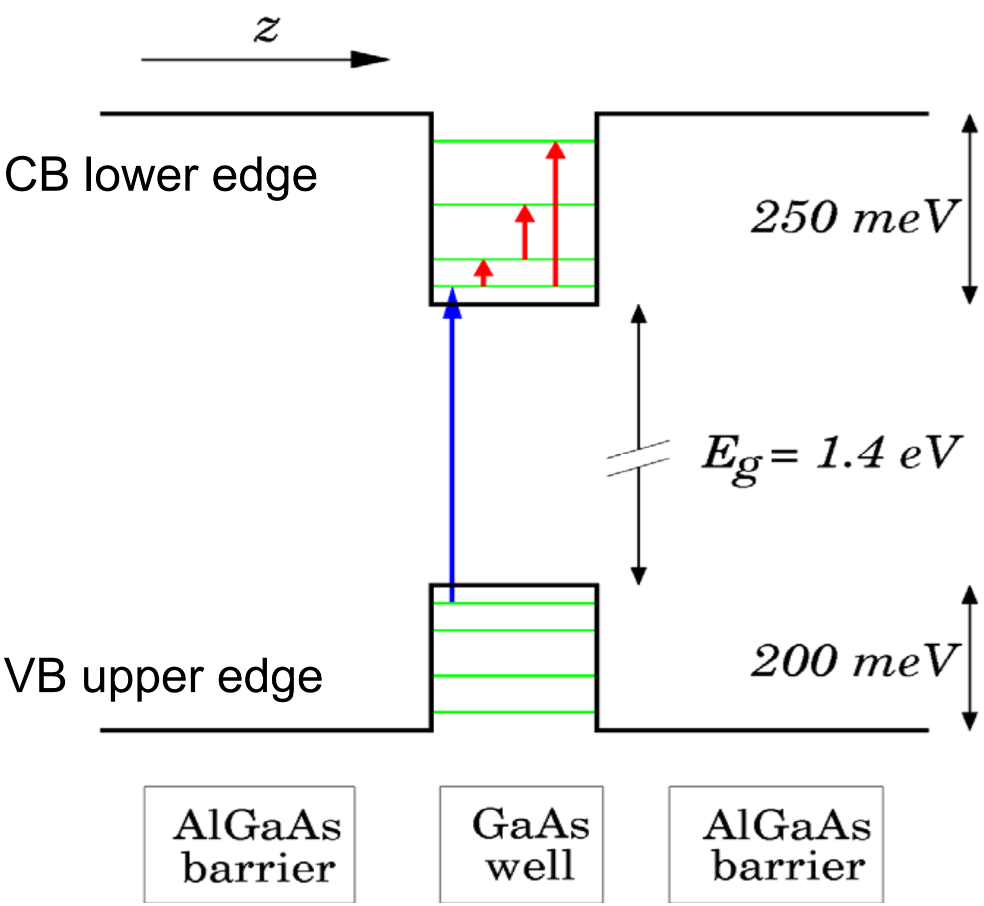




Optical excitations of insulators:

- interband transitions
- excitons (bound electron-hole pairs)

Electronic transitions in doped quantum wells



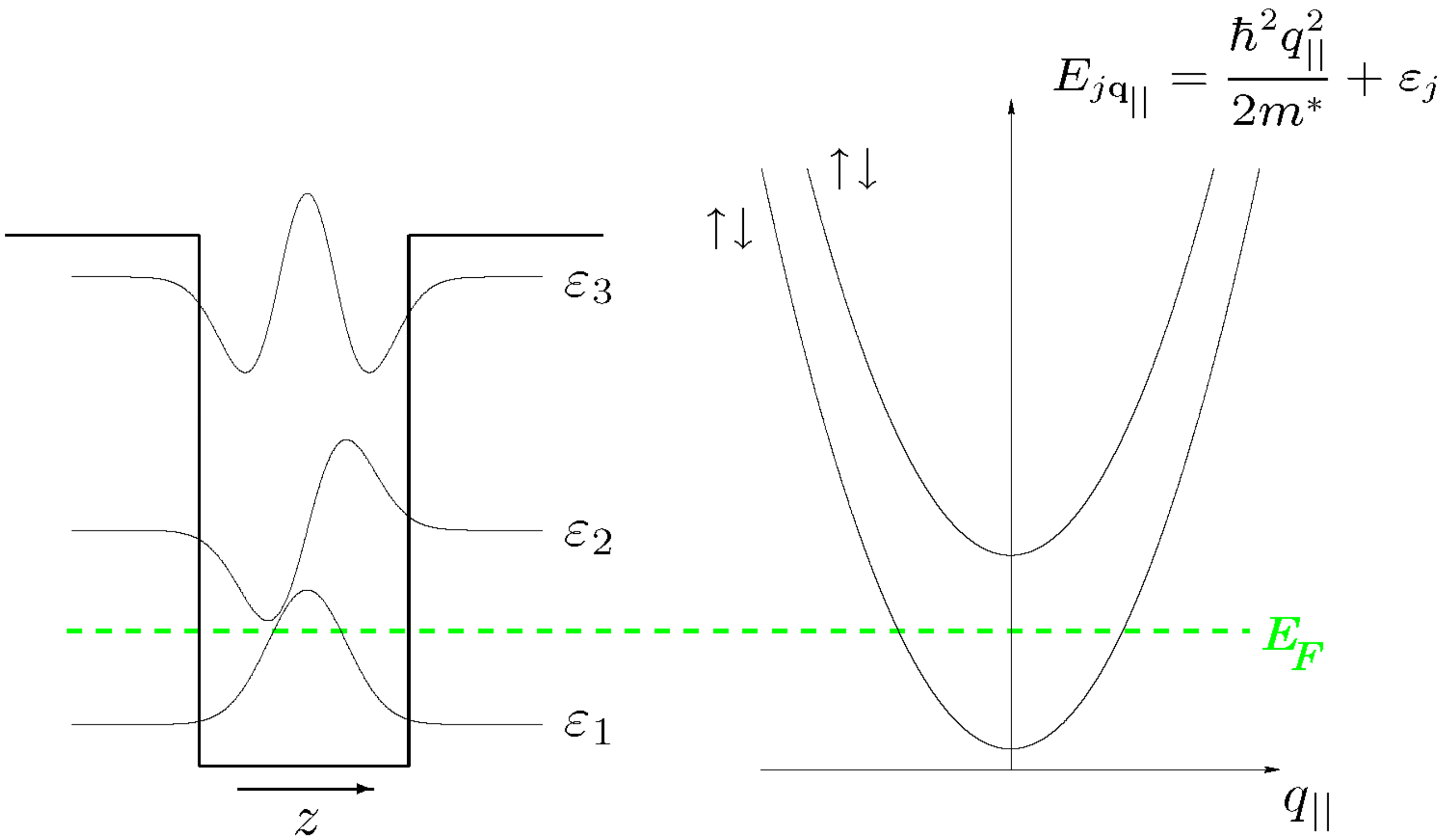
Interband transitions:
of order eV
(visible to near-IR)

