TDDFT for extended systems I: Plasmons

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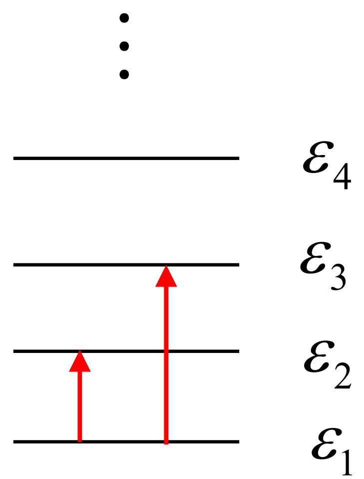
Single-particle versus collective excitations

$$\chi_s(\mathbf{r},\mathbf{r}',\omega) = \sum_{j,k}\left(f_k - f_j\right)\frac{\varphi_k^*(\mathbf{r})\varphi_j(\mathbf{r})\varphi_j^*(\mathbf{r}')\varphi_k(\mathbf{r}')}{\omega - \boxed{(\varepsilon_j - \varepsilon_k)} + i\eta}$$



Electronic excitation spectra in materials contain contributions from single-particle excitations between Kohn-Sham levels.

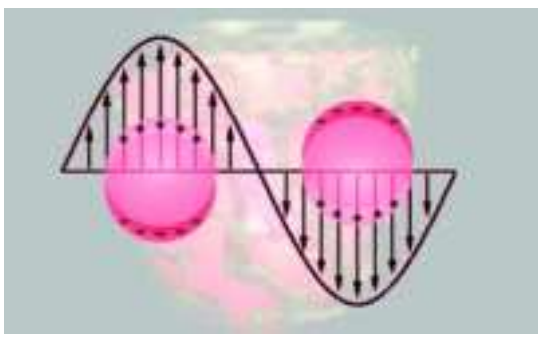
These are automatically included through the KS response function.

Single-particle versus collective excitations

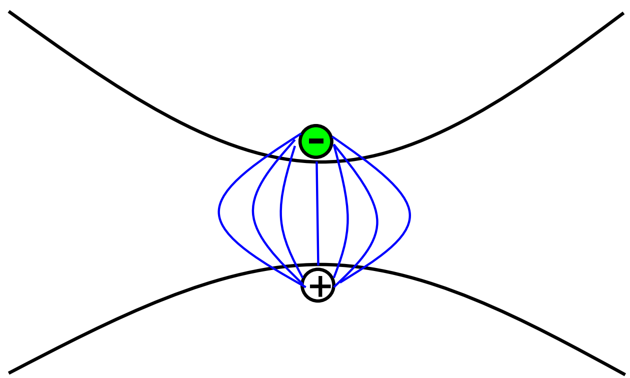
$$\chi = \chi_s + \chi_s \boxed{f_{Hxc}} \chi$$

But there are **collective excitations** that do **not** have a counterpart in the KS spectrum!

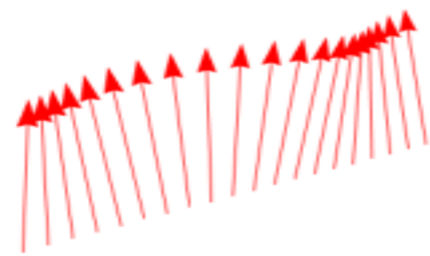
Plasmons



Excitons



Magnons

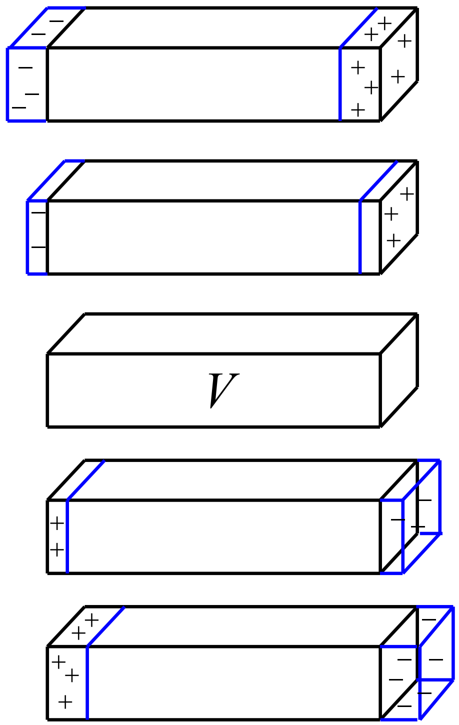


► **Not excitations between eigenstates of the many-body system**
► **Quasiparticle-like collective excitations with finite lifetimes**

Outline

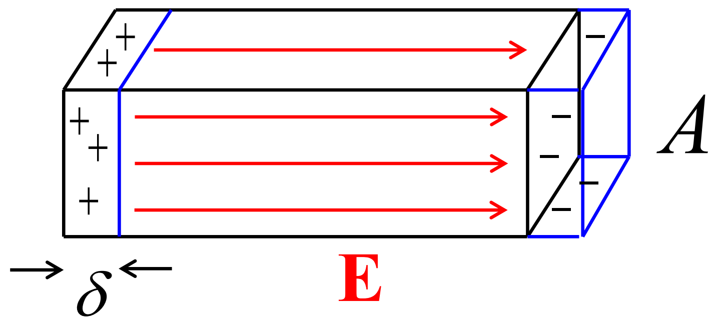
- Classical plasma oscillations
- Experimental observation of plasmons
- The homogeneous electron gas:
  how to calculate plasmons
- Plasmons in TDDFT
- Plasmon damping
- Nanoscale systems and plasmonics

Classical bulk motion of charge in a solid



A slab of electrons moving back and forth on top of
a slab of neutralizing positive charge: **plasma oscillations**.

Classical bulk motion of charge in a solid



Total charge on one side:

$$enA\delta$$

Uniform electric field caused by surface charge: $E = 4\pi en\delta$

Total force on all electrons: $F = enVE = -4\pi n^2 e^2 V\delta$

Set force equal to total mass times acceleration: $F = M\ddot{\delta}$

$$-4\pi n^2 e^2 V\delta = mnV\ddot{\delta} \quad \Rightarrow \quad \ddot{\delta} = -\frac{4\pi n e^2}{m}\delta$$

Plasma frequency: $\omega_{pl}^2 = \dfrac{4\pi n e^2}{m}$

Table 2 Volume plasmon energies, in eV

Material	Observed	Calculated $\hbar\omega_p$	Calculated $\hbar\tilde{\omega}_p$
Metals			
Li	7.12	8.02	7.96
Na	5.71	5.95	5.58
K	3.72	4.29	3.86
Mg	10.6	10.9	
Al	15.3	15.8	

includes ionic background

Plasmons: experiment

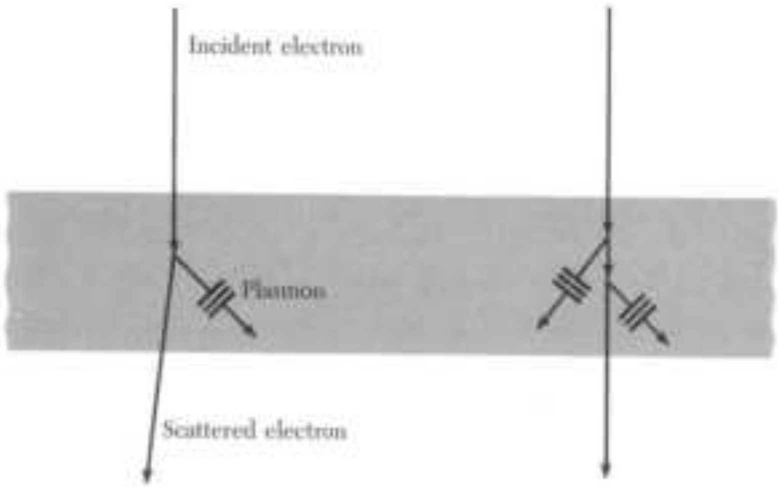


Figure 6 Creation of a plasmon in a metal film by inelastic scattering of an electron. The incident electron typically has an energy 1 to 10 keV; the plasmon energy may be of the order of 10 eV. An event is also shown in which two plasmons are created.

Plasmons are quantized excitations of collective longitudinal waves of the electron gas.

They are not optically excited, but by scattering with electrons or photons.

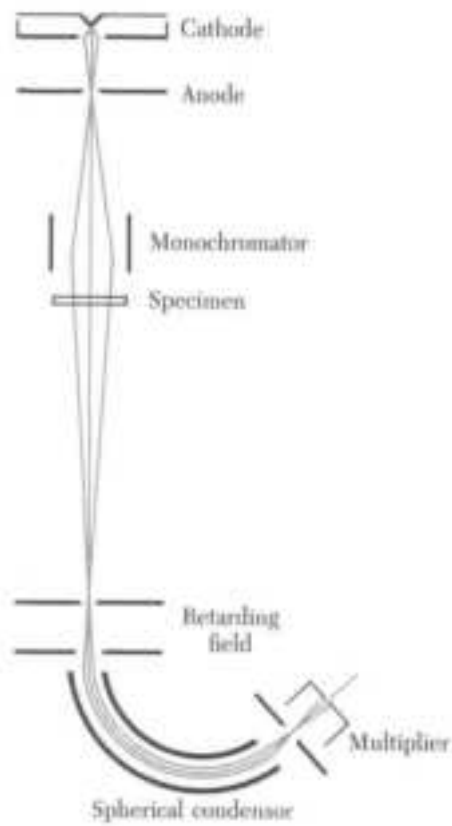


Figure 7 A spectrometer with electrostatic analyzer for the study of plasmon excitation by electrons. (After J. Daniels et al.)

