

Plasmonics and non-local interactions from TDDFT: graphene and metal surfaces

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Outline

- Linear response theory and excited states
- Plasmons on metal surfaces and influence of adsorbates
- Plasmons in graphene coupled to substrates

- Total energies from RPA: graphene at metal surfaces

Linear density response function

Single-particle DFT equation:

$$[\hat{T} + \hat{V}_{eff}] \varphi_n(r) = \varepsilon_n \varphi_n(r)$$

Eigenvalues and wave functions do not represent physical excitations!

Excited state properties can be obtained from the linear density response function defined by.

$$\delta n(\mathbf{r}, t) = \int d\mathbf{r}' \chi(\mathbf{r}, t; \mathbf{r}', t') V(\mathbf{r}', t')$$

for some external perturbation $V(r,t)$

Non-interacting response function follows from 1. order perturbation theory on DFT states:

$$\chi_{\mathbf{G}\mathbf{G}'}^0(\mathbf{q}, \omega) = \sum_{n,m} (f_n - f_m) \frac{\langle \varphi_n | e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \varphi_m \rangle \langle \varphi_m | e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}} | \varphi_n \rangle}{\omega - \varepsilon_n + \varepsilon_m + i\eta}$$

Linear density response function

The interacting response function can be calculated from the Dyson equation:

$$\chi(\omega) = \chi^0(\omega) + \chi^0(\omega) f_{Hxc}(\omega) \chi(\omega)$$

The Hartree-exchange-correlation kernel is defined as

$$f_{Hxc}(\mathbf{r}, t; \mathbf{r}', t') = \frac{\delta v_{Hxc}[n](\mathbf{r}, t)}{\delta(\mathbf{r}', t')}$$

We use the frequency independent approximations:

$$f_{Hxc}^{RPA} = \frac{1}{|\mathbf{r} - \mathbf{r}'|}, \quad f_{Hxc}^{ALDA} = f_{Hxc}^{RPA} + \left. \frac{d^2 E_{xc}^{LDA}[n]}{dn^2} \right|_{n=n(\mathbf{r})}$$

All calculations have been performed with the code GPAW, which uses the Projector Augmented Wave method to implicitly represent all-electron wavefunctions

Dielectric constants of simple semiconductors

Microscopic dynamical dielectric function:

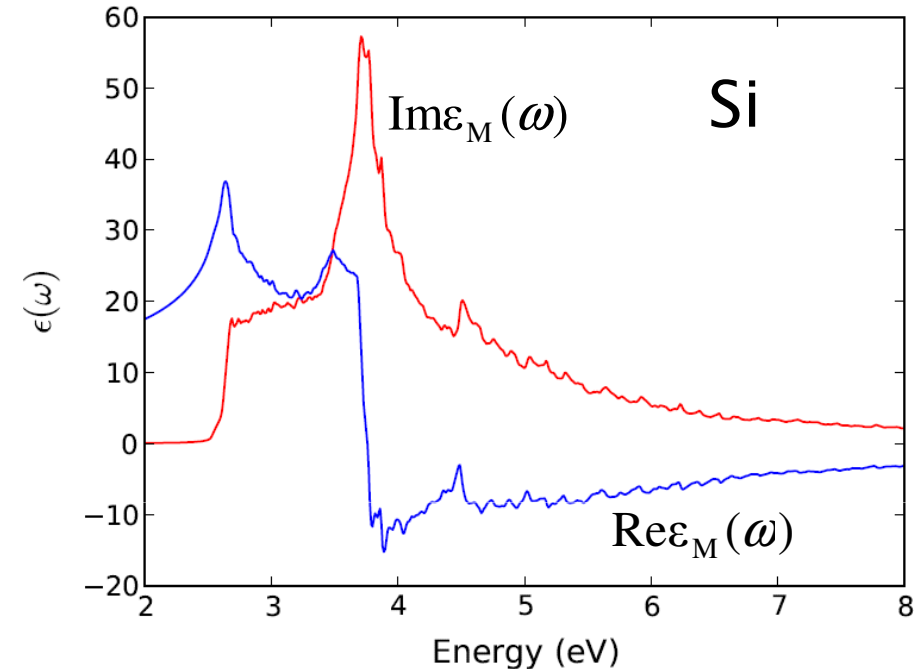
$$\epsilon_{\mathbf{G}\mathbf{G}'}^{RPA}(\mathbf{q}, \omega) = \delta_{\mathbf{G}\mathbf{G}'} - \frac{4\pi}{|\mathbf{q} + \mathbf{G}|^2} \chi_{\mathbf{G}\mathbf{G}'}^0(\mathbf{q}, \omega)$$

Macroscopic dielectric constant

$$\epsilon_M(\mathbf{q}, \omega) = \frac{1}{\epsilon_{00}^{-1}(\mathbf{q}, \omega)}$$

Calculated dielectric optical constants:

$$\epsilon^\infty = \epsilon_M(\mathbf{q} = 0, \omega = 0)$$



Crystal	C	Si	SiC	AlP	GaAs
RPA, NLF	5.98	13.99	7.18	9.04	15.12
RPA, LF	5.58	12.58	6.58	7.83	13.67
ALDA, LF	5.83	13.21	6.89	8.27	14.32
RPA, NLF (Ref. 30)	5.98	14.04	7.29	9.10	14.75
RPA, LF (Ref. 30)	5.55	12.68	6.66	7.88	13.28
ALDA, LF (Ref. 30)	5.82	13.31	6.97	8.33	13.98
Expt. (Ref. 39)	5.70	11.90	6.52	7.54	11.10