Intersubband transitions:
of order meV
(mid- to far-IR)

10 meV = 2.4 THz

C.A. Ullrich, TDDFT book, Chapter 18

Quantum well subbands

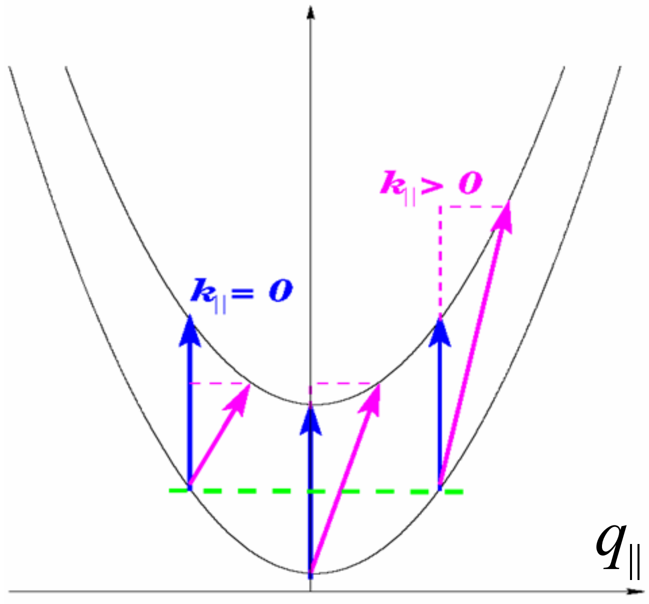


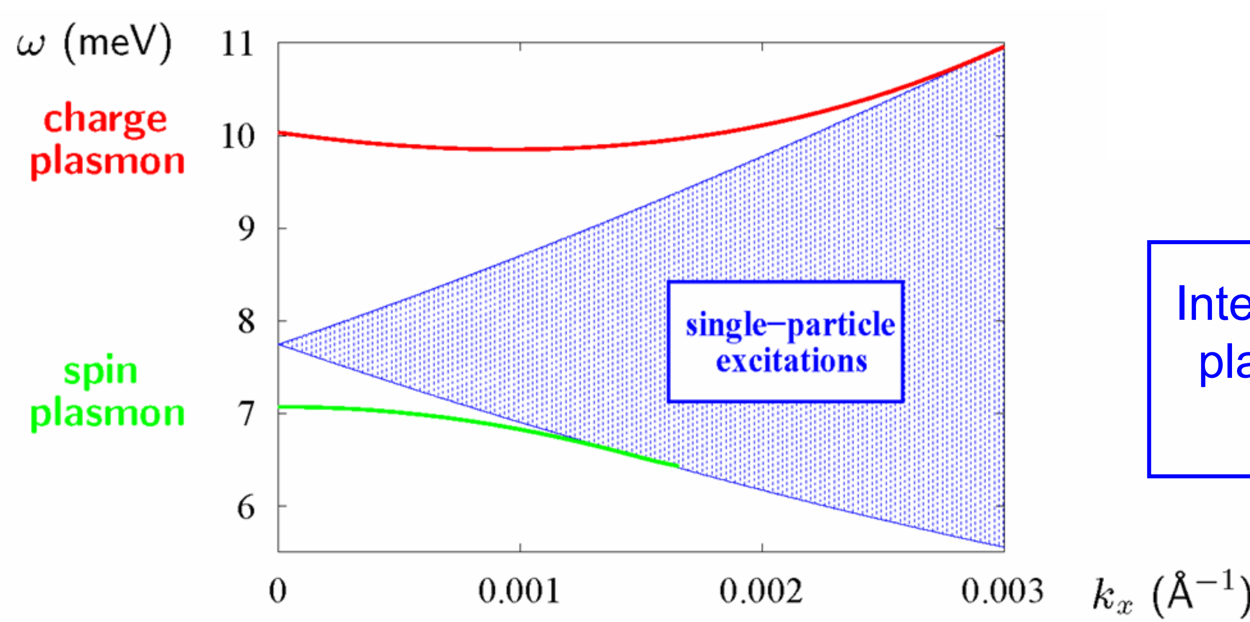
Electrons in a quantum well:

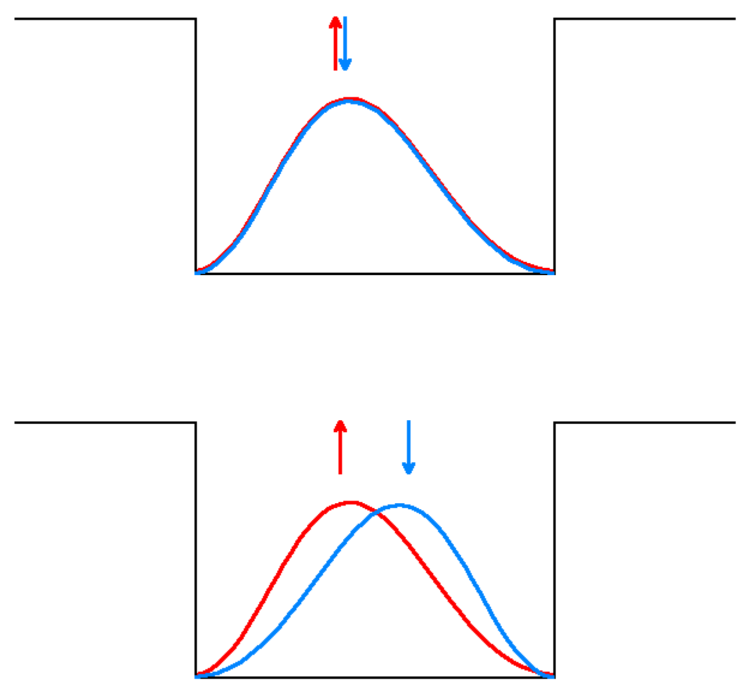
►quantized in z-direction (discrete subbands)

►free in the x-y plane (each subband is parabolic)

Single-particle and collective excitations







Intersubband charge and spin plasmons: ↑ and ↓ densities in and out of phase

TDCDFT for intersubband plasmons

Since this is a "1D" system, we can integrate the continuity equation:

$$\frac{\partial j_1}{\partial z} = i\omega n_1 \quad \Rightarrow \quad j_1(z,\omega) = i\omega \int_{-\infty}^{z} n_1(z',\omega)\,dz'$$

and we can construct the xc scalar potential from the xc vector potential:

$$\frac{\partial V_{xc,1}}{\partial z} = i\omega A_{xc,1} \quad \Rightarrow \quad V_{xc,1}(z,\omega) = i\omega \int_{-\infty}^{z} A_{xc,1}(z',\omega)\,dz'$$

We only need the zz component of the xc stress tensor:

$$\sigma_{xc,zz}(z,\omega) = \left(\zeta_{xc} + \frac{4}{3}\eta_{xc} \right) \frac{\partial \mathrm{v}(z,\omega)}{\partial z}$$

where $$\zeta_{xc} + \frac{4}{3}\eta_{xc} = -\frac{n_0^2(z)}{i\omega} \left(f_{xc}^{L}(n,\omega) - \frac{d^2 e_{xc}^{unif}}{dn^2} \right)_{n=n_0(z)}$$

f_{xc}^{dyn}

Explicit expression for the scalar xc kernel in 1D

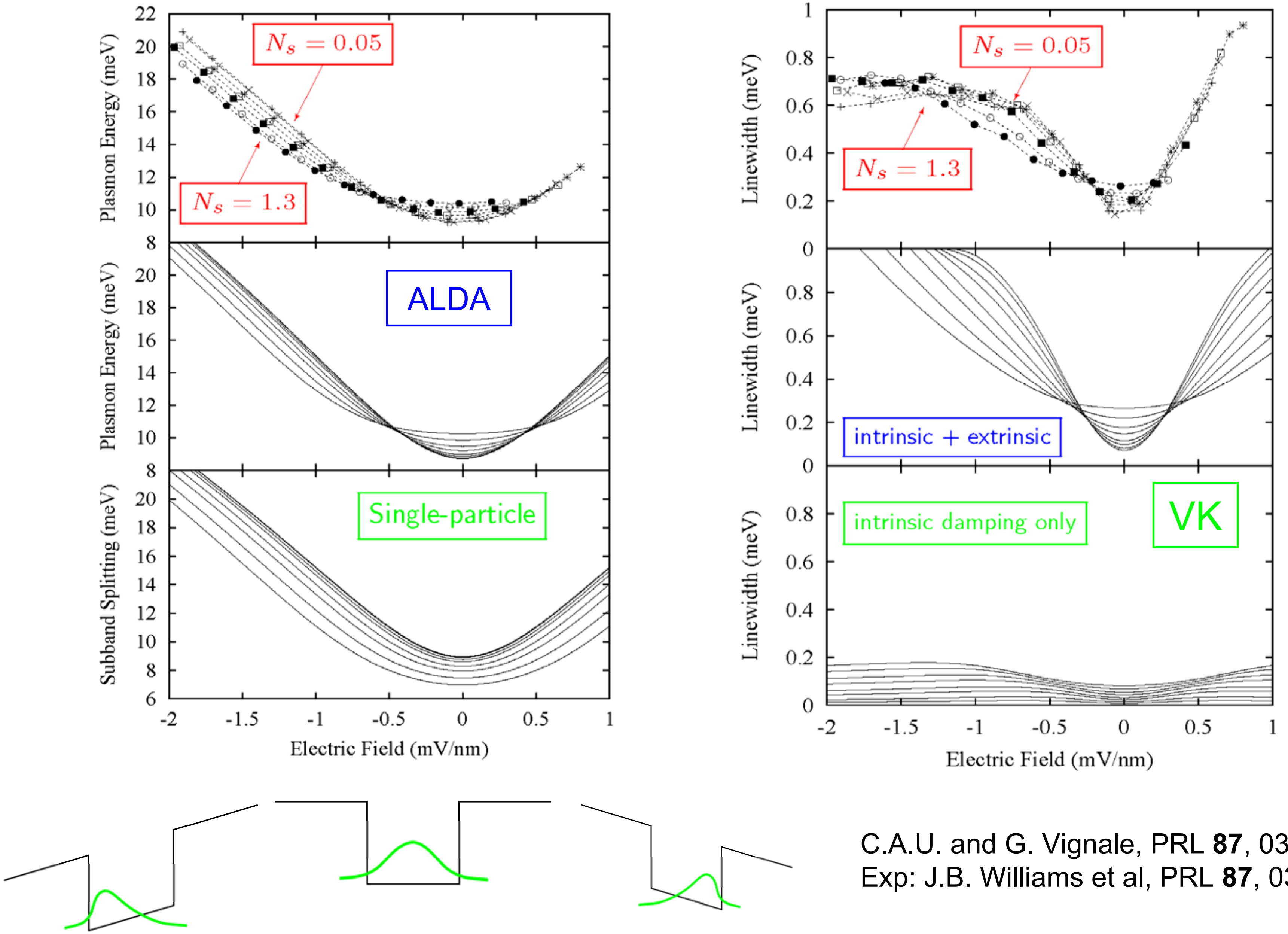
$$
\begin{aligned}
f_{xc}^{VK}(z,z',\omega) &= f_{xc}^{L}(z,\omega)\delta(z-z') \\
&\quad - f_{xc}^{dyn}(z,\omega)\frac{n_0'(z)}{n_0(z)}\theta(z-z') - f_{xc}^{dyn}(z',\omega)\frac{n_0'(z')}{n_0(z')}\theta(z'-z) \\
&\quad + \int dz''\theta(z''-z)\theta(z''-z')f_{xc}^{dyn}(z'',\omega)\left(\frac{n_0'(z'')}{n_0(z)}\right)^2
\end{aligned}
$$