Electron loss spectra

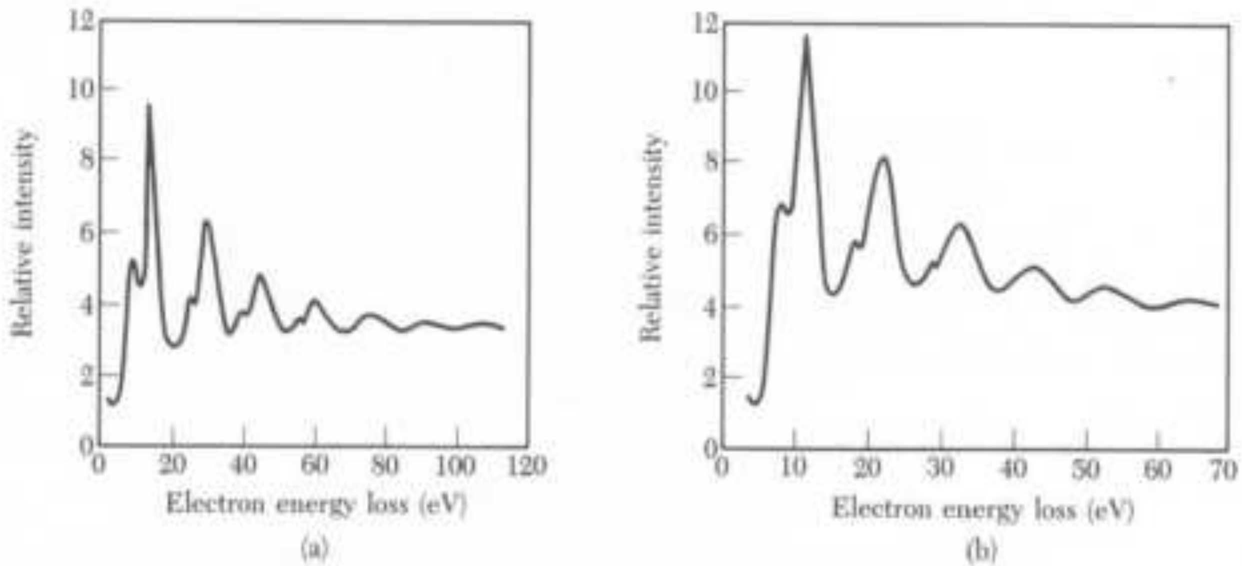
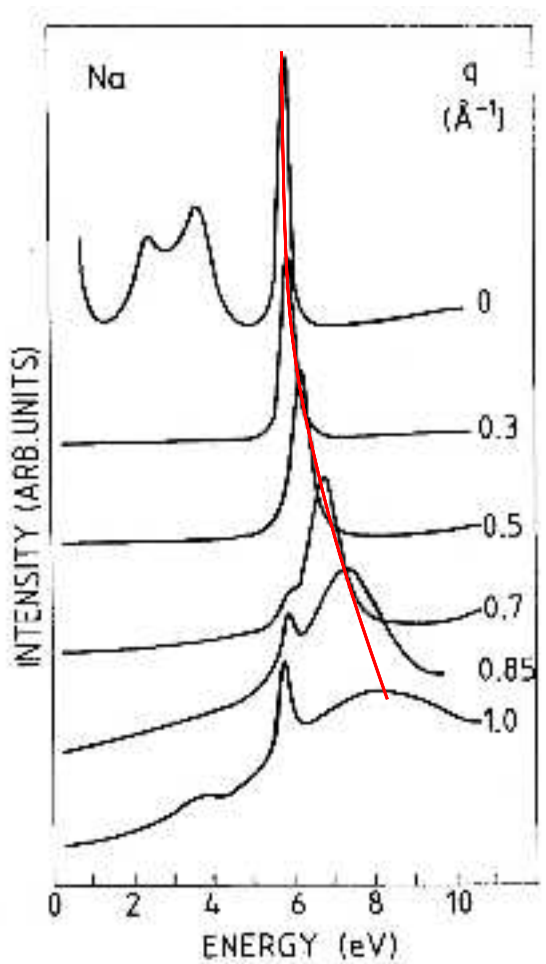


Figure 8 Energy loss spectra for electrons reflected from films of (a) aluminum and (b) magnesium, for primary electron energies of 2020 eV. The 12 loss peaks observed in Al are made up of combinations of 10.3 and 15.3 eV losses, where the 10.3 eV loss is due to surface plasmons and the 15.3 eV loss is due to volume plasmons. The ten loss peaks observed in Mg are made up of combinations of 7.1 eV surface plasmons and 10.6 eV volume plasmons. Surface plasmons are the subject of Problem 1. (After C. J. Powell and J. B. Swan.)

Electron loss spectra



at low momentum: surface and volume plasmon

at large momentum transfer:

- double scattering
- Landau damping

A. vom Felde, J. Sprösser-Prou, and J. Fink, PRB **40**, 10181 (1989)

The history of plasmons

PHYSICAL REVIEW VOLUME 85, NUMBER 2 JANUARY 15, 1952

A Collective Description of Electron Interactions: II. Collective *vs* Individual Particle Aspects of the Interactions

DAVID PINES
Randal Morgan Laboratory of Physics, University of Pennsylvania, Philadelphia, Pennsylvania

AND

DAVID BOHM*
Palmer Physical Laboratory, Princeton University, Princeton, New Jersey

(Received September 28, 1951)

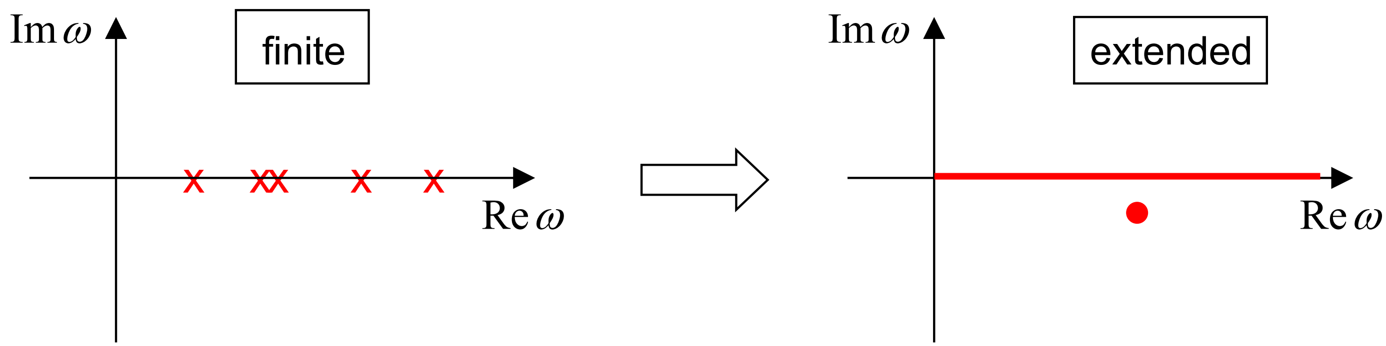
Plasmons: proposed by David Pines in 1952-55

David Pines
1924-2018

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)

The homogeneous electron gas

Kohn-Sham response function:

$$\chi_s(\mathbf{r},\mathbf{r}',\omega) = \sum_{j,k}^{\infty} (f_k - f_j) \frac{\varphi_j(\mathbf{r})\varphi_k^*(\mathbf{r})\varphi_j^*(\mathbf{r}')\varphi_k(\mathbf{r}')}{\omega - (\varepsilon_j - \varepsilon_k) + i\eta}$$

Homogeneous electron gas:

$$\varphi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

Jens Lindhard
1922-1997

Lindhard function:

$$\chi_s(q,\omega) = 2\int \frac{d^3k}{(2\pi)^3} \left[\frac{\theta(k_F - k)}{\omega - \mathbf{k}\cdot\mathbf{q} - q^2/2 + i\eta} - \frac{\theta(k_F - k)}{\omega + \mathbf{k}\cdot\mathbf{q} + q^2/2 + i\eta} \right]$$

Giuliani and Vignale, *Quantum Theory of the Electron Liquid* (2005)

The homogeneous electron gas

Full interacting response function:

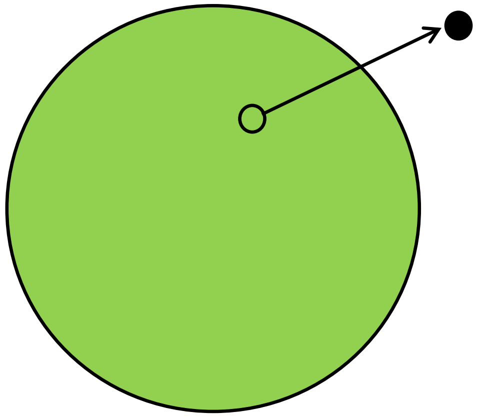
$$\chi(q,\omega) = \frac{\boxed{\chi_s(q,\omega)}}{1-[v_q + f_{xc}(q,\omega)]\chi_s(q,\omega)}$$

Poles of the full response function:

Poles of the Lindhard function give the particle-hole continuum

note: $v_q = \frac{4\pi}{q^2}$ Fourier transform of the 3D Coulomb potential

Particle-hole continuum



In the ground state, all single-particle states inside the **Fermi sphere** are filled. A **particle-hole excitation** connects an occupied single-particle state inside the Fermi sphere with an empty state outside.

$$\chi_s(q,\omega) = 2\int \frac{d^3k}{(2\pi)^3}\left[\frac{\theta(k_F - k)}{\omega - \mathbf{k}\cdot\mathbf{q} - q^2/2 + i\eta} - \frac{\theta(k_F - k)}{\omega + \mathbf{k}\cdot\mathbf{q} + q^2/2 + i\eta}\right]$$

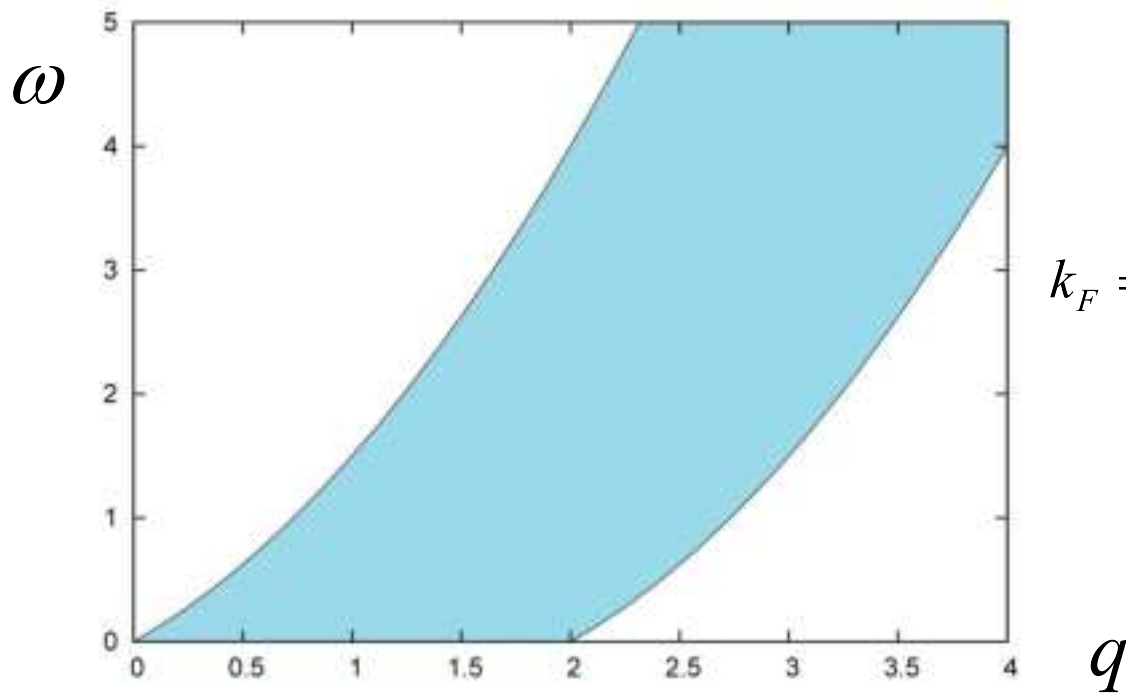
Denominator vanishes for frequency range

$$\frac{q^2}{2} - qk_F \le \omega \le \frac{q^2}{2} + qk_F$$

Particle-hole continuum

Denominator vanishes for frequency range

$$\frac{q^2}{2} - qk_F \ \le \ \omega \ \le \ \frac{q^2}{2} + qk_F$$



$k_F = 1$

Full interacting response function:

$$\chi(q,\omega) = \frac{\chi_s(q,\omega)}{\boxed{1-[v_q + f_{xc}(q,\omega)]\chi_s(q,\omega)}}$$

Poles of the full response function:

Vanishing denominator gives the plasmons

$$\Rightarrow \quad [v_q + f_{xc}(q,\omega)]\chi_s(q,\omega) = 1$$

Finding the plasmon dispersion

$$[v_q + f_{xc}(q,\omega)]\chi_s(q,\omega) = 1$$

► **numerically solution**: for a given q, find that ω which solves this equation.

