Plasmon resonances in reduced dimensions
--Insight from computational studies

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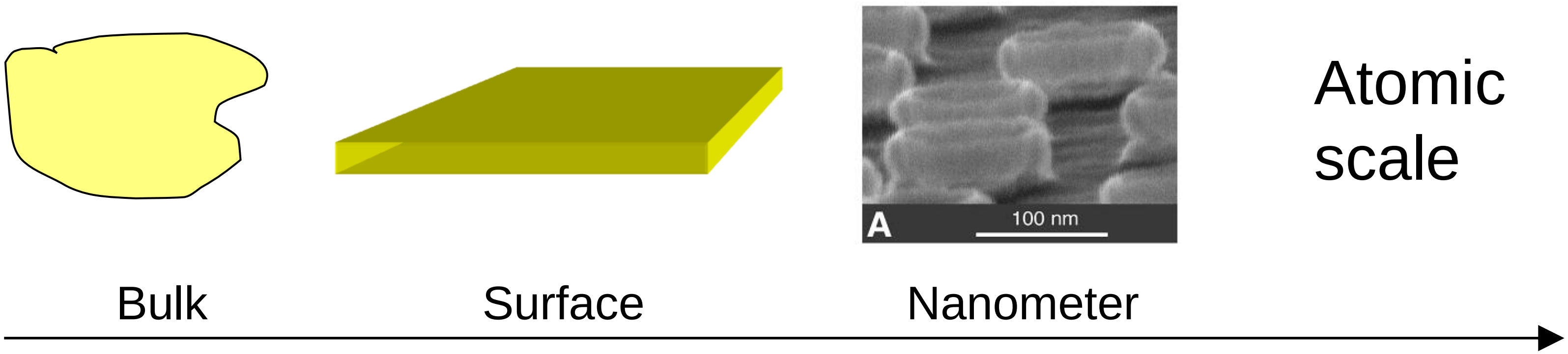
PhotoNano, Metamaterials: M. Käll, B. Kasemo, I. Zoric
US: W. Ho, P. Nordlander
PhotoNano(SSF), STINT

Surface plasmons in reduced dimensions



Fundamental issues

- Quantum characteristics of SP in low-D structures?
- Relationship between SP and electronic structures?
- How do the SPs couple to electrons/photons?
- What are the dynamics of such interactions?

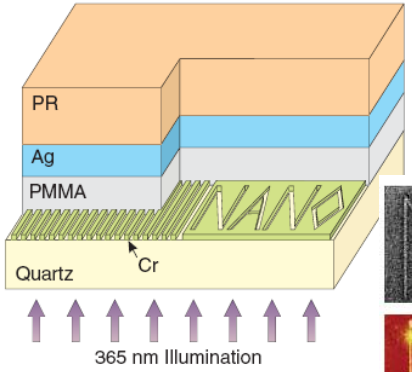
Nanophotonics/Nanoplasmonics: An Emerging Field

- Optical imaging

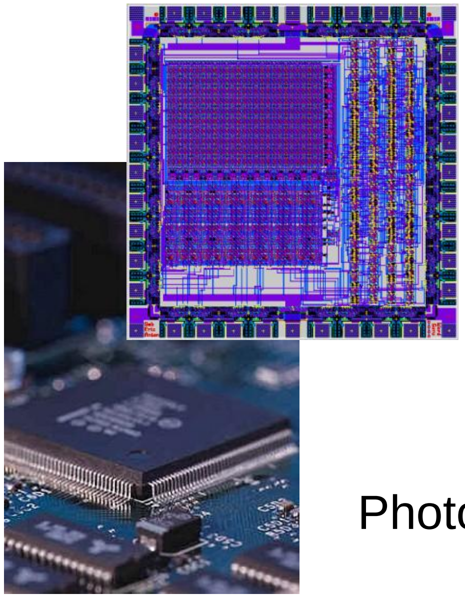
  Recovery of evanescent waves

- Photonic circuit

  Photon — SPs — Photon



Superlens



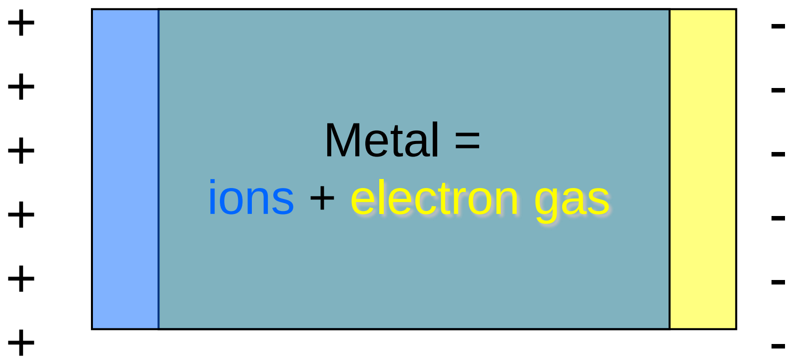
Photonic Circuit

- Surface Enhanced Raman Spectroscopy
- Chemical and biological sensing
- Surface reactions…

Superlens: X. Zhang et.al, Science 308, 534 (2005)

Bulk Plasmon

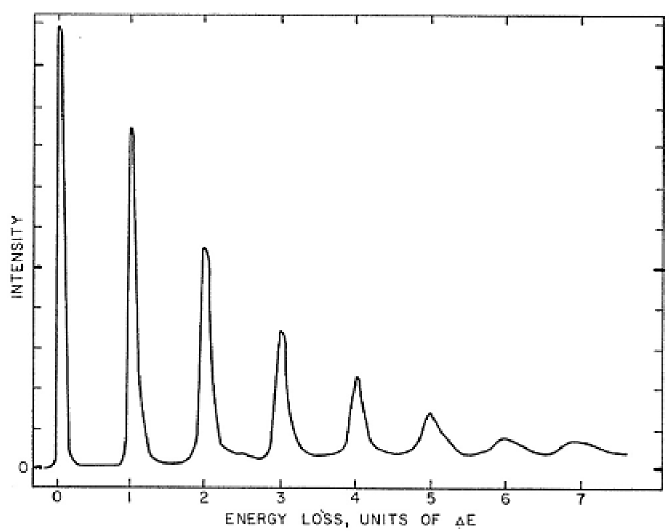
Plasmon is a quanta of collective oscillation of conducting electrons



Bulk plasmon energy depends only on electron density n

$$\omega_P = \sqrt{\frac{4\pi n e^2}{m_e}}$$

Electron Energy Loss Spectrum



Typical Plasmon Energies

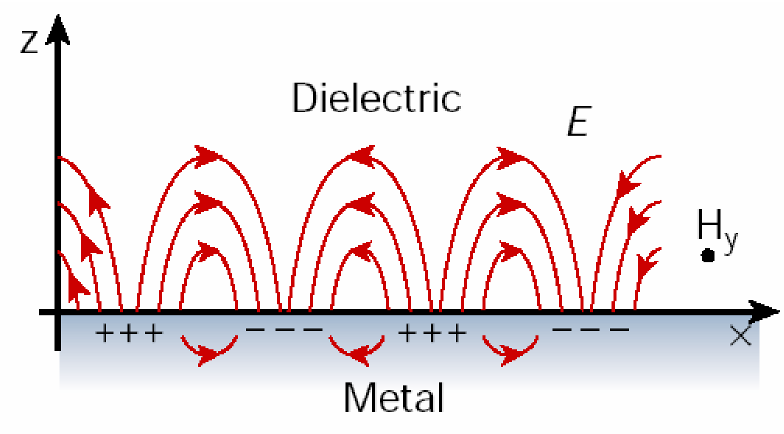
	ω_P (eV)
Na	5.9
Mg	10.6
Al	15.3
Ag	3.8
Au	3.8

$$\frac{\omega_P}{\sqrt{\mathrm{Re}\,\varepsilon_d}}$$

EELS spectrum: L. Marton, J. A. Simpson, H. A. Fowler, and N. Swanson, Phys. Rev. 126, 182 (1962)

Surface Plasmons

Wave nature: Charge density waves at surface

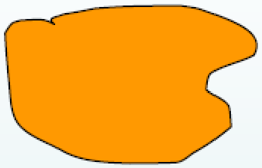


$$\omega_{Surf} = \frac{\omega_P}{\sqrt{2}}$$

W.L.Barnes, A.Dereux, and T.W.Ebbesen, Nature 424, 824 (2003).

The plasmon energies of a nanoparticle depend on its shape!