- long-range nature of the xc kernel explicitly visible
- satisfies Harmonic Potential Theorem and other symmetries

G. Vignale and W. Kohn, in "Electronic DFT" (Plenum, 1998)

Exercise: derive this expression!

Frequencies and linewidths of ISB plasmons



C.A.U. and G. Vignale, PRL **87**, 037402
Exp: J.B. Williams et al, PRL **87**, 037401

The small-matrix approximation in TDDFT

$$n_{1\sigma}(\mathbf{r},\Omega) = \int d^3\mathbf{r}'\chi^{KS}_{\sigma\sigma}(\mathbf{r},\mathbf{r}',\Omega)\sum_{\sigma'}\int d^3\mathbf{r}''\left[\frac{1}{|\mathbf{r}'-\mathbf{r}''|} + f_{xc,\sigma\sigma'}(\mathbf{r}',\mathbf{r}'',\Omega)\right]n_{1\sigma'}(\mathbf{r}'',\Omega)$$

Find those frequencies Ω where there is a finite solution of the response equation without any external perturbation (eigenmodes of the system).

consider only 2 levels:

$$\chi^{KS}_{\sigma\sigma}(\mathbf{r},\mathbf{r}',\omega) \approx \left[\frac{1}{\omega-\omega_{21}} - \frac{1}{\omega+\omega_{21}}\right]\varphi_1(\mathbf{r})\varphi_2(\mathbf{r})\varphi_1(\mathbf{r}')\varphi_2(\mathbf{r}')$$

define

$$S_{\sigma\sigma'} = 2\int d^3r\int d^3r'\left[\frac{1}{|\mathbf{r}-\mathbf{r}'|} + f_{xc,\sigma\sigma'}(\mathbf{r},\mathbf{r}',\Omega)\right]\varphi_1(\mathbf{r})\varphi_2(\mathbf{r})\varphi_1(\mathbf{r}')\varphi_2(\mathbf{r}')$$

$$\Omega^2_{\pm} = \omega^2_{21} + 2\omega_{21}\left(S_{\uparrow\uparrow} \pm S_{\uparrow\downarrow}\right)$$

Exercise: derive this!

+ Charge-Density excitation / singlet excitation

— Spin-Density excitation / triplet excitation

Atomic excitation energies with TDCDFT

C.A.Ullrich and K. Burke, JCP **121**, 28 (2004)

Velocity field of 1→2 excitation: $$\mathbf{v}^{12} = \frac{\varphi_1(r)\nabla\varphi_2(r) - \varphi_2(r)\nabla\varphi_1(r)}{n_0(\mathbf{r})}$$

Small-matrix approximation of TDCDFT with VK functional:

$$\Omega^2 = \Omega^2_{ALDA} - \frac{i\Omega}{\omega_{12}} \sum_{jk} \int d^3r\, \sigma^{12}_{xc,jk}(\mathbf{r},\Omega) \nabla_k \mathrm{v}^{12}_j(\mathbf{r})$$

compare with average rate of energy dissipation in a classic viscous fluid: $$\dot{E}_{diss} = -\sum_{jk} \int d^3r\, \sigma_{jk} \nabla_k \mathrm{v}_j$$

More general formalism for molecules: M. van Faassen, Int. J. Mod. Phys. B **20**, 3419 (2006)

Atomic excitation energies

lowest $^1S \to {}^1S$ (in eV)

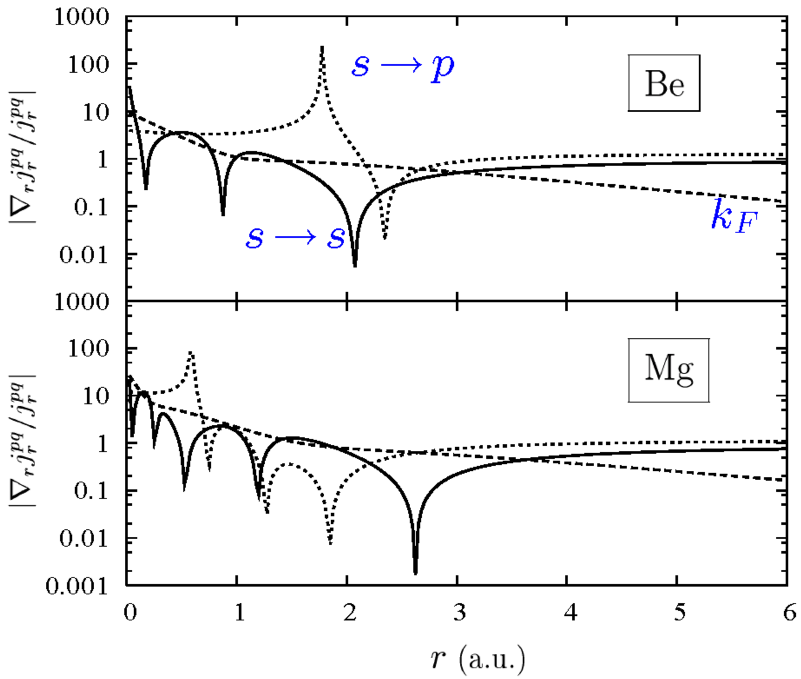
	Exp	bare KS	ALDA	VK
Be $2s \to 3s$	6.78	5.56	5.62	$5.67 - 0.04\,i$
Mg $3s \to 4s$	5.39	4.72	4.78	$4.83 - 0.05\,i$
Ca $4s \to 5s$	4.13	3.77	3.81	$3.87 - 0.06\,i$
Sr $5s \to 6s$	3.79	3.50	3.54	$3.59 - 0.06\,i$