► **analytic solution:** expand to second order in q

Random Phase Approximation (RPA):

$$\underbrace{v_q \chi_s(q,\omega) - 1}_{\text{RPA dielectric function}} = 0$$

Analytic plasmon dispersion

$$\chi_s(q,\omega) = 2\int \frac{d^3k}{(2\pi)^3}\left[\frac{\theta(k_F-k)}{\omega-\mathbf{k}\cdot\mathbf{q}-q^2/2+i\cancel{\eta}} - \frac{\theta(k_F-k)}{\omega+\mathbf{k}\cdot\mathbf{q}+q^2/2+i\cancel{\eta}}\right]$$

$$\chi_s(q,\omega) = \frac{1}{2\pi^2}\int_0^{k_F} k^2 dk \int_0^{\pi} \sin\theta d\theta \left[\frac{1}{\omega-\mathbf{k}\cdot\mathbf{q}-q^2/2} - \frac{1}{\omega+\mathbf{k}\cdot\mathbf{q}+q^2/2}\right]$$

$$= \frac{1}{\pi^2\omega^2}\int_0^{k_F} k^2 dk \int_0^{\pi} \sin\theta d\theta [kq\cos\theta + q^2/2] \quad + \quad O(q^4)$$

One finds

$$\chi_s(q,\omega) = \frac{k_F^3}{3\pi^2}\frac{q^2}{\omega^2}\left[1+\frac{3k_F^2 q^2}{5\omega^2}+\ldots\right]$$

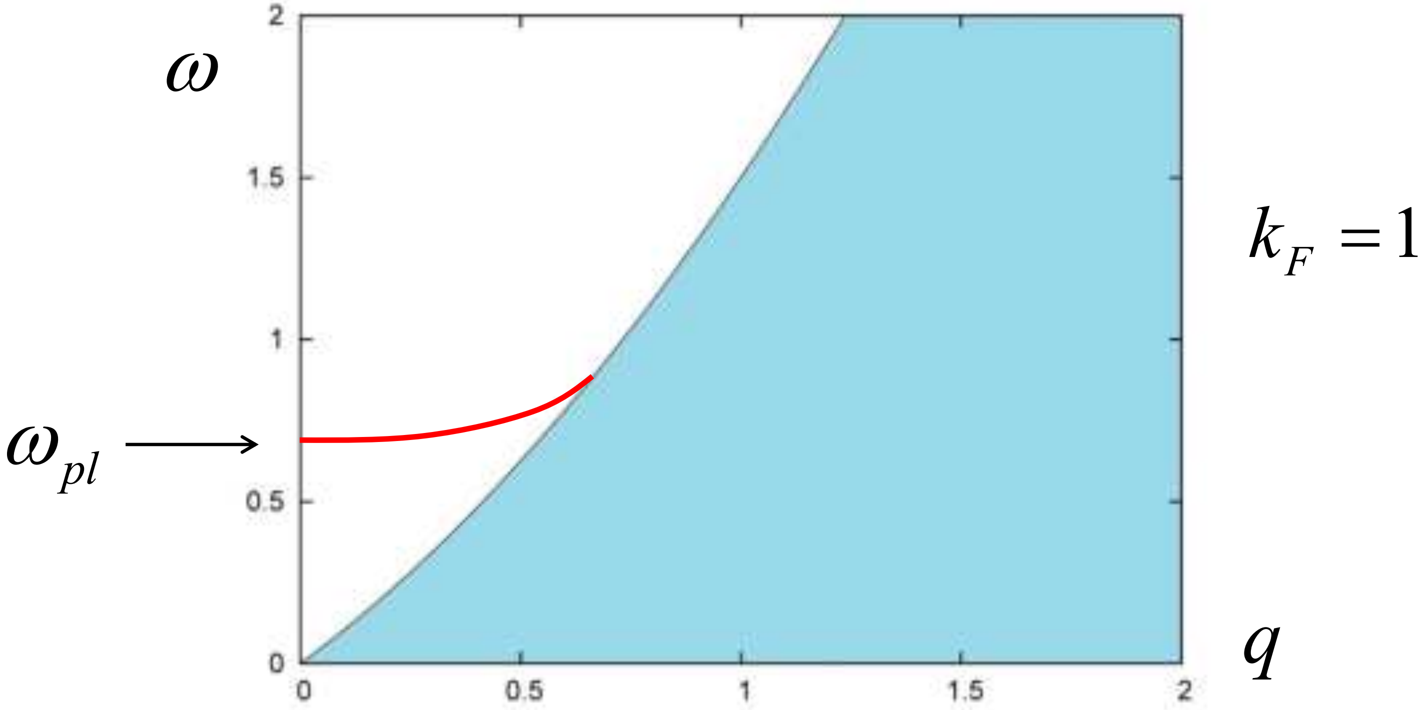
Analytic plasmon dispersion

$$\left.\begin{array}{l}\left[\dfrac{4\pi}{q^2}+f_{xc}(q,\omega)\right]\chi_s(q,\omega)=1\\[2ex] \chi_s(q,\omega)=\dfrac{k_F^3}{3\pi^2}\dfrac{q^2}{\omega^2}\left[1+\dfrac{3k_F^2q^2}{5\omega^2}+\ldots\right]\end{array}\right\}$$

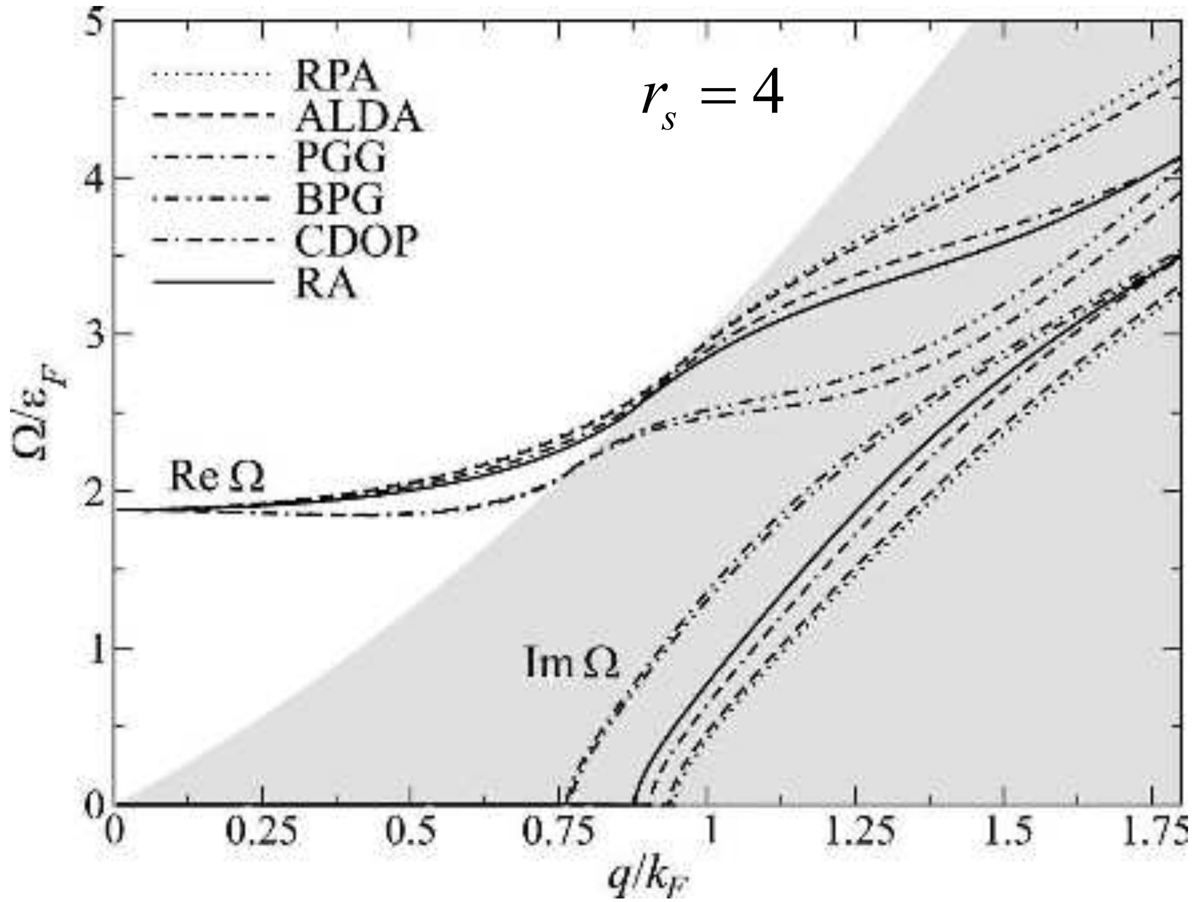
To order q^2, one finds

$$\boxed{\omega(q)=\omega_{pl}\left[1+\left(\frac{3k_F^2}{10\omega_{pl}^2}+\frac{1}{8\pi}f_{xc}(0,\omega_{pl})\right)q^2\right]}$$