Bulk:

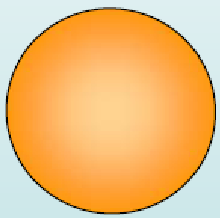


$$\omega_B = \sqrt{\frac{4\pi e^2 n}{m_e}}$$

Surface:

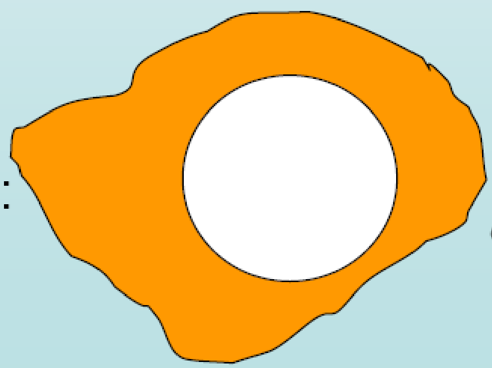
$$\omega_{surf} = \frac{\omega_B}{\sqrt{2}}$$

Sphere:



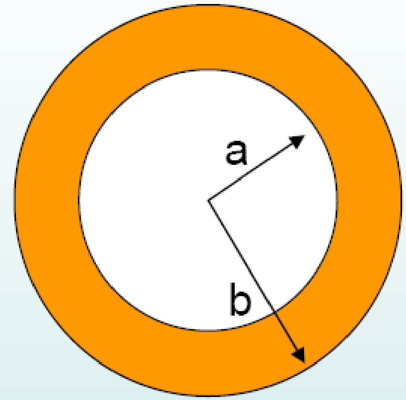
$$\omega_{S,l} = \omega_B \sqrt{\frac{l}{2l+1}}$$

Cavity:



$$\omega_{C,l} = \omega_B \sqrt{\frac{l+1}{2l+1}}$$

Nanoshell:



$$x = \frac{a}{b}$$

$$\omega_{l\pm}^2 = \frac{\omega_B^2}{2}\left[1 \pm \frac{1}{2l+1}\sqrt{1+4l(l+1)x^{2l+1}}\right]$$

The plasmon energies of a nanoshell depends on the aspect ratio x

Plasmon energies of a nanoshell can be tuned!!!

Geometry is denoted (a,b)

Ocean waves

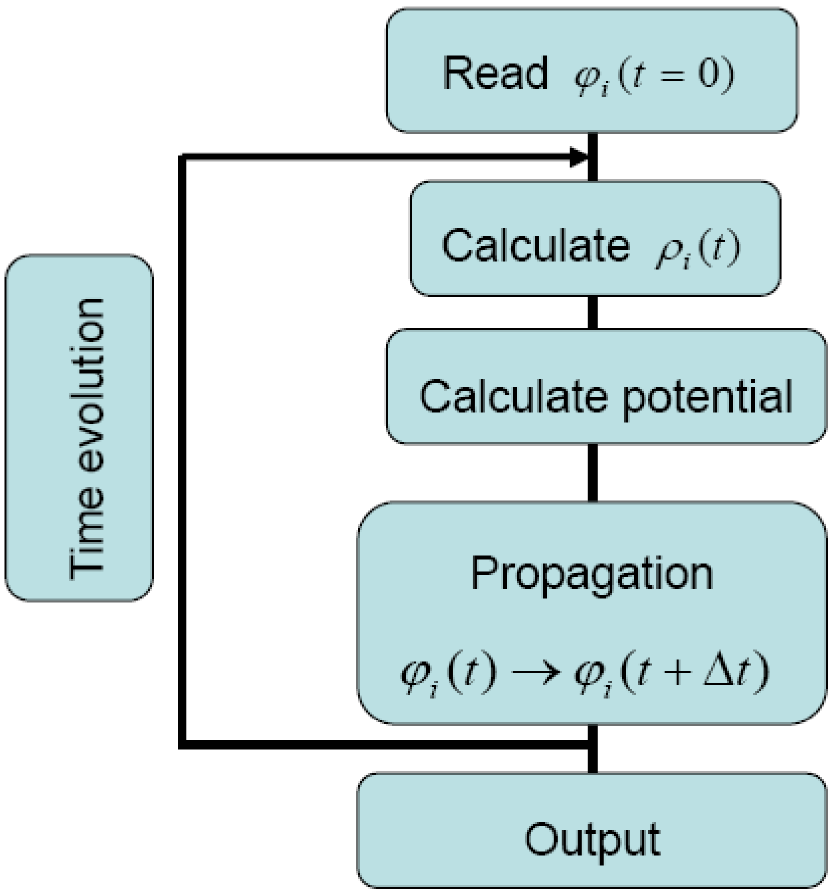
Collective plasmon behaviors of water

- Periodic oscillations
- Collective, all water molecules participate
- Intrinsic/fixed frequencies
- Deflected by islands & guided by habor or channels
- Decays on the beaches (surface damping)
- …………

TDDFT: Time-dependent Density Functional Theory

Octopus program

$$\varphi_i(t) \to \varphi_i(t+\Delta t)$$



Time evolution

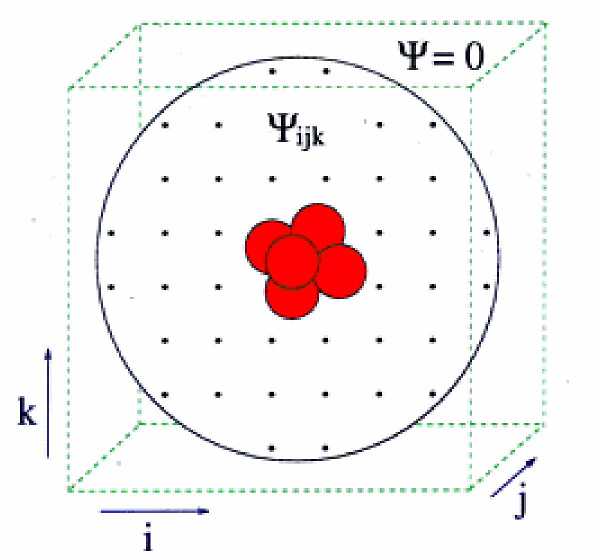
$$i\frac{\partial \varphi(t)}{\partial t} = \hat{H}(t)\varphi(t)$$

$$\varphi(t+\Delta t) = T\exp\{-i\int_t^{t+\Delta t} d\tau \hat{H}(\tau)\}\varphi(t)$$

$$\varphi(t+\Delta t) \approx \exp\{-i\hat{H}(\tau)dt\}\varphi(t)$$
$$= U(t+\Delta t, t)\varphi(t)$$

- Grid representation of W.F.
- FFT in position-momentum spaces
- many-many >100000 time steps

Real-space representation



Real-space 3D grid representation

$$[-\frac{1}{2}\nabla^2 + v_{eff}(r_i)]\varphi_j(r_i) = \varepsilon_j \varphi_j(r_i)$$

$$v_{eff}(r_i) = v_{ext}(r_i) + v_H(r_i) + v_{xc}(r_i)$$

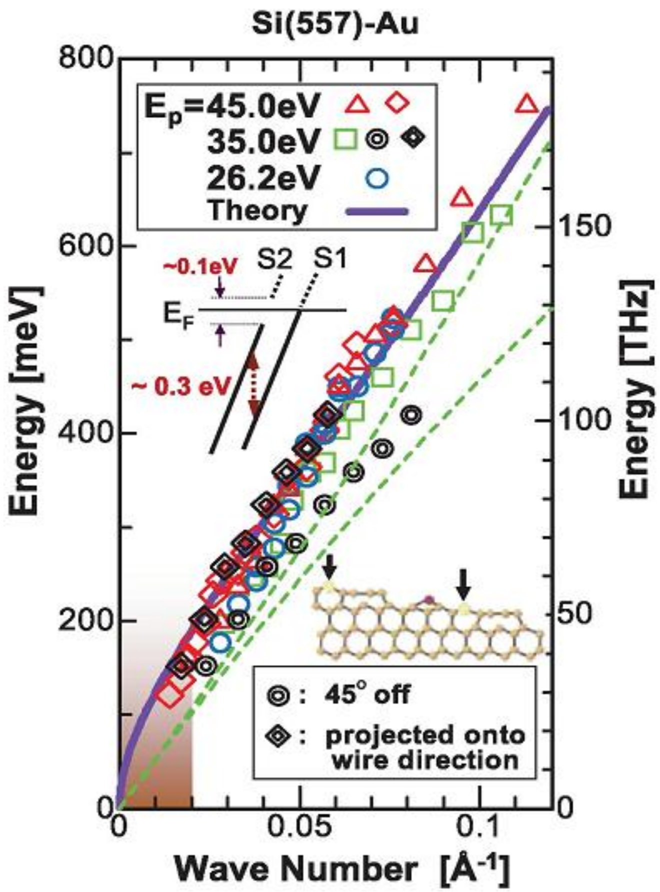
$$\nabla^2 v_H(r_i) = -4\pi\rho(r_i)$$

Poisson equation:	$\nabla^2\phi(\vec{r}) = f(\vec{r})$
Eigenvalue equation:	$\nabla^2\phi(\vec{r}) + v(\vec{r},\phi)\phi(\vec{r}) = \lambda\phi(\vec{r})$