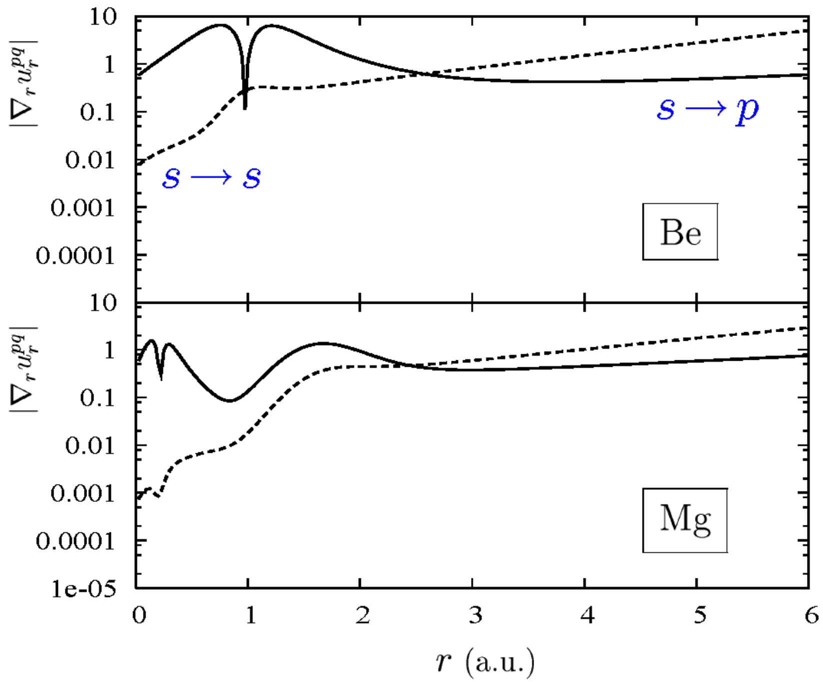
lowest $^1S \to {}^1P$ (in eV)

	Exp	bare KS	ALDA	VK
Be $2s \to 2p$	5.28	3.50	5.08	$6.24 - 0.69\,i$
Mg $3s \to 3p$	4.35	3.39	4.57	$4.86 - 0.09\,i$
Ca $4s \to 4p$	2.93	2.39	3.38	$3.22 - 0.06\,i$
Sr $5s \to 5p$	2.69	2.22	3.11	$-1.63 - 0.06\,i$

C.A.Ullrich and K. Burke, JCP **121**, 28 (2004)

Analysis of the VK functional for atoms





conditions for validity of the VK functional:

$$\left|\frac{\nabla n_0}{n_0}\right|, \left|\frac{\nabla j_\nu}{j_\nu}\right|, \left|\frac{\nabla v_\nu}{v_\nu}\right| << k_F, \frac{\omega}{v_F}$$

OK for s→s, but badly violated for s→p!

Analysis of the VK functional for atoms

► Frequency shifts:

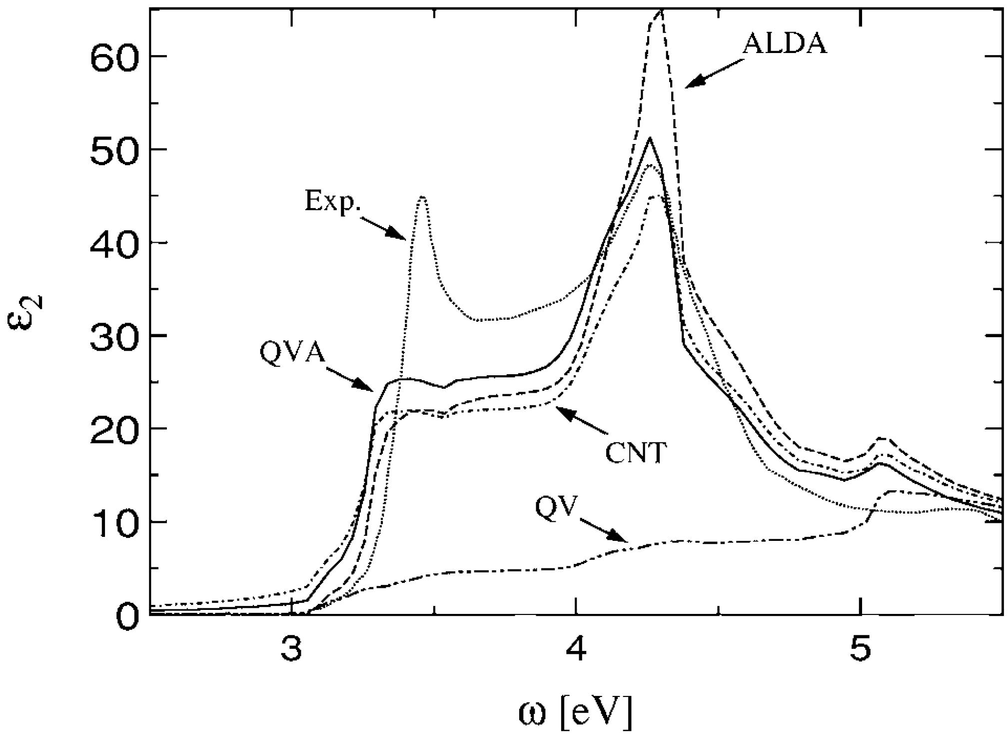
- Generally in the right direction; but only small for s→s, and tend to overshoot for s→p excitations
- need more accurate $f_{xc}^{L,T}(\omega)$, especially around nucleus (r_s<<1)
- excitations with large ∇j are problematic. Need higher gradients. [partial cure: Tao and Vignale, PRL **97**, 036403 (2006)]

► Imaginary parts:

- small but finite, often of the same order as frequency shifts.
- unphysical: a finite system ought to have zero linewidth. Difficult to achieve for a functional with the homogeneous electron gas as reference system!