Plasmon dispersion

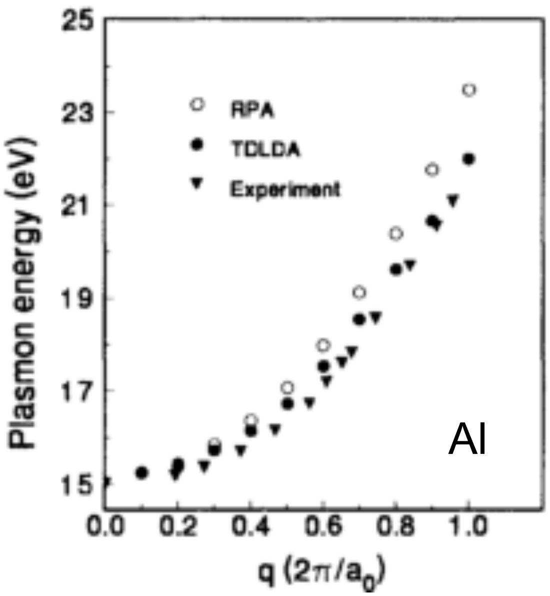


Plasmon dispersion

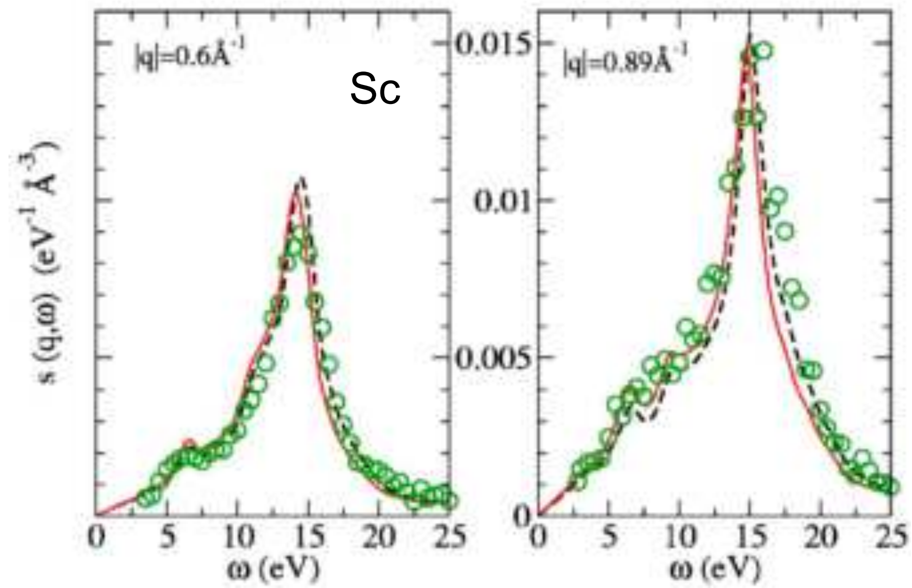


K. Tatarczyk, A. Schindlmayr, and M. Scheffler, PRB **63**, 235106 (2001)

Plasmon excitations in bulk metals



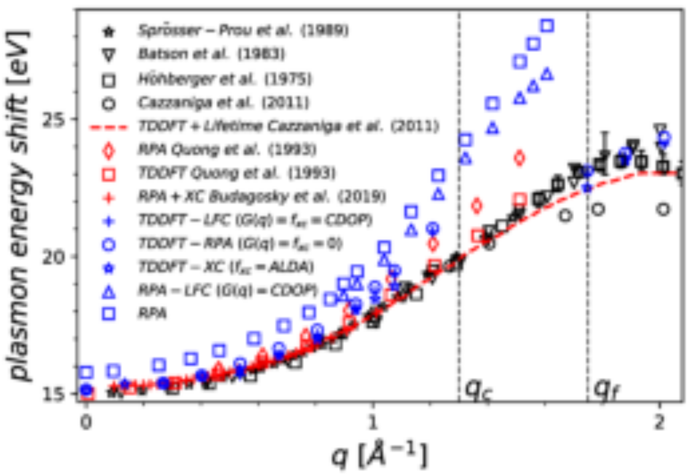
Quong and Eguiluz,
PRL **70**, 3955 (1993)



Gurtubay et al., PRB **72**, 125114 (2005)

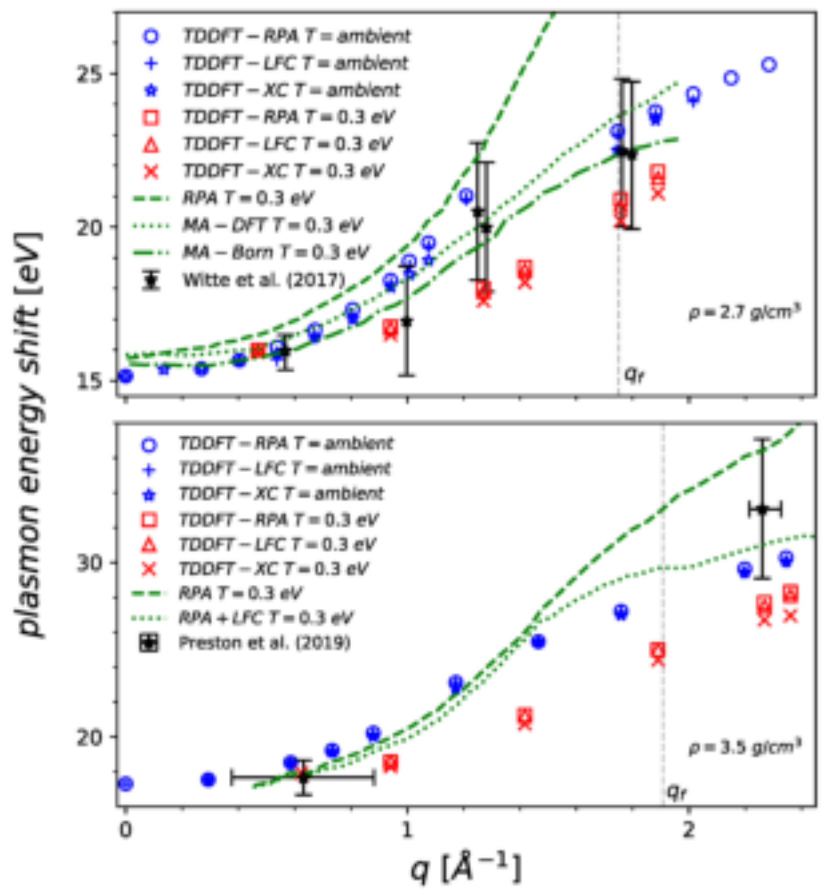
- In general, plasmons in (simple) metals are very well described by ALDA.
- Time-dependent Hartree (=RPA) already gives the dominant contribution
- f_{xc} typically gives some (minor) corrections (and damping!)
- This is also the case for 2DEGs in doped semiconductor heterostructures

Plasmon excitations in bulk metals



Plasmon dispersions of sodium at ambient and high pressure

K. Ramakrishna, A. Cangi, T. Dornheim, A. Baczewski, J. Vorberger, PRB **103**, 125118 (2021)



Plasmons in different dimensions

Bulk plasmon:

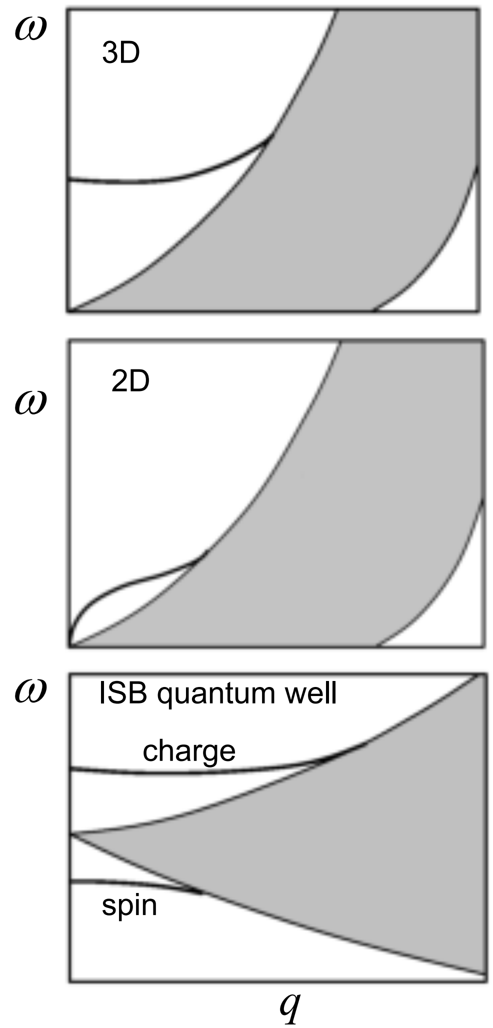
$$\omega(q) = \omega_p + \alpha q^2 + \dots$$

2D plasmon:

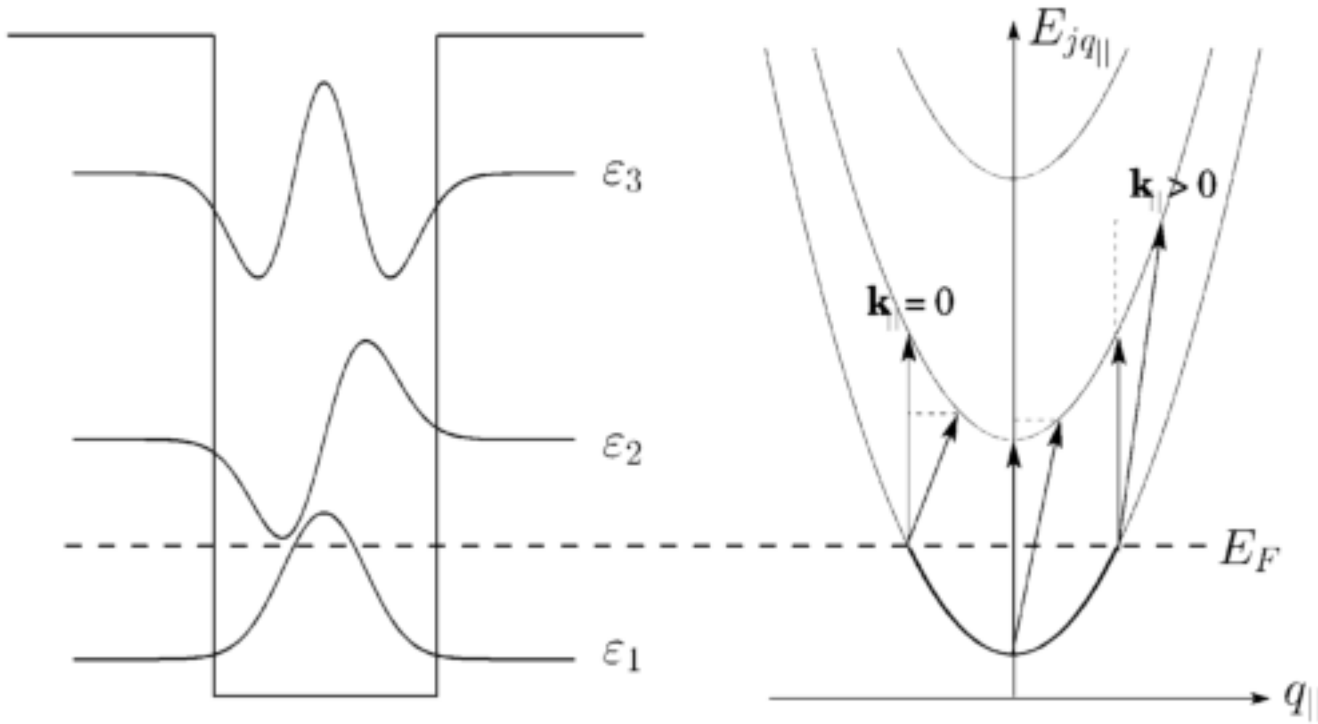
$$\omega(q) = \beta\sqrt{q} + \dots$$

Intersubband plasmons:

$$\omega(q) = (\varepsilon_2 - \varepsilon_1) \pm \Delta_{Hxc}^{c,s} + \dots$$



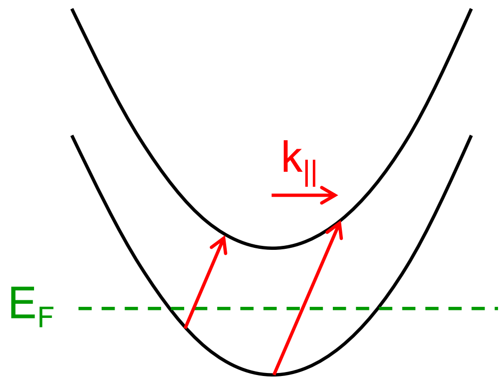
Excitations in nanostructures



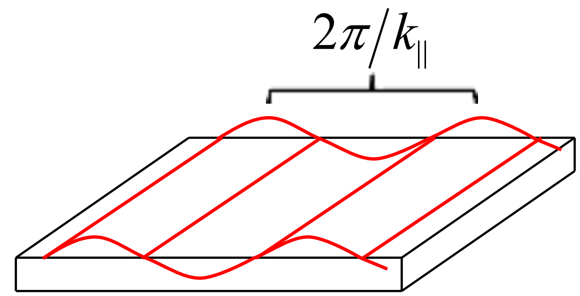
Vertical excitations: no momentum change, $k_{||} = 0$