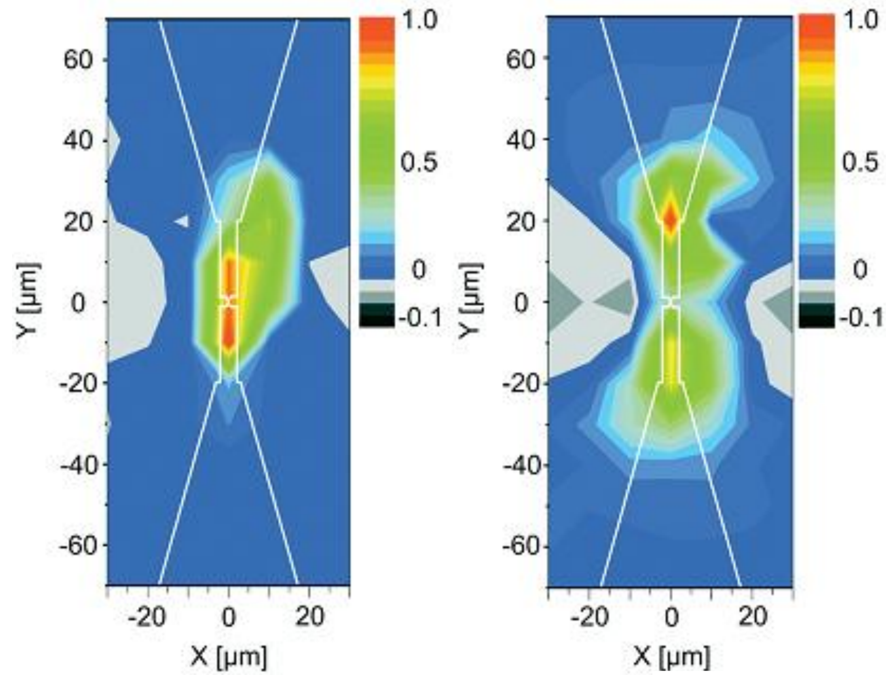
Thomas L. Beck, Rev. Mod. Phys. 72,1041 (2000), J.R. Chelikowsky powerpoint

Plasmons in linear atomic chains

Plasmon dispersion of Au chains



Light induced conductance in break junctions

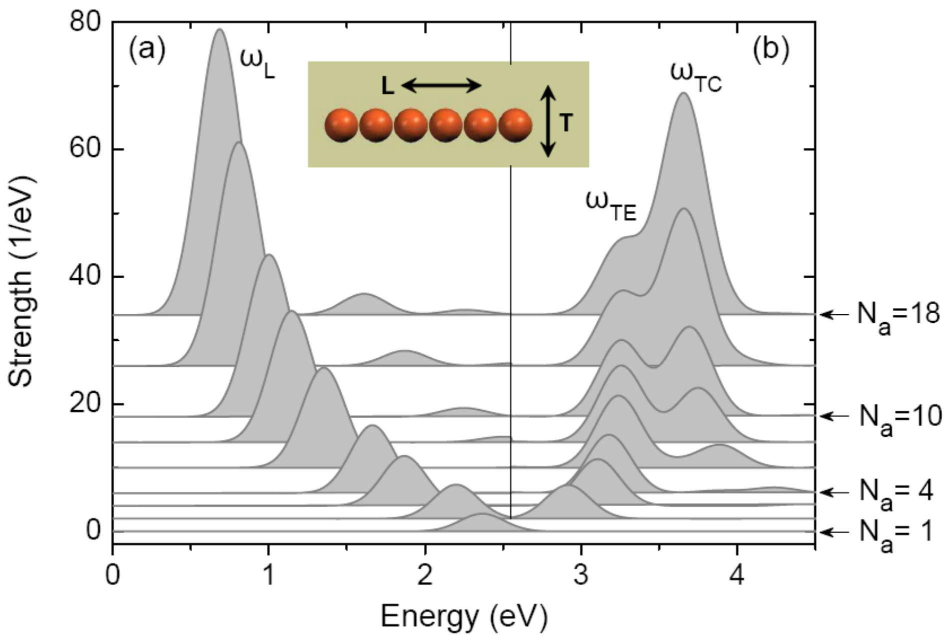


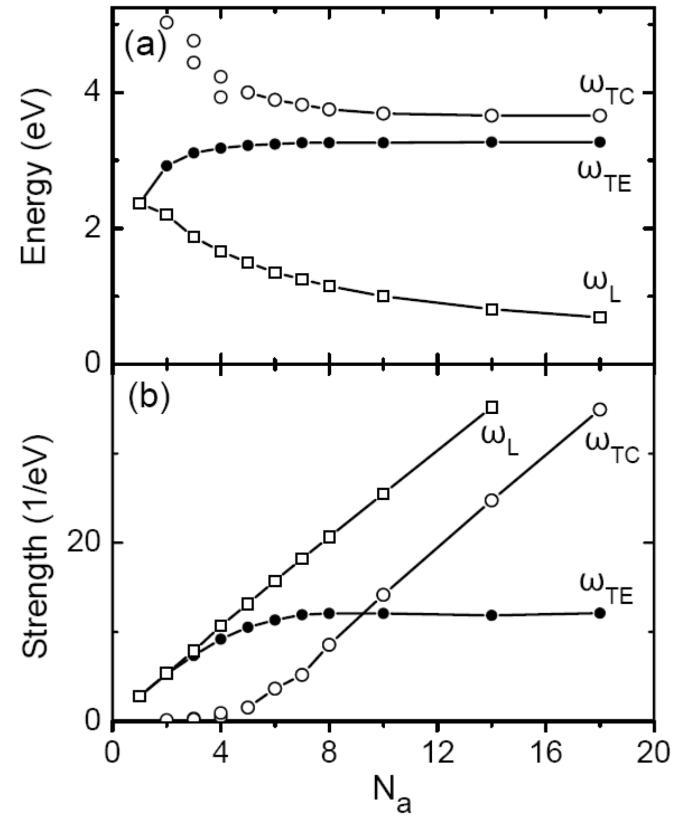
STM tip induced light emission

Atomic chain: T.Nagao, et al, PRL 97, 116802 (2006).
Break junction: D.C.Guhr, et al, PRL 99, 086801 (2007).

Optical excitation of atom chains: Na
-Longitudinal vs transverse plasmons

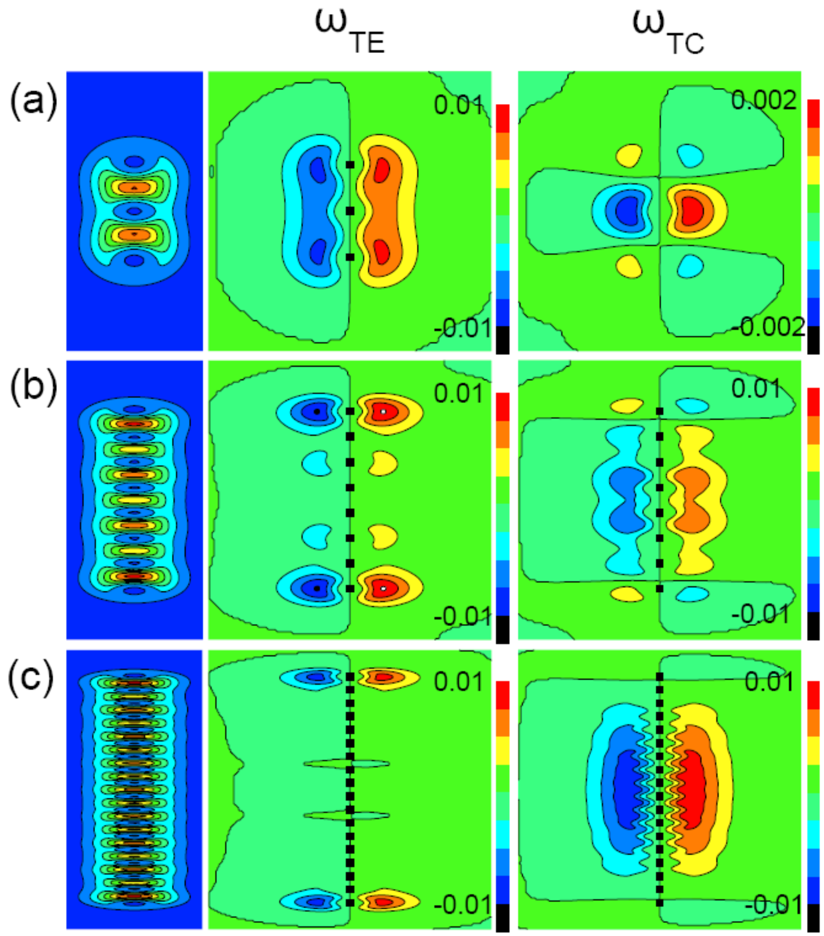
Atomic models, LR-TDLDA (Octopus)





J. Yan, Z. Yuan, and S. Gao, Phys. Rev. Lett. 98, 216602 (2007)

End and central resonances in 1D



1D analog of surface and bulk plasmons in 2D systems

Comparison with a classical model

- Ellipsoidal model

$$\alpha(\omega) = \frac{4\pi abc}{3} \frac{\epsilon(\omega) - \epsilon_m}{\epsilon_m + n_i[\epsilon(\omega) - \epsilon_m]},$$