TDCDFT for bulk semiconductors

Berger, de Boeij, and van Leeuwen, PRB **75**, 035116 (2007)



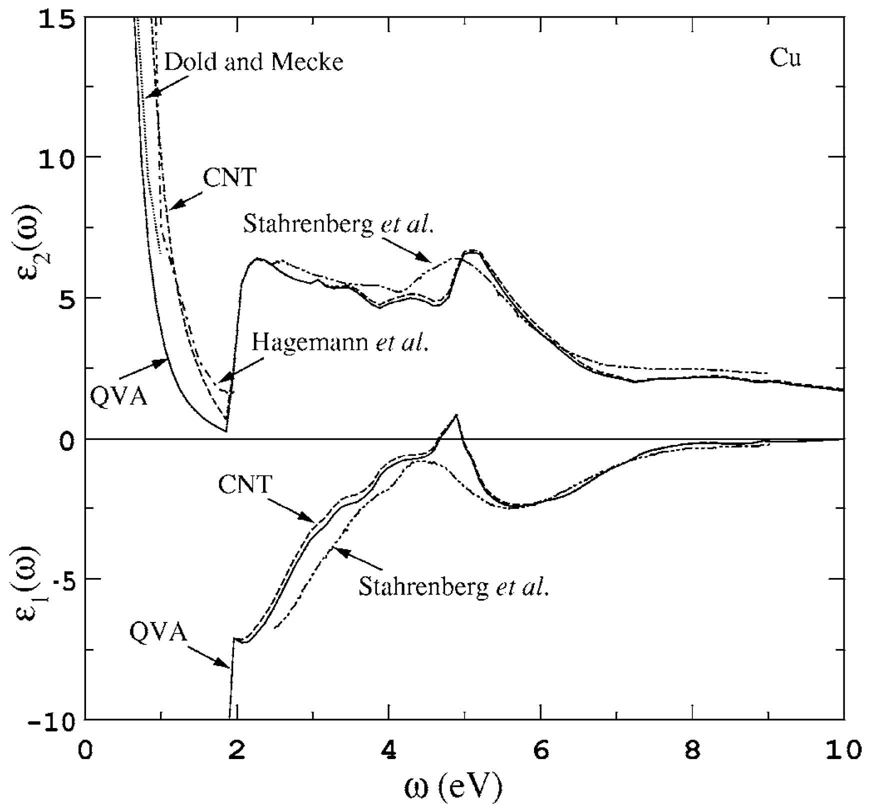
CNT: Conti, Nifosi, Tosi
QV: Qian, Vignale

Experiment:
Lautenschlager, Garriga, Vina and Cardona, PRB **36**, 4821 (1987)

- if shear modulus is ignored (CNT,QVA), marginal improvement over ALDA.
- including transverse shear modulus (QV), spectrum collapses.
- like in atoms, the inhomogeneity is too large; VK conditions violated
- usage of VK for insulators questionable, but can perhaps be improved

Macroscopic dielectric function of metals

Berger, Romaniello, van Leeuwen, and de Boeij, PRB **74**, 245117 (2006)



- cures deficiencies of ALDA (low-frequency Drude-like tail of spectrum)
- again, the transverse shear modulus causes trouble. Results are better if it is neglected. However, this might be fixed if we had better expressions for the shear modulus.

The VK functional: summary and words of caution

► Relies on a "double-LDA": both the ground-state density and external perturbation are assumed to be slowly varying.
In practice, these conditions are often violated, which can be a source of serious problems!

► Depends crucially on order of limits: q→0 first, then ω→0. Does therefore not reduce to ALDA in the ω→0 limit, due to xc shear modulus of electron liquid which stays finite.
The discontinuity in f_{xc} is a very subtle point, and sometimes seems to lead to unphysical results, depending on the system. How to take the static limits properly is still subject of research.

► VK is based on the electron gas, which is an infinite reference system. Therefore, excitation energies have an imaginary part.
For finite systems, this is unphysical, but for extended systems, this is the correct physics.

► Required input for VK functional is only approximately known.
Need more accurate expressions for $f_{xc}^{L}(n,\omega)$, $f_{xc}^{T}(n,\omega)$ especially at high densities.

Ultranonlocality in DFT: "upgrades"

► Band insulators:

$$f_{xc}(\mathbf{k},\mathbf{k},0) \xrightarrow[k\to 0]{} \frac{\alpha}{k^2} \quad \Rightarrow \quad \textbf{Polarization DFT}$$

Gonze, Ghosez, and Godby, PRL **74**, 4035 (1995)

► TDDFT:

$$f_{xc}(\mathbf{k},\mathbf{k}',\omega) \xrightarrow[k\to 0]{} \alpha(\omega)\frac{\mathbf{k}\cdot\mathbf{k}'}{k^2} \quad \Rightarrow \quad \textbf{TDCDFT}$$

Vignale and Kohn, PRL **77**, 2037 (1996)

► Spin-TDDFT:

$$f^{unif}_{xc,\sigma\sigma'}(\mathbf{k},\omega) \xrightarrow[k\to 0]{} \frac{A(\omega)}{k^2}\frac{\sigma\sigma' n^2}{4n_\sigma n_{\sigma'}} + B_{\sigma\sigma'}(\omega) \quad \Rightarrow \quad \textbf{TDSCDFT}$$

Situation even worse: ultranonlocality appears in the homogeneous case!