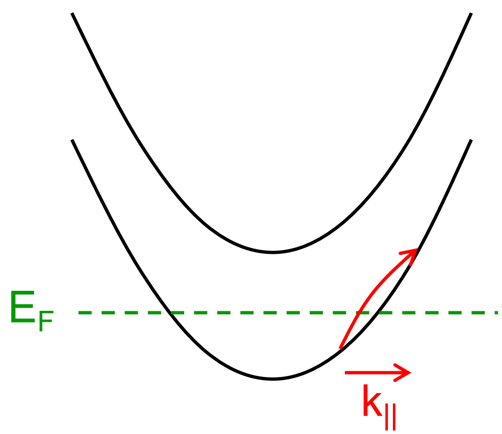
Nonvertical excitations: finite momentum transfer, $k_{||} > 0$

Inter- versus intrasubband dynamics

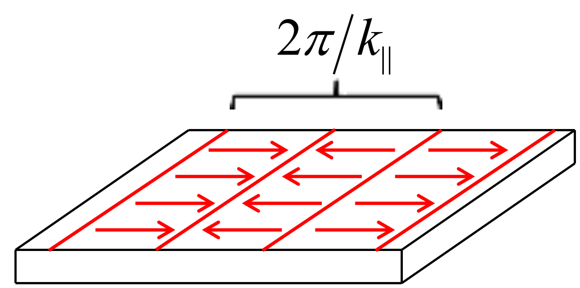


intersubband plasmon: <u>perpendicular</u> to the plane

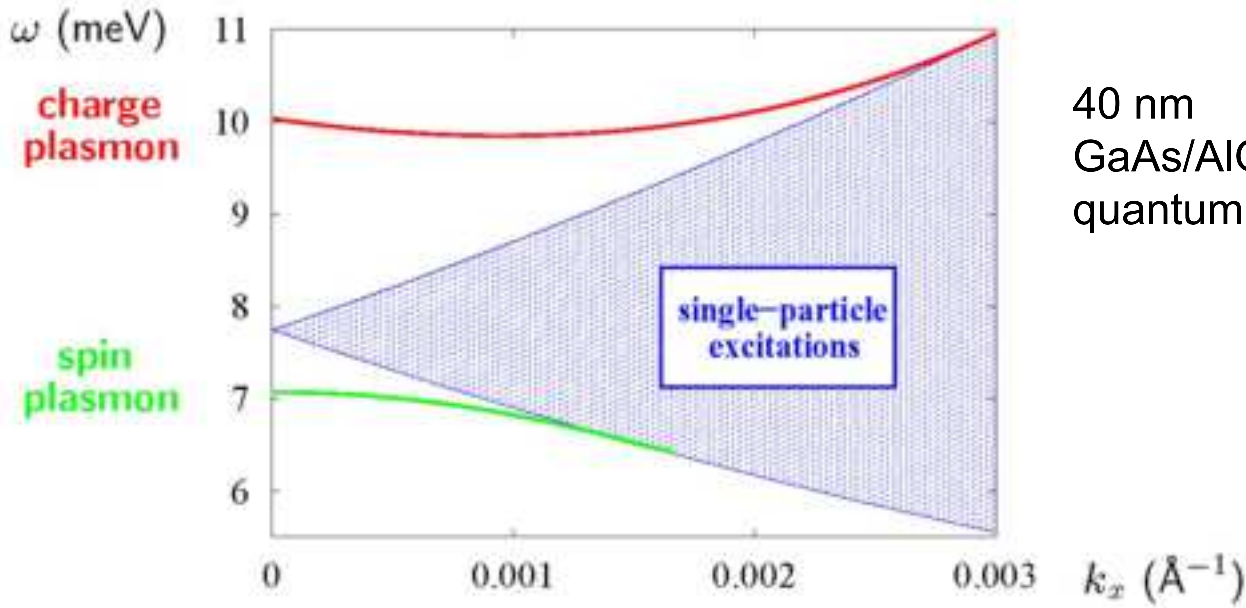




intrasubband plasmon (charge/spin-density wave): <u>within</u> the plane



Intersubband plasmon dispersions



40 nm GaAs/AlGaAs quantum well

charge

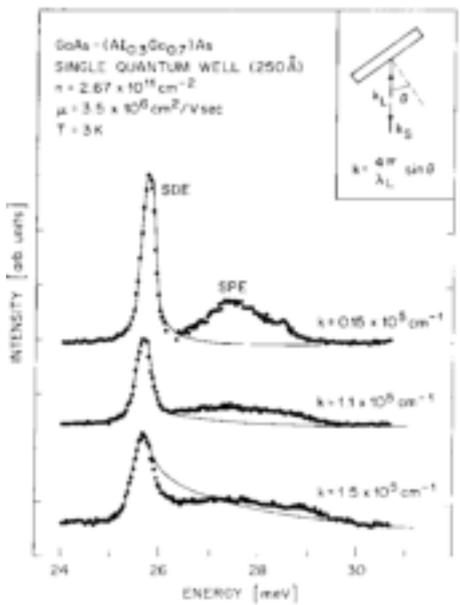
spin

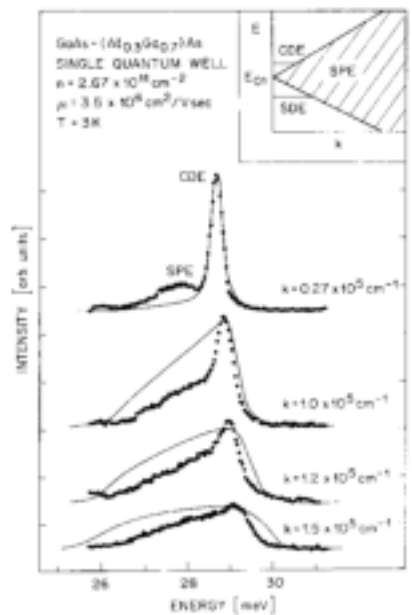
Inelastic light scattering

VOLUME 63, NUMBER 15 PHYSICAL REVIEW LETTERS 9 OCTOBER 1989

Large Exchange Interactions in the Electron Gas of GaAs Quantum Wells

A. Pinczuk, S. Schmitt-Rink, G. Danan, J. P. Valladares, L. N. Pfeiffer, and K. W. West
AT&T Bell Laboratories, Murray Hill, New Jersey 07974





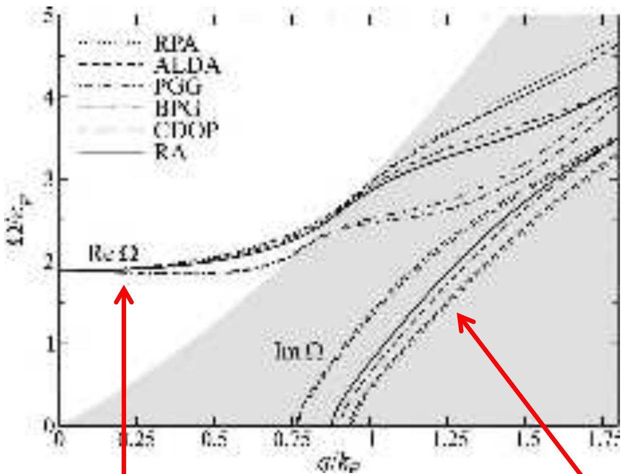
"depolarized"

spin plasmons

"polarized"

charge plasmons

Plasmon damping: adiabatic xc kernel



$$\left[\frac{4\pi}{q^2} + f_{xc}^{adia}(q)\right]\chi_s(q,\omega) = 1$$

Adiabatic xc kernel: ω is real outside the particle-hole continuum

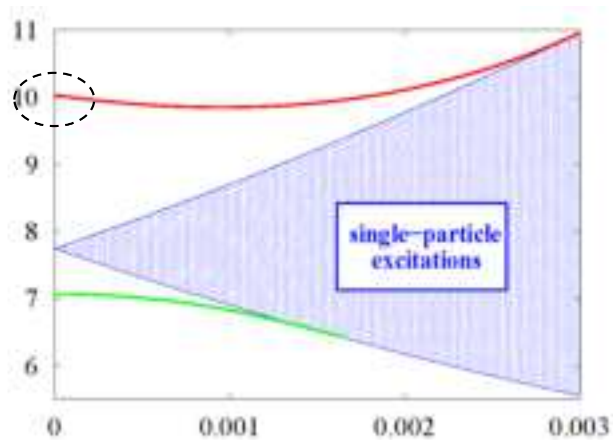
infinite plasmon lifetime

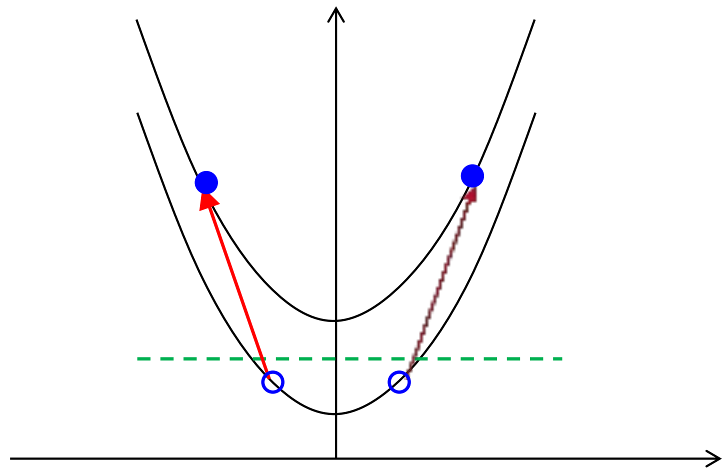
Should have finite (but large) lifetime!