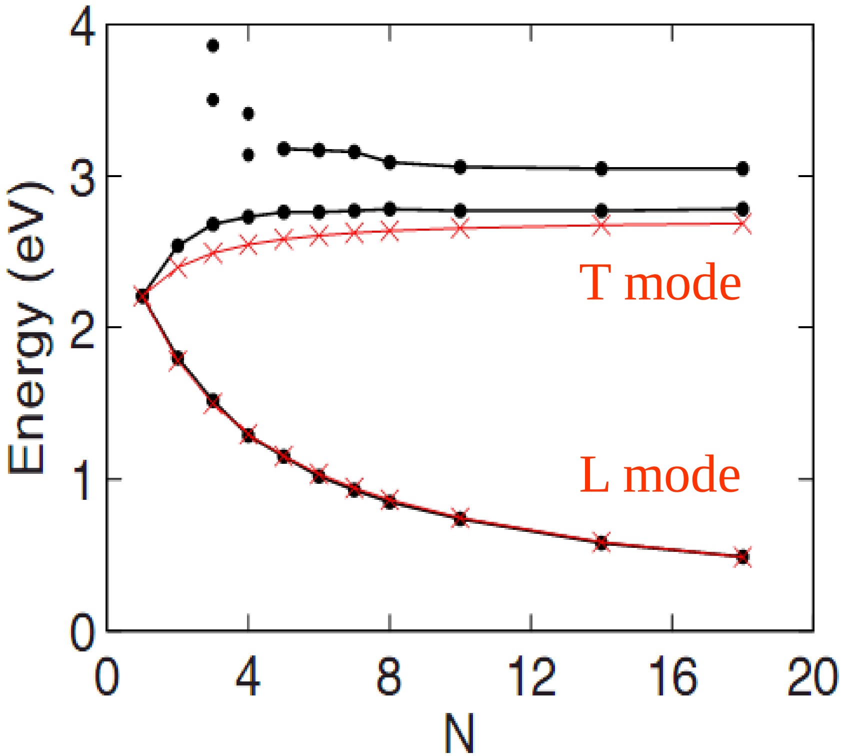
$$\omega_P = \frac{\omega_{P0}}{\sqrt{n_i}}$$

n_i is the structural factor

i=a,b,c represents the main axes

- Parameters

$$\omega_{P0} = 3.83\text{eV}, \text{r} = 3\text{A}$$



One L mode with dispersion

One T mode dispersionless

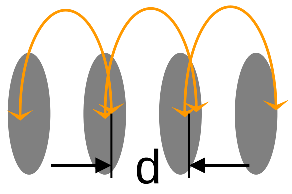
J. Yan and SW Gao, Phys. Rev. B78, 235413 (2008)

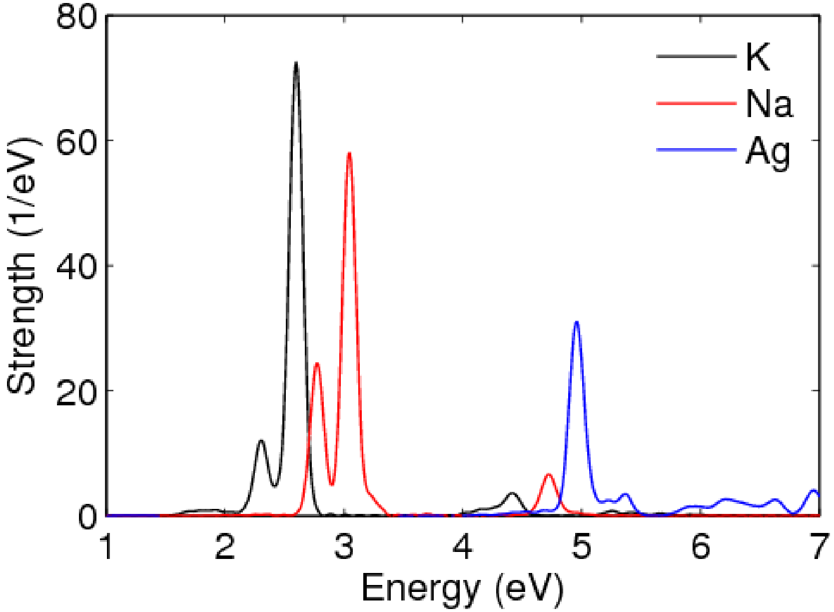
Strength and origin of the TE mode

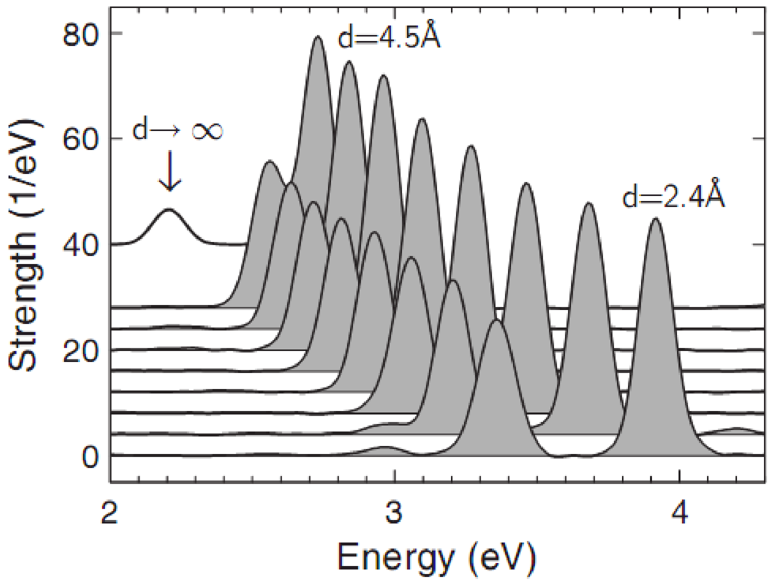
Intratomic binding

	S_{TE}	E_B (eV)
K (4s):	2	4.34
Na (3s):	4	5.14
Ag (5s):	6	7.58

Interatomic coupling



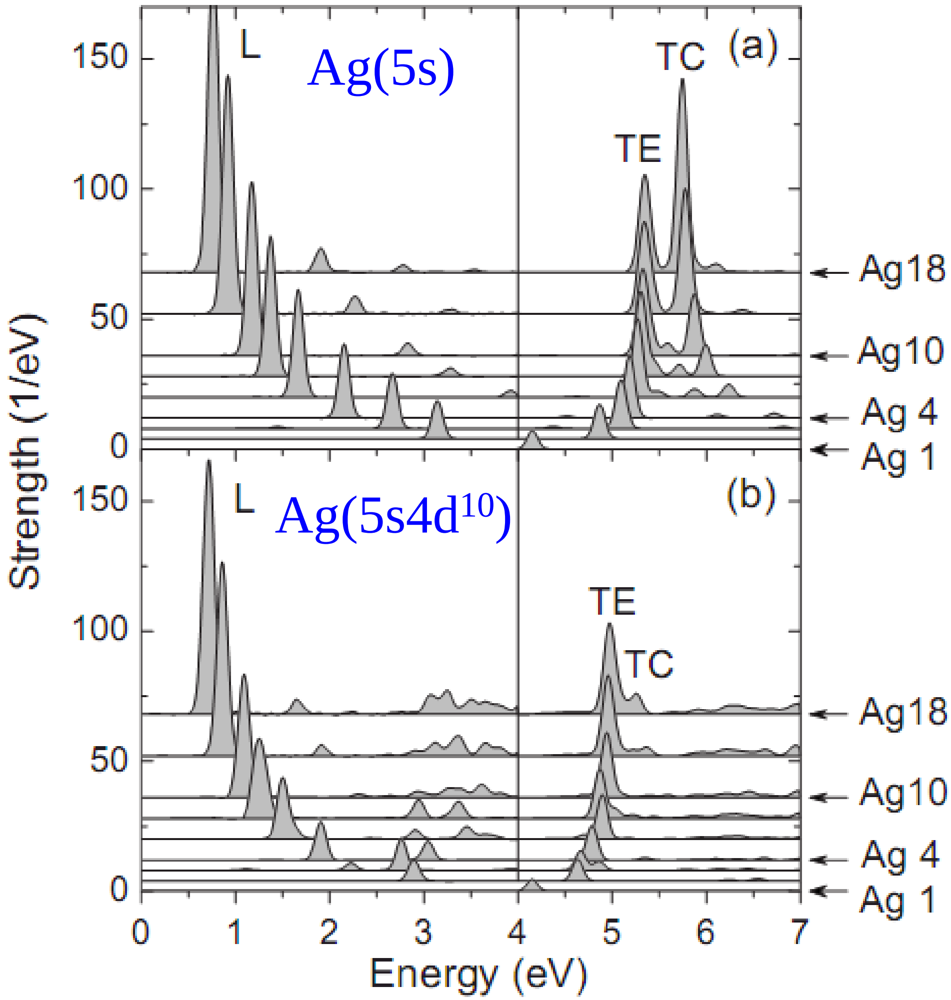


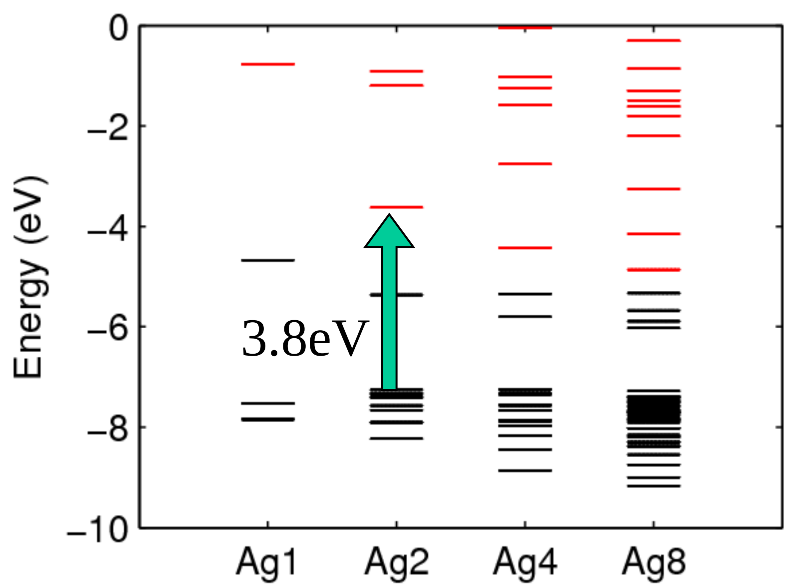


Jun Yan and Shiwu Gao, Phys. Rev. B78, 235413 (2008)