Qian, Constantinescu, Vignale, PRL **90**, 066402 (2003)

Spin-dependent generalization of VK functional

Qian, Constantinescu, Vignale,
PRL **90**, 066402 (2003)

- spin-dependent generalization of the xc viscoelastic stress tensor
- depends on velocity gradients

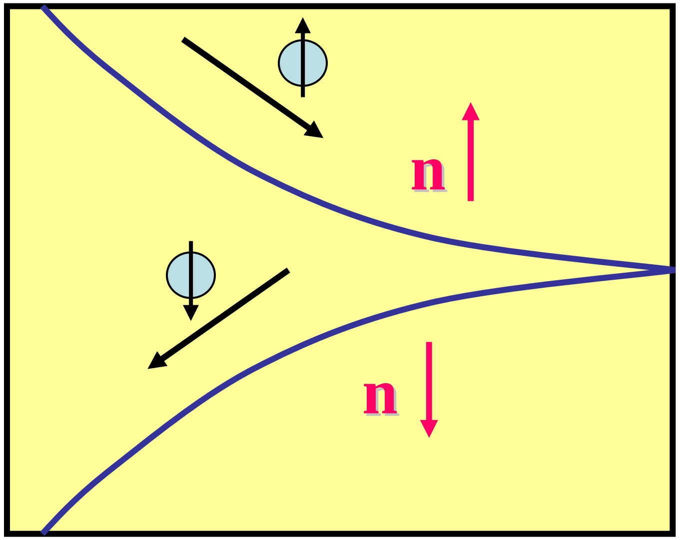
$$\mathbf{A}_{xc,1\sigma}(\mathbf{r},\omega)=\mathbf{A}^{ALDA}_{xc,1\sigma}(\mathbf{r},\omega)-\frac{1}{i\omega n_\sigma(\mathbf{r})}\sum_{\sigma'}\nabla\cdot\overleftrightarrow{\sigma}_{xc,\sigma\sigma'}(\mathbf{r},\omega)$$
$$+\frac{n_\uparrow(\mathbf{r})n_\downarrow(\mathbf{r})\rho_{\uparrow\downarrow}(\mathbf{r},\omega)}{i\omega}\sum_{\sigma'}\frac{\sigma\sigma'}{n_\sigma(\mathbf{r})n_{\sigma'}(\mathbf{r})}\mathbf{j}_{\sigma'}(\mathbf{r},\omega)$$

$\rho_{\uparrow\downarrow}(\omega)$
spin-transresistivity

- new term, depends on the velocities themselves
- disappears in the static limit ($\rho_{\uparrow\downarrow}\sim\omega$)
- real part: spin mass
- imaginary part: spin Coulomb drag

The spin Coulomb drag effect

Even in the purest material (no spin-flip), spin currents decay due to Coulomb interaction between different spin populations.



SCD counteracts spin diffusion in opposite directions.

⇒ **Spin-transresistivity** $\rho_{\uparrow\downarrow}$

$$D_s = D_{ni} \frac{S}{S_{ni}} \frac{1}{1 + \left|\rho_{\uparrow\downarrow}\right| / \rho_{Drude}}$$

spin diffusion constant

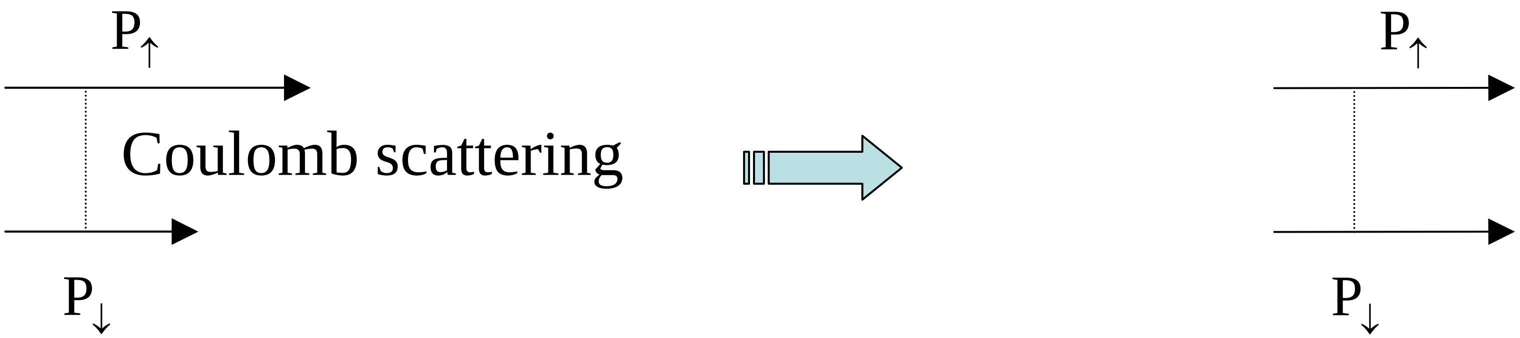
spin stiffness

Theory: I. D'Amico and G. Vignale, EPL **55**, 566 (2001), PRB **65**, 85109 (2002) PRB **68**, 045307 (2003)

Experiment: C.P. Weber, N. Gedik, J.E. Moore, J. Orenstein, J. Stephens, and D. D. Awschalom, Nature **437**, 1330 (2005)