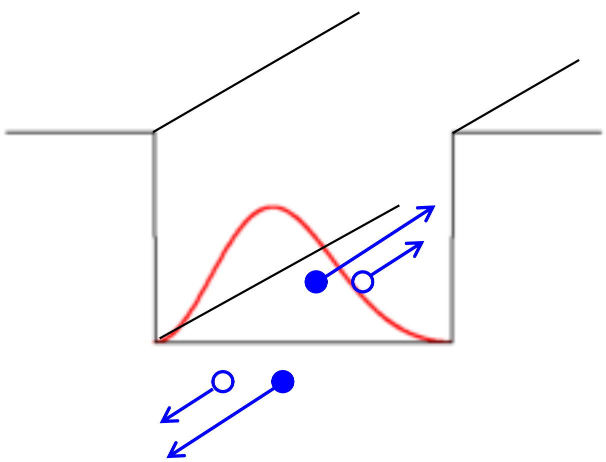
Plasmon decays into individual particle-hole excitations (Landau damping)

How does TDDFT do this? $f_{xc}(q,\omega)$

Intrinsic plasmon damping mechanism







► Plasmon has energy and momentum different from any single p-h pair
→ plasmon is robust

► But, can find two p-h pairs at right energy, and combined right total momentum
→ (weak) decay channel, requires Coulomb correlation beyond ALDA

The VK-functional of current-TDDFT

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

xc viscoelastic stress tensor:

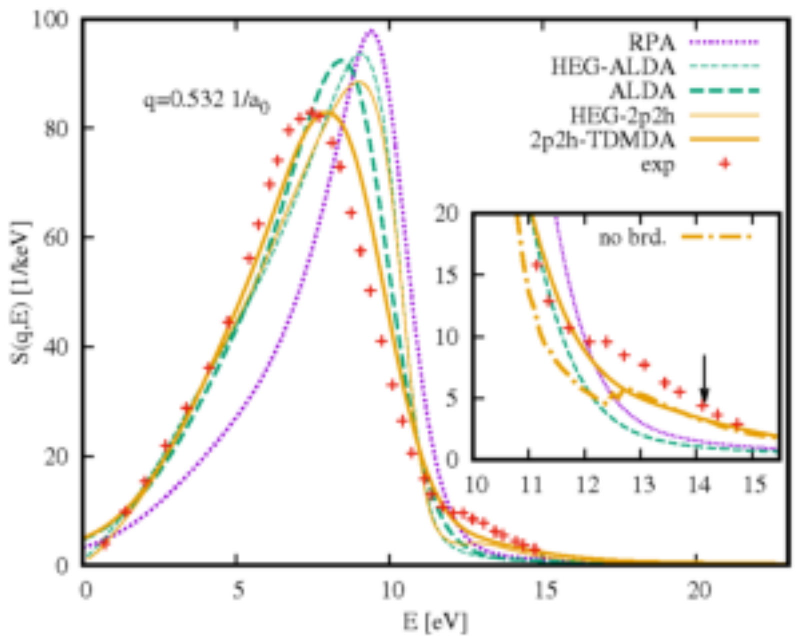
$$\sigma_{xc,\mu\nu}(\omega) = \eta_{xc}\left(\nabla_\nu u_{1,\mu} + \nabla_\mu u_{1,\nu} - \frac{2}{3}\nabla \cdot \mathbf{u}_1 \delta_{\mu\nu}\right) + \zeta_{xc} \nabla \cdot \mathbf{u}_1 \delta_{\mu\nu}$$

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

G. Vignale and W. Kohn, PRL **77**, 2037 (1996)
G. Vignale, C.A.U., and S. Conti, PRL **79**, 4878 (1997)
C.A.U. and G. Vignale, PRB **65**, 245102 (2002)

Gives correct description of plasmon damping, but tends to overdamp as soon as the plasmon is less ”hydrodynamic”. Not recommended for excitations in atoms and molecules.

Double plasmons



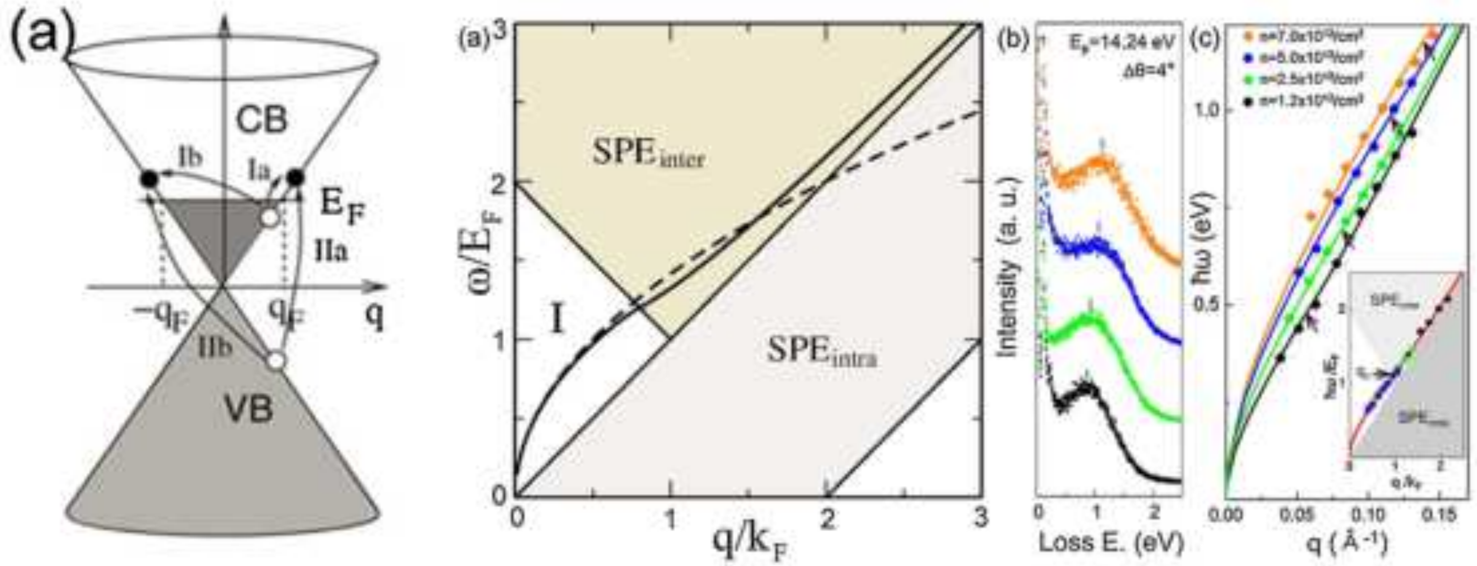
dynamic structure factor of sodium

► Another many-body effect beyond the adiabatic approximation:
Double (or multiple plasmons)

► Can be captured by $f_{xc}(q,\omega)$ that is constructed from correlated calculations

M. Panholzer, M. Gatti and L. Reining, PRL **120**, 166402 (2018)

Plasmons in doped graphene

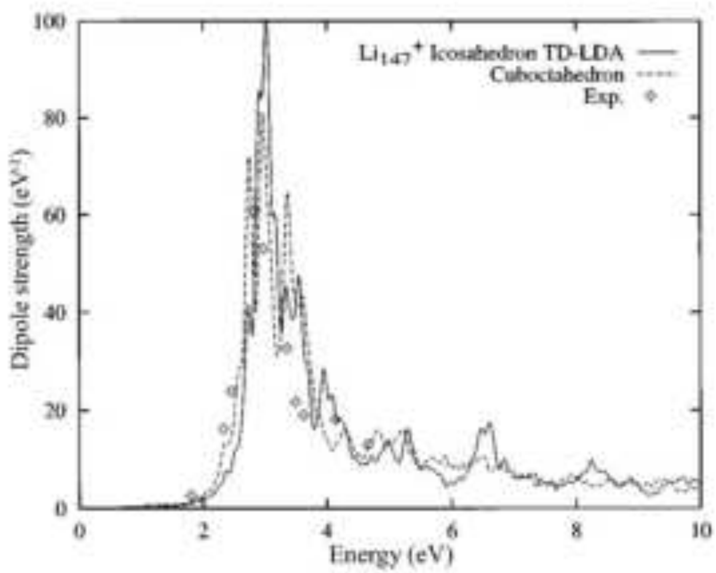


Luo et al.. Mat. Sci. Eng. **R74**, 351 (2013); Shin et al., Appl. Phys. Lett. 99, 082110 (2011)

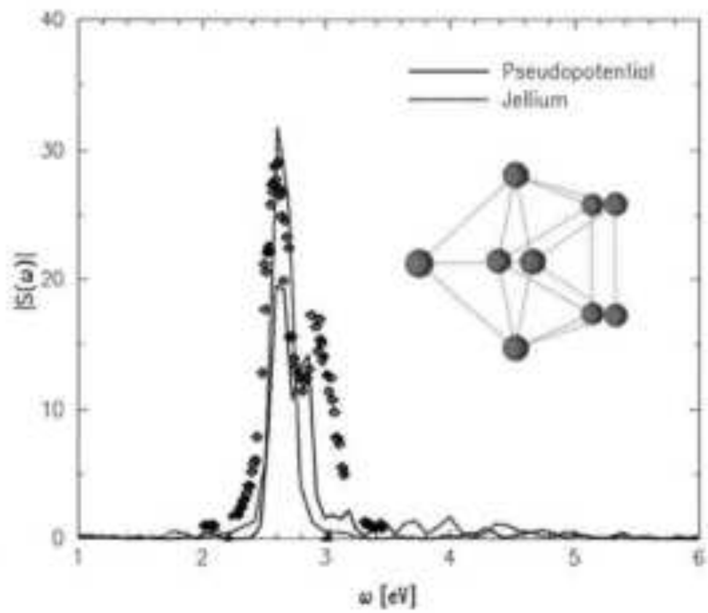
- Low loss, good tunability, good material properties
- Topological materials (transition metal dichalcogenides, MoS_2): strong spin-orbit coupling, valley effects
- TDDFT: standard xc functionals not applicable (Dirac Fermions)

  Polini, Tomadin, Asgari & MacDonald, PRB **78**, 115426 (2008)
  Grigorenko, Polini & Novoselov, Nature Photonics **6**, 749 (2012)
  T. Stauber, J. Phys: Condens. Mat. **26**, 123201 (2014)
  M. Anderson, F. Perez and C.A. Ullrich, PRB **104**, 245422 (2021)

Plasmon excitations in metal clusters



Yabana and Bertsch, PRB **54**, 4484 (1996)

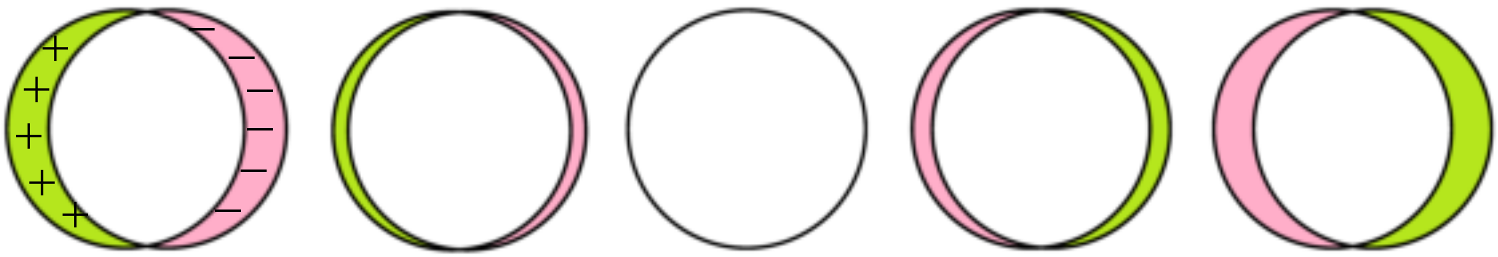


Calvayrac et al., Phys. Rep. **337**, 493 (2000)

Surface plasmons ("Mie plasmon") in metal clusters are very well reproduced within ALDA.