Ag: anisotropic screening of d-electrons

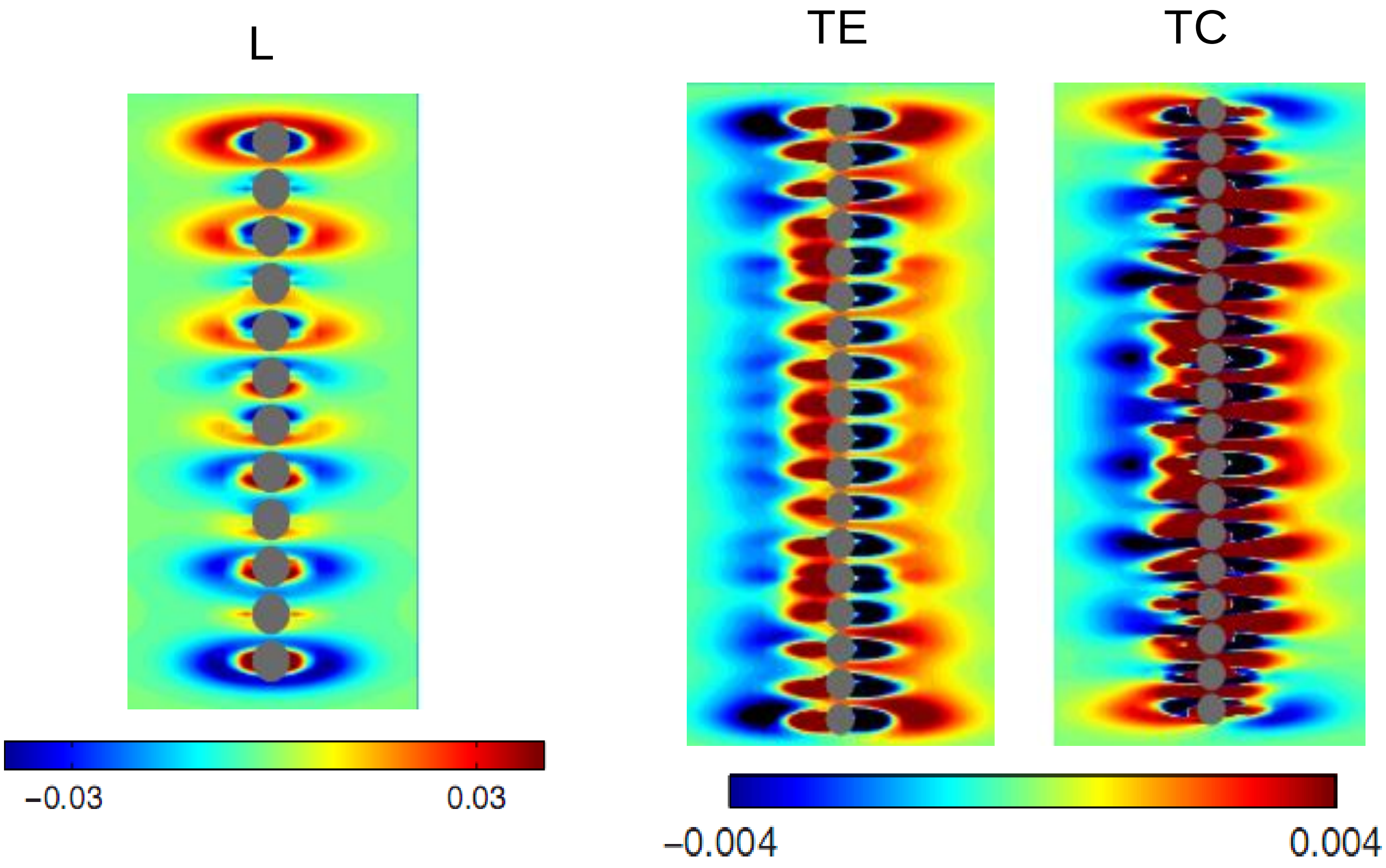
Would d-electrons simply damp (redshift) all chain modes?





L mode, No screening!
TC mode screened!
TE mode, only slightly

Dynamic screening of d-electrons: Ag



What we learned in 1D atomic chains

- 1 L and 2 T modes (TE, and TC)
- L and TC classical like, TE quantum
- Free electron dispersion in L mode vs. expt
- Screening is anisotropic in linear chains
  - L mode, no screening
  - TE no screening,
  - TE strongly damped

Dresponse: LR+TDLDA

Y. Zhe and S. Gao, Comput. Phys. Commun. 180, 466 (2009)

$$n_{\text{ind}}(\mathbf{r},\omega) = \int d^3r'\,\chi(\mathbf{r},\mathbf{r}',\omega)V_{\text{ext}}(\mathbf{r}',\omega)$$

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \frac{1}{\Omega}\sum_{\mathbf{q}}^{\text{BZ}}\sum_{\mathbf{G},\mathbf{G}'} e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}\chi_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}$$

$$\chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \frac{2}{N_k\Omega}\sum_{\mathbf{k}}^{BZ}\sum_{n,n'}\frac{f_{n,\mathbf{k}}-f_{n',\mathbf{k}+\mathbf{q}}}{\omega+\epsilon_{n,\mathbf{k}}-\epsilon_{n',\mathbf{k}+\mathbf{q}}+i\eta}$$
$$\times\langle n,\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|n',\mathbf{k}+\mathbf{q}\rangle\langle n',\mathbf{k}+\mathbf{q}|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n,\mathbf{k}\rangle$$

$$\chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) + \sum_{\mathbf{G}_1,\mathbf{G}_2}\chi^0_{\mathbf{G}\mathbf{G}_1}(\mathbf{q},\omega)\left\{K^{\text{Coulomb}}_{\mathbf{G}_1\mathbf{G}_2}+K^{\text{XC}}_{\mathbf{G}_1\mathbf{G}_2}\right\}\chi_{\mathbf{G}_2\mathbf{G}'}(\mathbf{q},\omega)$$

Ground states calculated from *abinit package*

- Full band structure, screening included
- Parameter free

Parallelization over k-summation

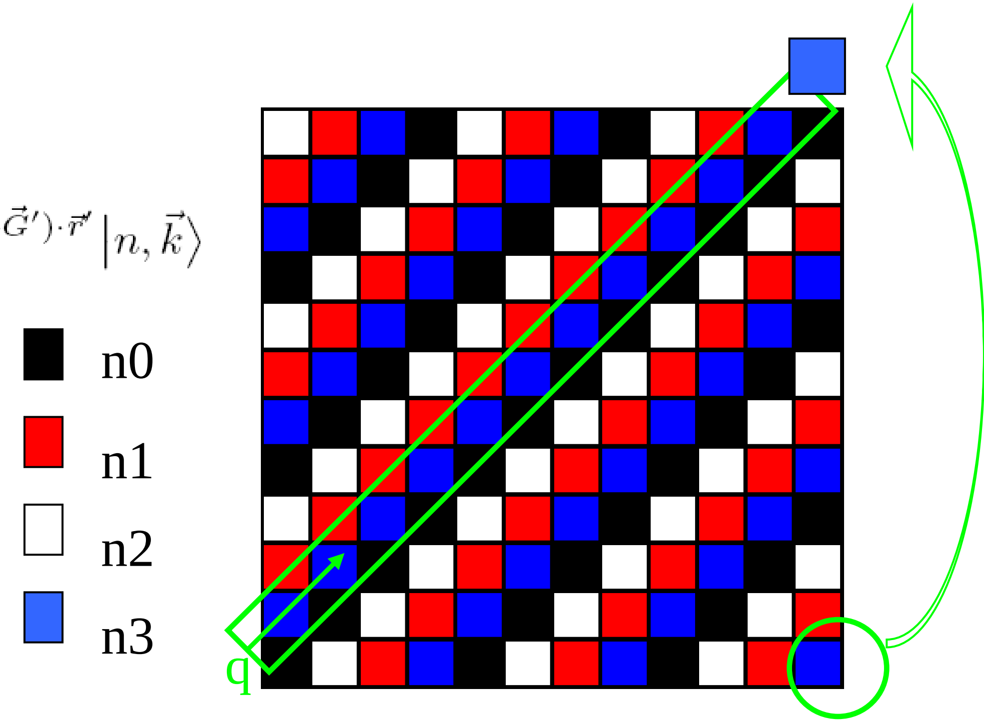
Distribution of k-points for a given q

$$\chi^0_{\vec{G}\vec{G}'}(\vec{q},\omega)$$

$$= \frac{2}{N_k\Omega}\sum_{\vec{k}}^{BZ}\sum_{n,n'}\frac{f_{n,\vec{k}}-f_{n',\vec{k}+\vec{q}}}{\omega+\epsilon_{n,\vec{k}}-\epsilon_{n',\vec{k}+\vec{q}}+i\eta}$$

$$\times \quad \langle n,\vec{k}|e^{-i(\vec{q}+\vec{G})\cdot\vec{r}}|n',\vec{k}+\vec{q}\rangle\langle n',\vec{k}+\vec{q}|e^{i(\vec{q}+\vec{G}')\cdot\vec{r}'}|n,\vec{k}\rangle$$