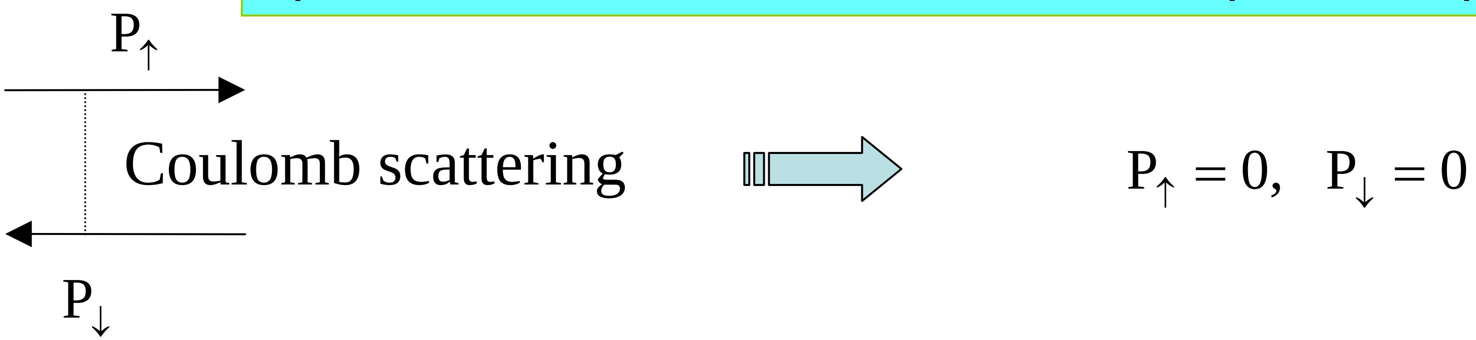
The spin Coulomb drag effect

Spin+ Charge mode → **Charge mode**



SCD ‘pumps’ momentum from faster to slower population

Spin mode → **complete damping**



SCD damps *both* spin populations

P_{tot} conserved, $P_{\uparrow,\downarrow}$ *not* conserved

Spin-resolved excitation spectrum in TDSCDFT

(complex) excitation frequency

$$\Omega_{\pm\sigma}^2 \approx \omega_{pq\sigma}^2 + 2\omega_{pq\sigma} S_{\pm\sigma}$$

linewidth

$$\Gamma_{\pm} \approx \mathrm{Im}\, S_{\pm\sigma}$$

$\omega_{pq\sigma}$ = bare single-particle excitation frequency between levels p and q

$$S_{\pm\sigma} = \left(S_{\sigma\bar{\sigma}}^{H+ALDA} \pm S_{\sigma\bar{\sigma}}^{H+ALDA}\right) + \left(S_{\sigma\bar{\sigma}}^{VE} \pm S_{\sigma\bar{\sigma}}^{VE}\right) + \left(S_{\sigma\bar{\sigma}}^{SCD} \pm S_{\sigma\bar{\sigma}}^{SCD}\right)$$

Hartree + ALDA: real
(no dissipation)

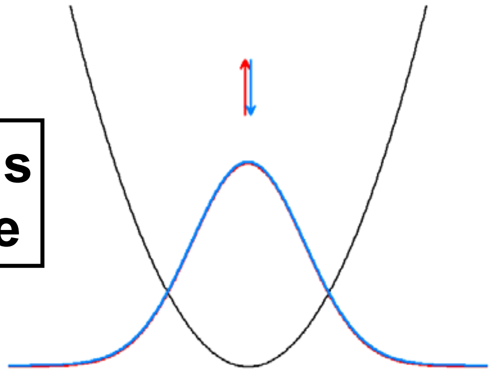
Viscoelastic + SCD: complex
(dissipative)

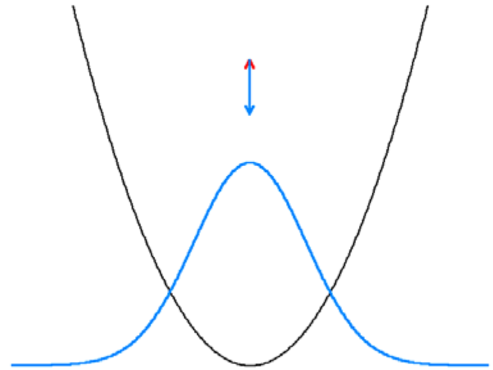
$$\left(S_{\sigma\bar{\sigma}}^{SCD} \pm S_{\sigma\bar{\sigma}}^{SCD}\right) = \frac{ie^2\omega}{\omega_{pq\sigma}^2} \int d^3r \left[\frac{n_{\bar{\sigma}}}{n_\sigma} \left|\vec{j}_{pq\sigma}\right|^2 \mp \vec{j}_{pq\bar{\sigma}} \cdot \vec{j}_{pq\sigma} \right] \rho_{\uparrow\downarrow}(\omega; n_\uparrow, n_\downarrow)$$

structure of a (complex) power loss
term in an AC spintronics circuit

Intersubband plasmons in parabolic quantum wells

Kohn's mode





Charge-density excitation (CDE)

$$\Gamma^{VE}_{CDE} = 0, \quad \Gamma^{SCD}_{CDE} = 0$$

Spin-density excitation (SDE)

Γ^{VE}_{SDE} small, Γ^{SCD}_{SDE} not small

Total linewidth: $$\Gamma_{\pm} = \Gamma^{disorder}_{\pm} + \Gamma^{VE}_{\pm} + \Gamma^{SCD}_{\pm}$$

⇨ Linewidth of spin plasmons dominated by SCD effect.
Proposal for experimental study using inelastic light scattering.

I. D'Amico and C.A.Ullrich, PRB **74**, 121303(R) (2006)

End of the second lecture

Today's summary:

► The VK functional in TDCDFT works great for polarizabilities of polymers and linewidths of collective plasmon excitations

► The situation is less clear for excitations in atoms and molecules and optical spectra of metals and insulators. These seem hard to capture with electron-gas based functionals.

► VK is promising, but needs improvements (e.g. local → semilocal)

► For spin-dependent dynamics, TDSCDFT leads to the spin Coulomb drag effect, which is of interest in the field of spintronics.

Tomorrow:

- Dynamics in the time domain: memory and dissipation in TDKS
- A rigorous extension of the LDA: TDDefFT versus TDCDFT
- Time-dependent optimized effective potential