Plasmonics: mainly using classical electrodynamics, not quantum response, but TDDFT becoming more and more widely used

Mie plasmons

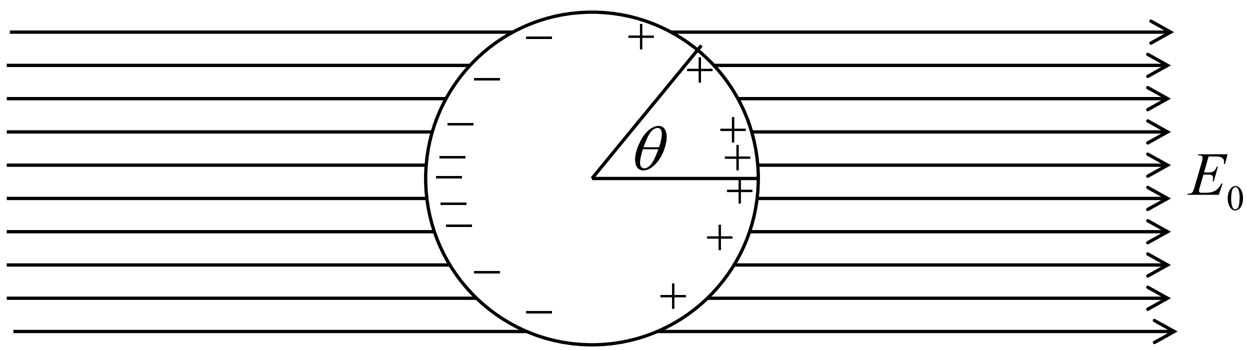


Oscillation of a uniformly charged sphere against neutralizing background.

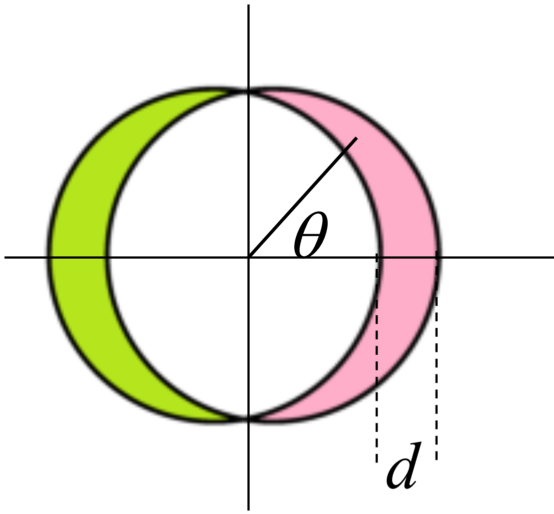
A standard result from electrostatics:
conducting sphere in a uniform electric field:

Surface charge density:

$$\sigma = \frac{3}{4\pi} E_0 \cos\theta$$



Mie plasmons



Displacing two charged spheres, we find

$$\sigma = en\,d\cos\theta$$

This surface charge is identical to what one gets in an electric field, so

$$\sigma = \frac{3}{4\pi}E_0\cos\theta = en\,d\cos\theta$$

Total force on all electrons: $$F = enVE_0 = -\frac{4\pi}{3}n^2e^2Vd$$

Set force equal to total mass times acceleration: $$F = mnV\ddot{d}$$

$$\Rightarrow \ddot{d} = -\frac{4\pi ne^2}{3m}d \Rightarrow \boxed{\omega_{sphere}^2 = \frac{4\pi ne^2}{3m} = \frac{\omega_p^2}{3}}$$

Mie scattering

Rayleigh scattering: $\lambda >> d$

Rayleigh scattering intensity: $I \sim I_0 \dfrac{1+\cos^2\theta}{\lambda^4}$

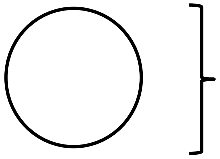
(explains why sky is blue)

Gustav Mie
1869-1957

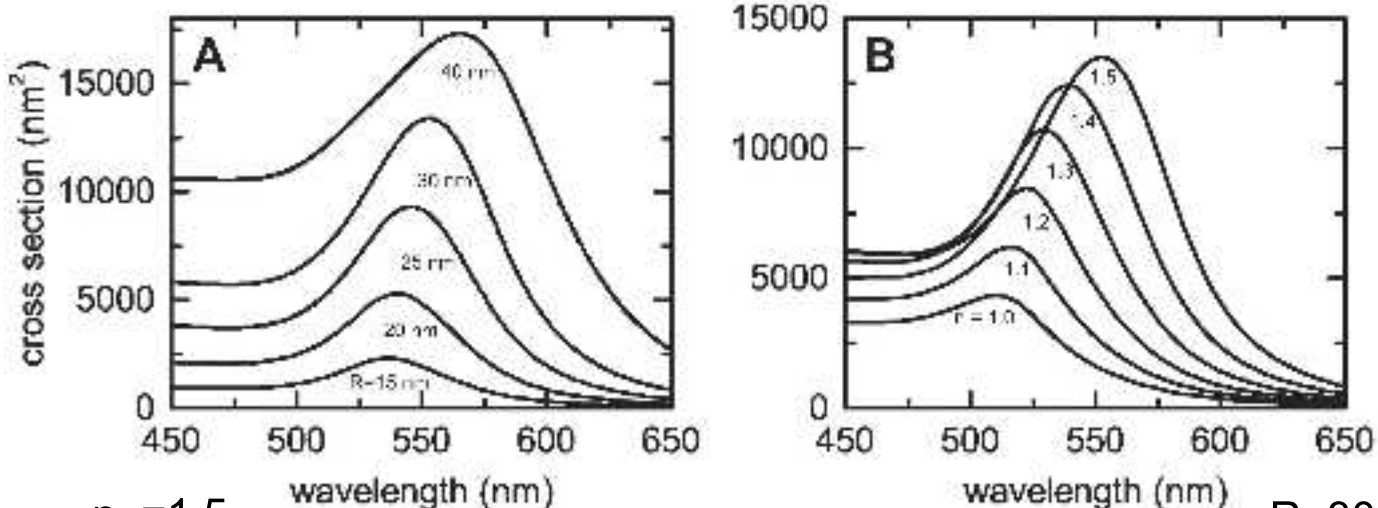
Rayleigh-Gans-Debye scattering: $\lambda << d$

Mie scattering: $\lambda \approx d$

Metal nanoparticles:



diameter d: 1 – 100 nm



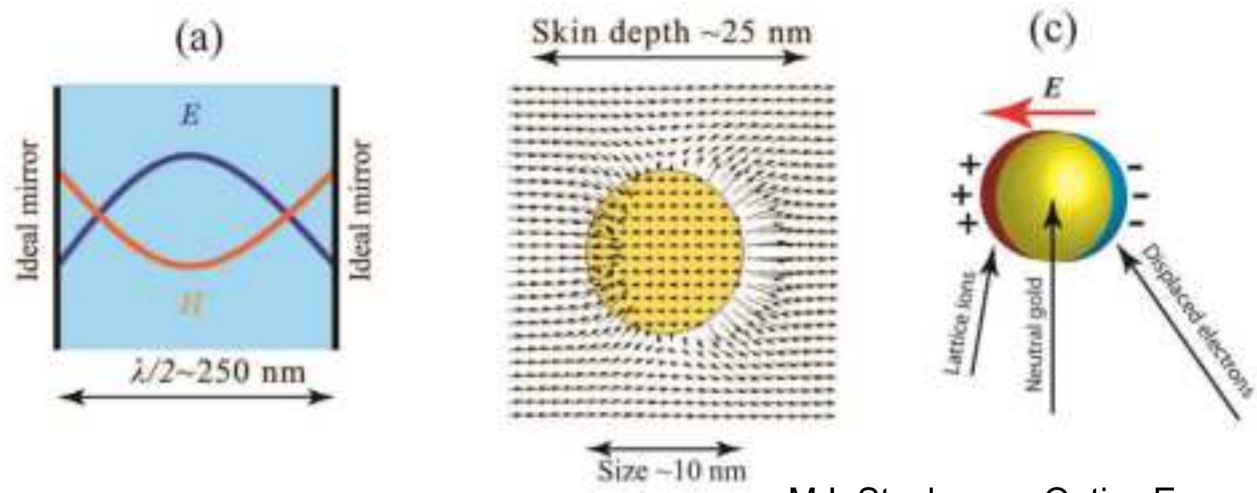
n_m=1.5

R=30 nm

Absorption changes with particle size and refractive index of the medium.

M.A. van Dijk, PhD thesis (2007)

Localization of optical fields: nanoplasmonics



M.I. Stockman, Optics Express(2011)

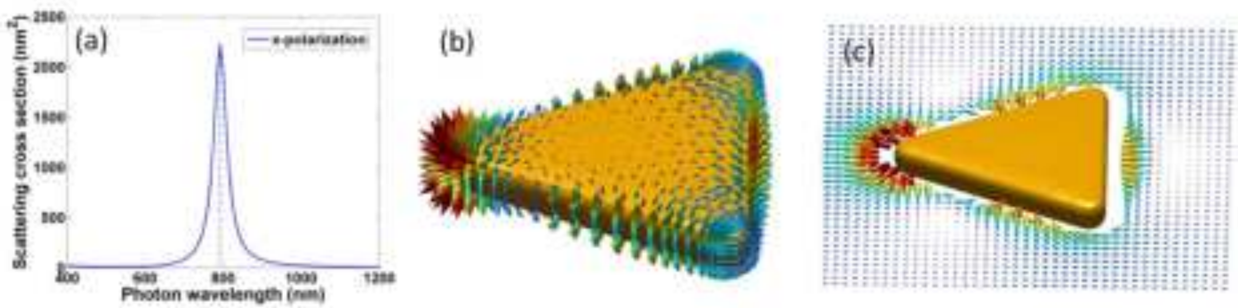


Figure 4.4.: **(a)** Scattering cross section of a gold nanotriangle ($55 \times 50 \times 8$ nm, n_b = 1.34). The panels **(b)** and **(c)** show the electric field at the resonance energy of 792 nm at the particle surface and on the outside, respectively. (Also see Fig. 3.7.)