- Summation over k-->k+q pairs in parallels, stripe-wise
- Much less memory for wave functions storage



K-mesh in a 2D square Brillouin zone

Parallelization of χ_0 and χ

- Block-wise distribution of χ_0 matrix

$$\begin{aligned}
&\chi^0_{\vec{G}\vec{G}'}(\vec{q},\omega) \\
&= \frac{2}{N_k\Omega}\sum_{\vec{k}}^{BZ}\sum_{n,n'}\frac{f_{n,\vec{k}}-f_{n',\vec{k}+\vec{q}}}{\omega+\epsilon_{n,\vec{k}}-\epsilon_{n',\vec{k}+\vec{q}}+i\eta} \\
&\times \langle n,\vec{k}|e^{-i(\vec{q}+\vec{G})\cdot\vec{r}}|n',\vec{k}+\vec{q}\rangle\langle n',\vec{k}+\vec{q}|e^{i(\vec{q}+\vec{G}')\cdot\vec{r}'}|n,\vec{k}\rangle
\end{aligned}$$

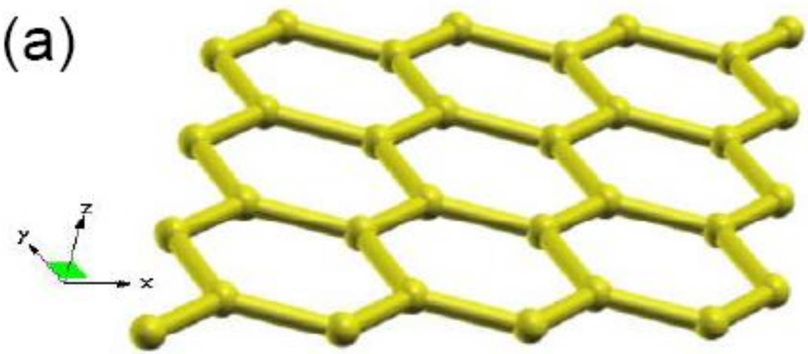
- Parallel solution of Dyson equation with scalapack

$$\chi_{\mathbf{GG}'}(\mathbf{q},\omega)=\chi^0_{\mathbf{GG}'}(\mathbf{q},\omega)+\sum_{\mathbf{G}_1,\mathbf{G}_2}\chi^0_{\mathbf{GG}_1}(\mathbf{q},\omega)\left\{K^{\text{Coulomb}}_{\mathbf{G}_1\mathbf{G}_2}+K^{\text{XC}}_{\mathbf{G}_1\mathbf{G}_2}\right\}\chi_{\mathbf{G}_2\mathbf{G}'}(\mathbf{q},\omega)$$

Surface plasmons in graphene

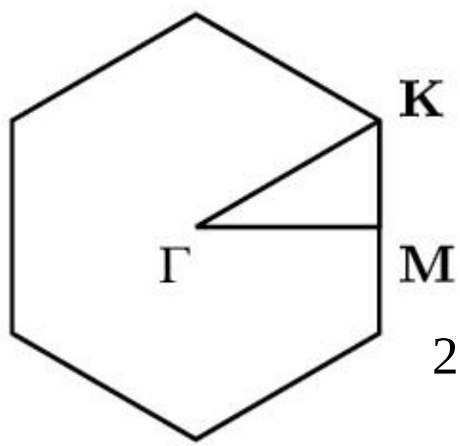
Atomic structure of graphene

(a)



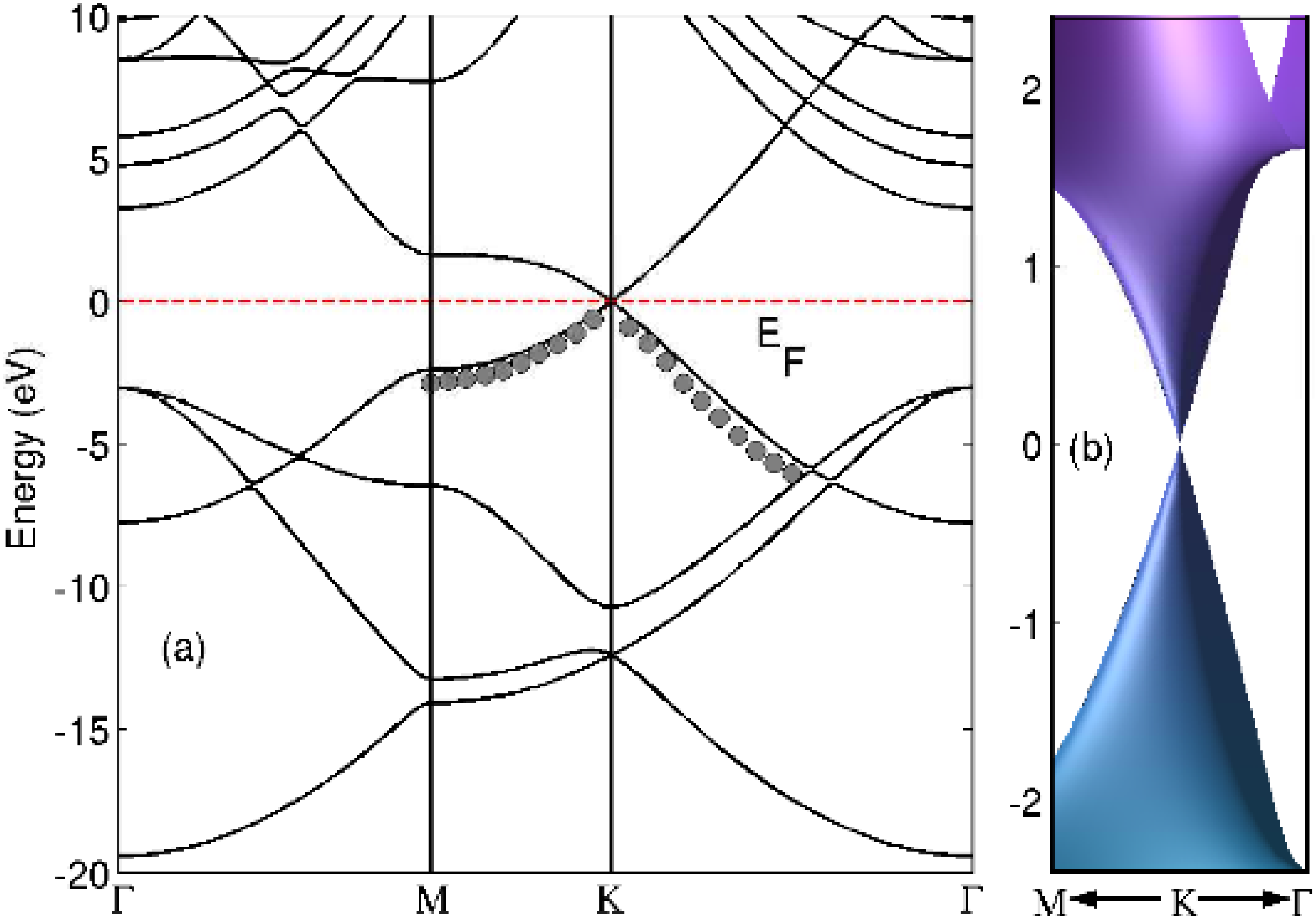
Honeycomb lattice

(b)

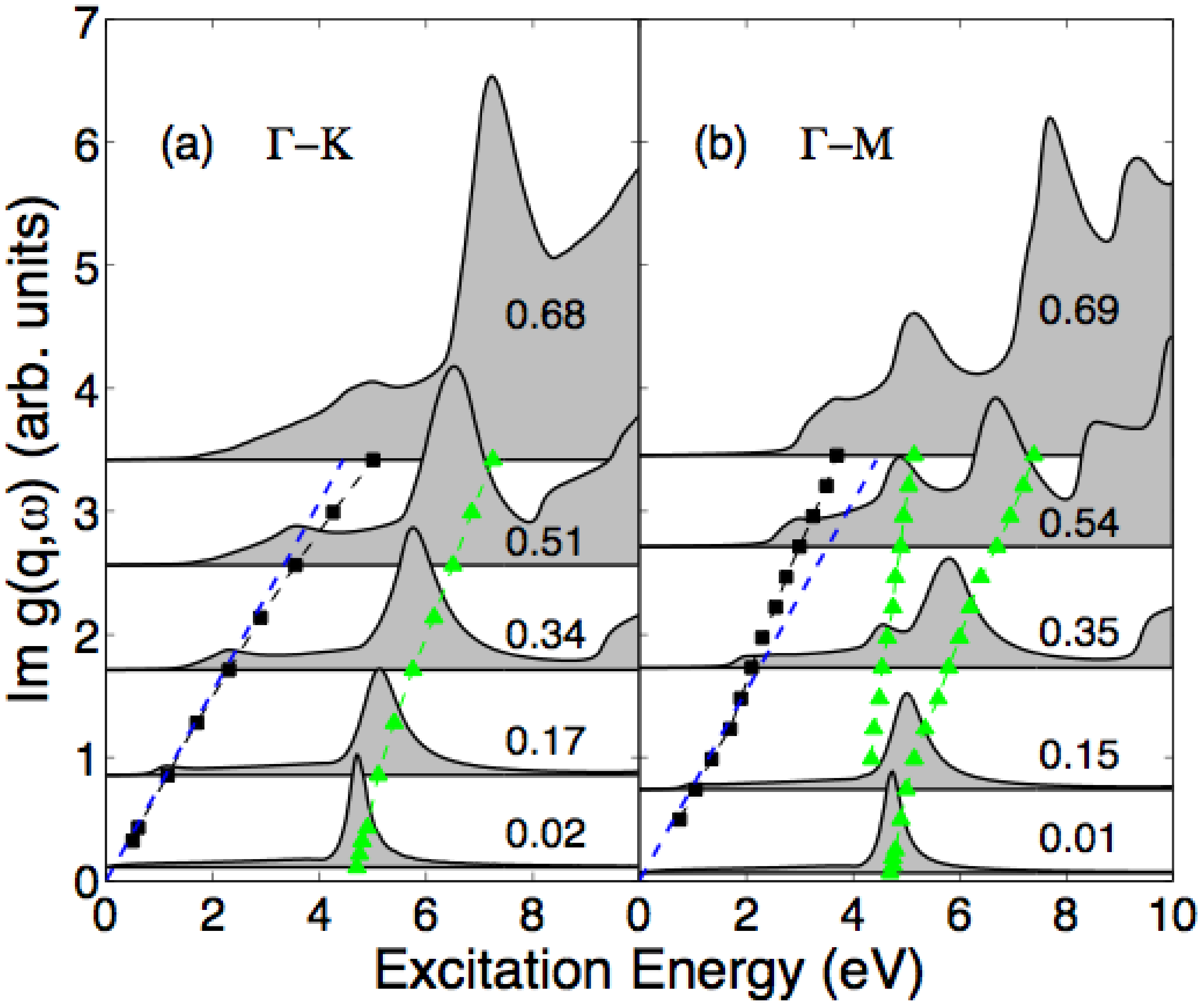


2DBZ

Band structure of graphene

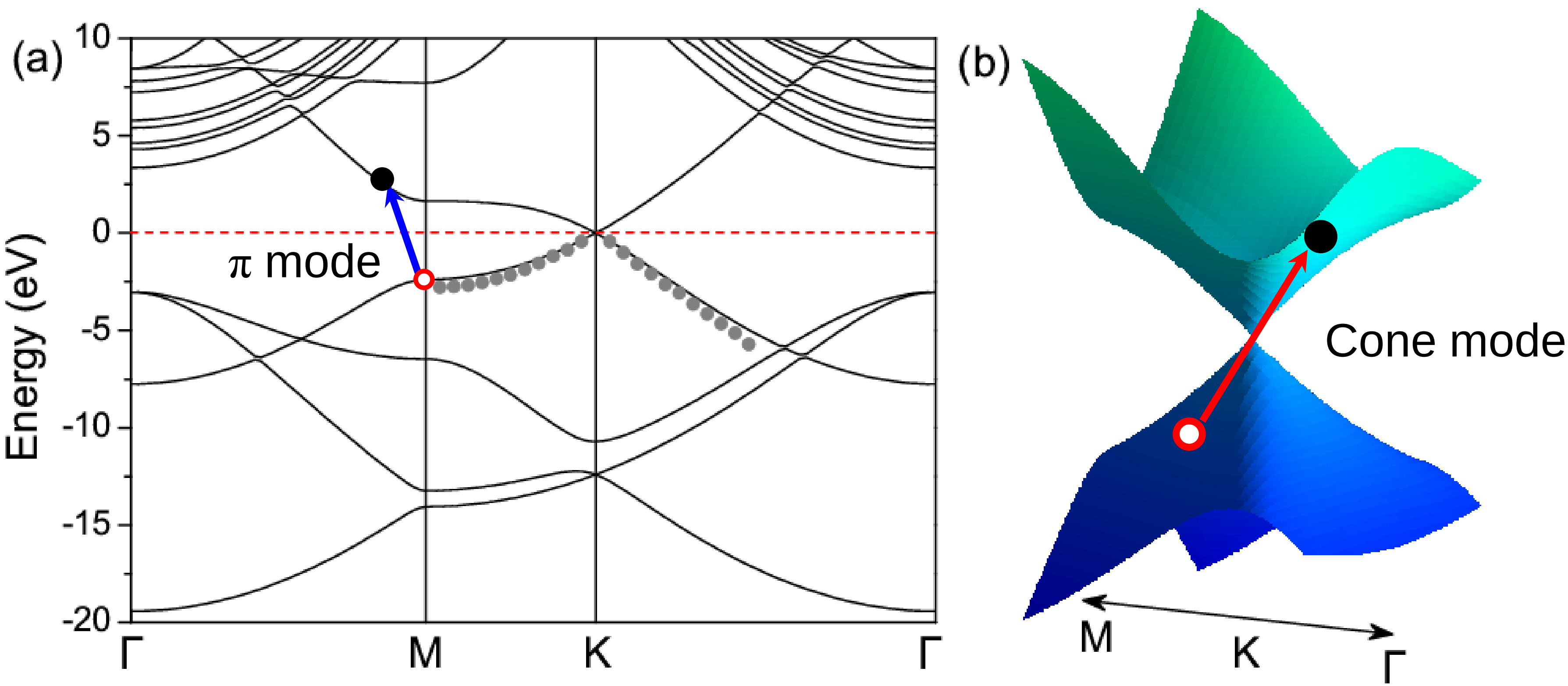


Loss spectrum of undoped graphene

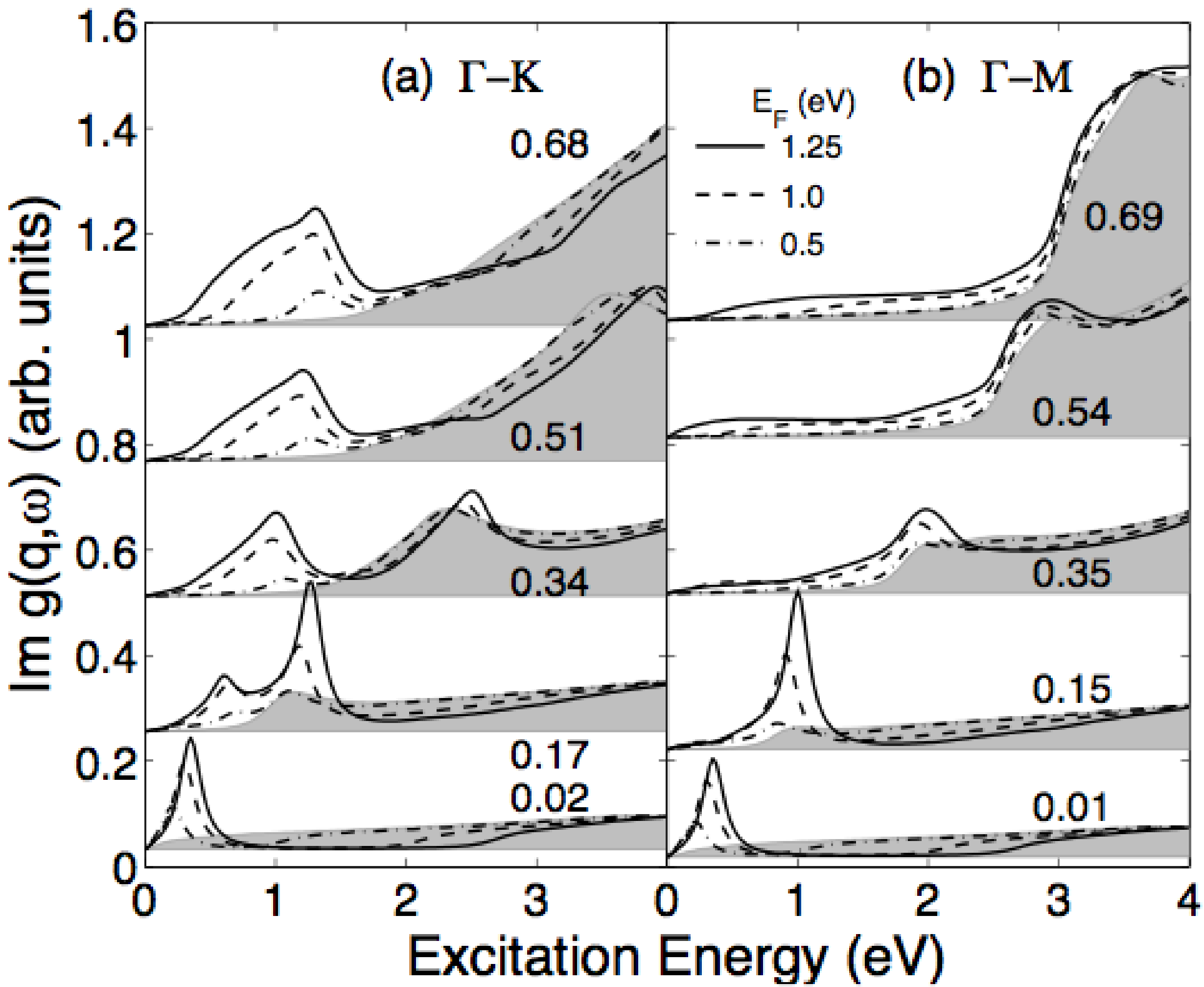


Plasmons in Graphene

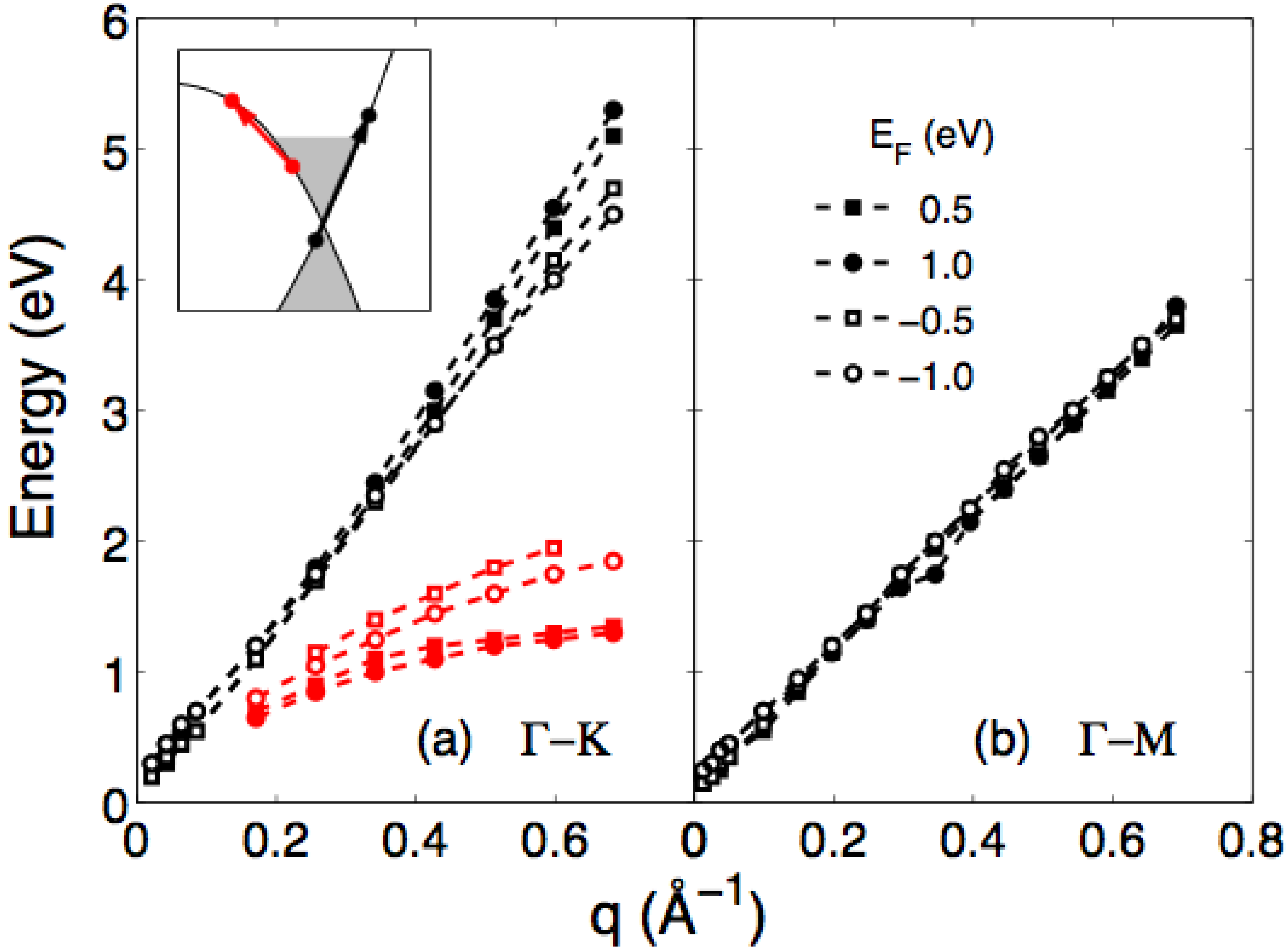
- π mode and cone mode



Electronic doping



Linear and nonlinear mode



Summary and outlook

Quantum plasmons at atomic scales

- Spatial quantization & size effects
- Collective oscillations vs interband transitions
- Plasmonic coupling & damping

Method/Code developments

- Optimization of TDDFT/Octopus
- Dresponse code, Yuan&Gao, CPC 180, 460 (2009)