A. Trügler, PhD thesis (2011)

Hot spots

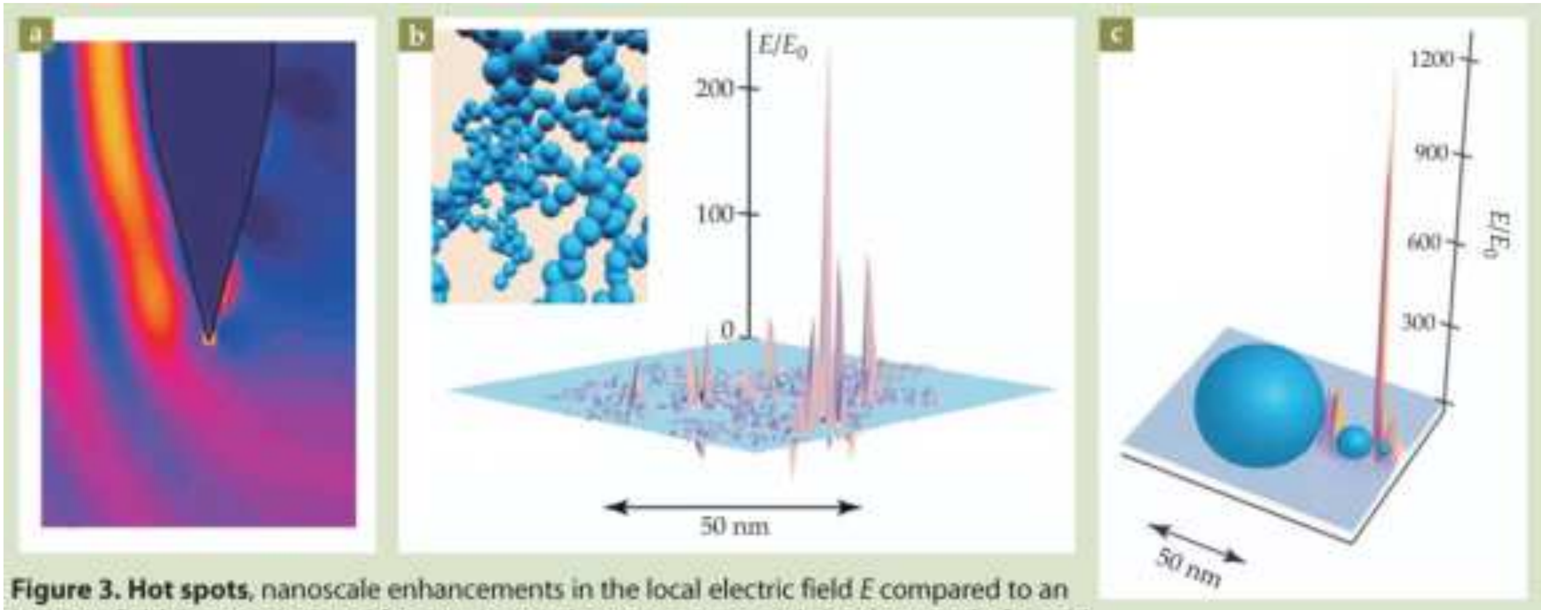


Figure 3. Hot spots, nanoscale enhancements in the local electric field E compared to an incident field E_0, are calculated for certain metal nanostructures: **(a)** the sharp end of a gold tip excited by a vertically polarized laser field (adapted from ref. 4); **(b)** a fractal cluster of silver nanoparticles (inset) whose resonance enhancement and specific morphologies can magnify, at the hottest spot, the local fields by a factor of nearly 300 (adapted from ref. 3); and **(c)** a self-similar nanolens whose geometrical arrangement of spheres concentrates optical energy, from bigger spheres to smaller ones, in the tight gaps between them.[5] In the hottest spot, the field is enhanced by a factor of 1200.

M.I. Stockman, Physics Today (2011)

Hot spots arise from the multiplication of the SP enhancement factors, constructive interference of SP fields from different particles, and additional enhancement due to sharp tips and small gaps.

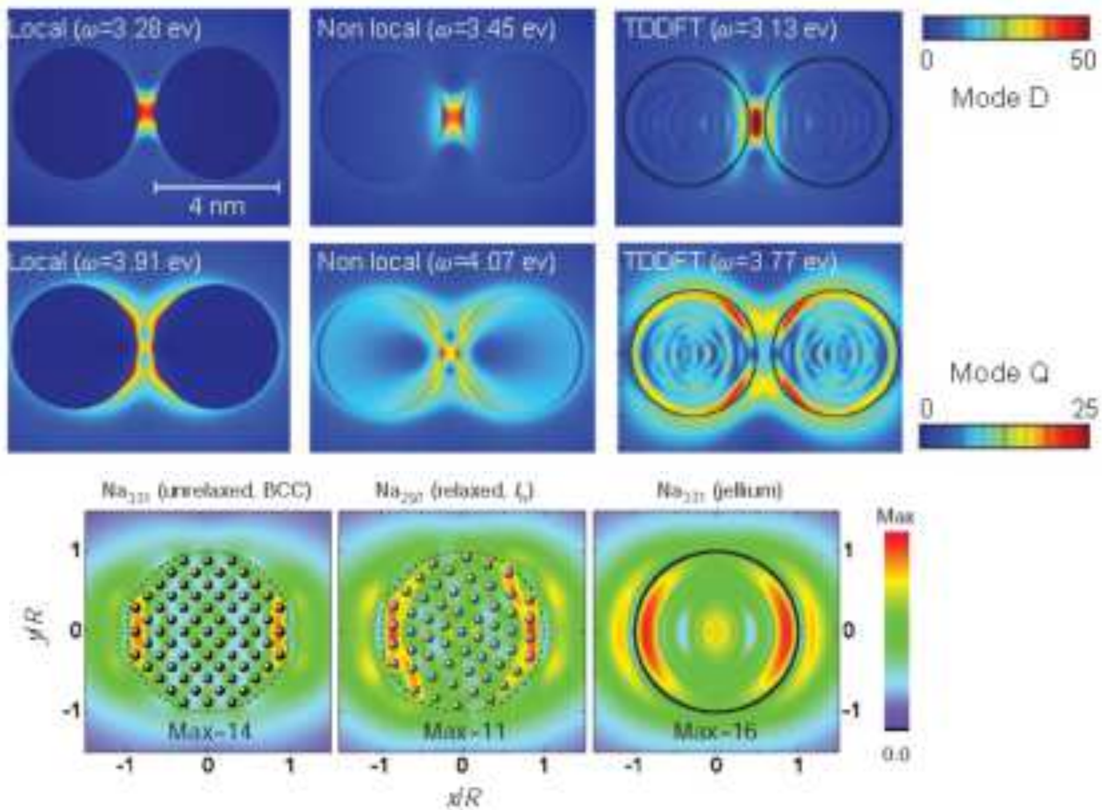
Nanoplasmonics with TDDFT: local E-fields

Plasmonics: mainly using classical electrodynamics, not quantum response

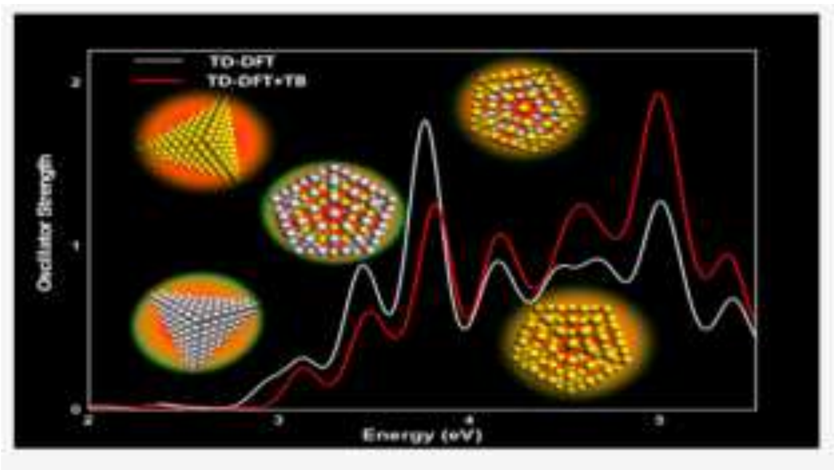
E.B. Guidez and C.M. Aikens, Nanoscale **6**, 11512 (2014)

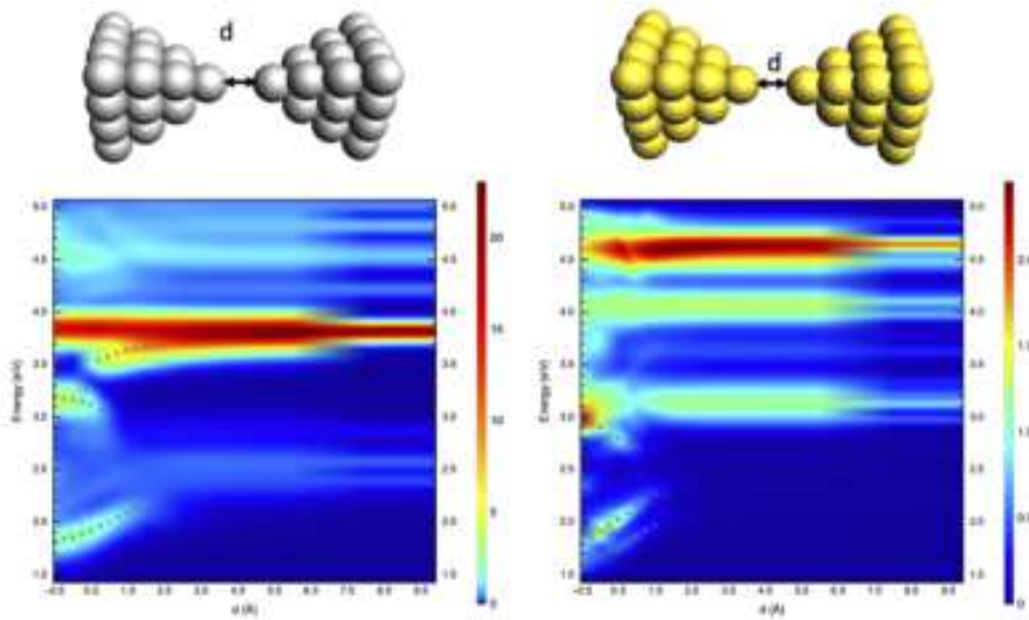
Quantum Plasmonics: from jellium to ab initio TDDFT calculations

A. Varas, P. Garcia-Gonzalez, J. Feist, F.J. Garcia-Vidal & A. Rubio, Nanophotonics **5**, 409 (2016)



Nanoplasmonics with TDDFT





Asadi-Aghbolaghi, Ruger, Jamshidi & Visscher,
J Phys. Chem. C **124**, 7946 (2020)
Jamshidi, Asadi-Aghbolaghi, Morad, Mahmoudi,
Sen, Maaza, and Visscher, JCP **156**, 074102 (2022)

TDDFT + TB approach

Summary

► **TDDFT is very good for collective plasmon excitations in metallic systems (mostly small corrections to RPA)**

► **There is a lot of activity applying TDDFT to nanoplasmonics (beyond linear response!)**

► **Challenges for TDDFT:**
- **plasmon damping, multiple plasmons (nonadiabatic xc effects)**
- **collective spin modes (no RPA, purely xc, hence very sensitive to choice of functional)**
- **Plasmons in graphene and topological 2D materials**
- **Coupling of plasmons to other excitations (polaritons, plexcitons...)**

N. H. March and M. P. Tosi, Advances in Physics **44**, 299 (1995)
S. M. Morton, D. W. Silverstein & L. Jensen, Chem. Rev. **111**, 3962 (2011)
E. B. Guidez and C. M. Aikens, Nanoscale **6**, 11512 (2014)
A. Varas, P. Garcia-Gonzalez, J. Feist, F.J. Garcia-Vidal & A. Rubio, Nanophotonics **5**, 409 (2016)
I. D'Amico, F. Perez & C.A. Ullrich, J. Phys. D: Appl. Phys. **52**, 203001 (2019)

Suggested exercises

1. Derive the small-q plasmon dispersions of an electron gas in 3D, 2D, and 1D

2. Obtain plasmons starting from the Casida equation in TDDFT. In other words, show that, for an electron gas,

$$\begin{pmatrix} \mathbf{A} & \mathbf{K} \\ \mathbf{K}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \Omega \begin{pmatrix} -\mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \Rightarrow \left[\frac{4\pi}{q^2} + f_{xc}^{adia}(q) \right] \chi_s(q,\omega) = 1$$

3. Convince yourself that the Tamm-Dancoff approximation fails completely for plasmons.

4. Write a simple Python code to calculate the full plasmon dispersions in RPA.