- Future: plasmon enhanced processes, light energy harvesting, water splitting, hydrogen storage, solor cells

Some results/on-going efforts

- Plasmon resonances in atomic chains

  Gao&Yuan, PRB05, Yan&Gao, PRL07, PRB08

- Quantum well plasmons, frequencies and linewidths Yuan&Gao, PRB06, Surf. Sci.08

- LR-TDLDA (Dresponse)

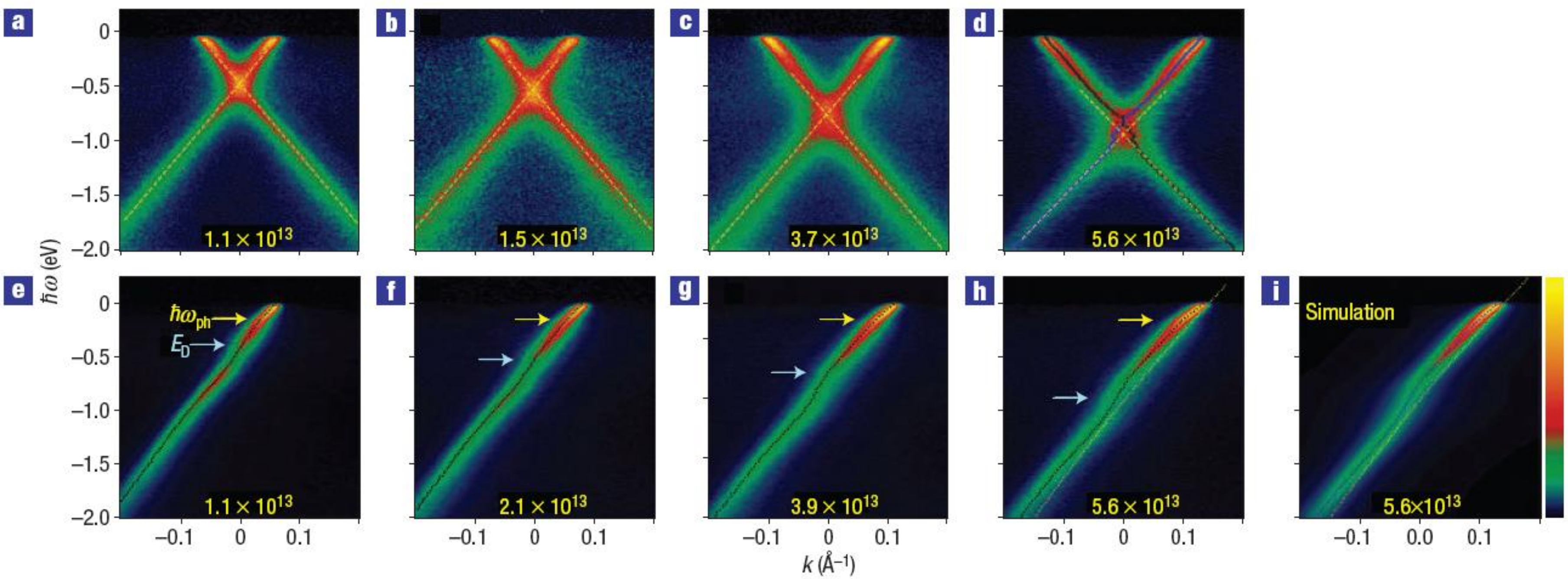
  Z. Yuan and S. Gao, CPC 180,460 (2009)

- Semiclassical theory of electron-plasmon coupling and Landau damping

- Photo-(plasmon) induced transport

Surface plasmon in graphene

- ARPES measurement near the Fermi level [*]
- Speculation: Electron-phonon vs electron-plasmon coupling



[*] A. Bostwick, *et. al.* Nat. Phys. **3**, 36 (2007)