Dielectric constants of simple semiconductors

Microscopic dynamical dielectric function:

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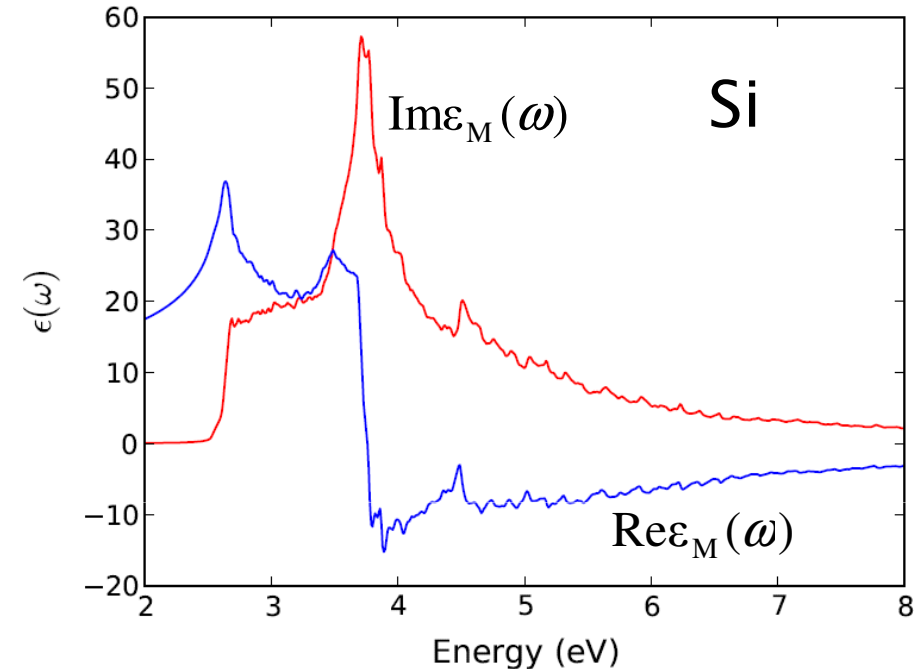
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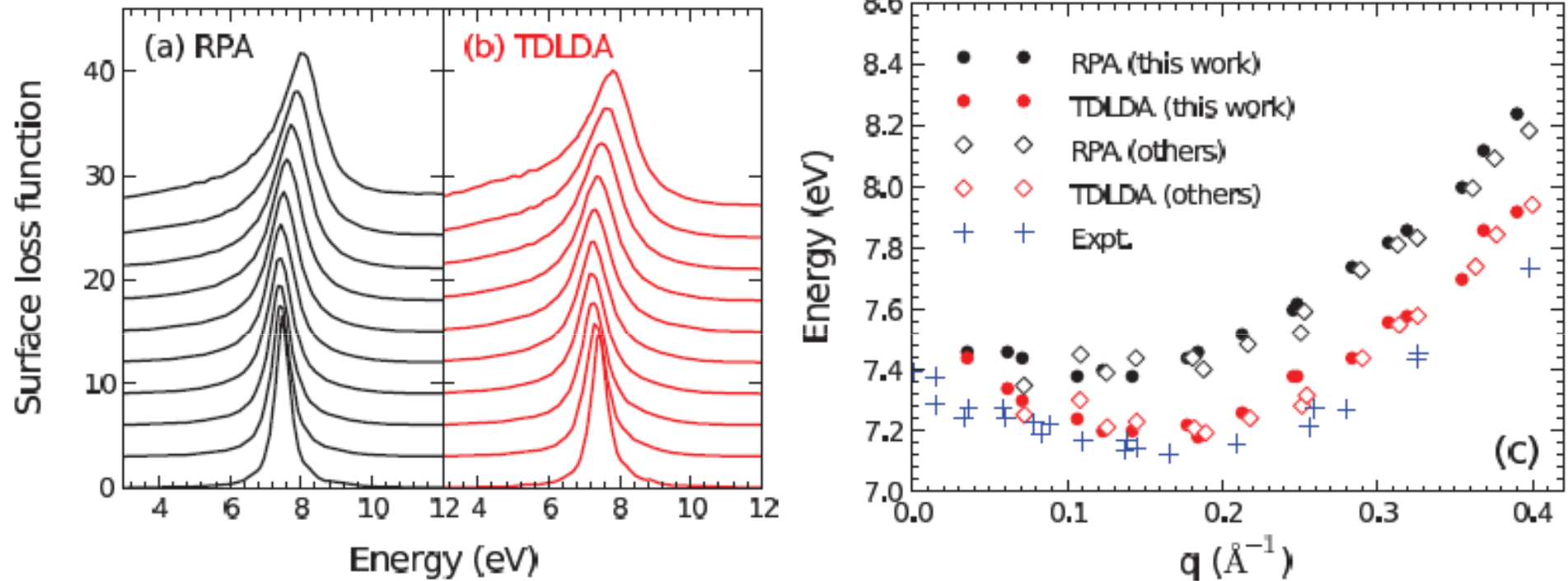
In the following we focus on the Electron Energy Loss Spectrum:

$$\text{EELS} = -\text{Im} \frac{1}{\epsilon_M(\mathbf{q}, \omega)}$$



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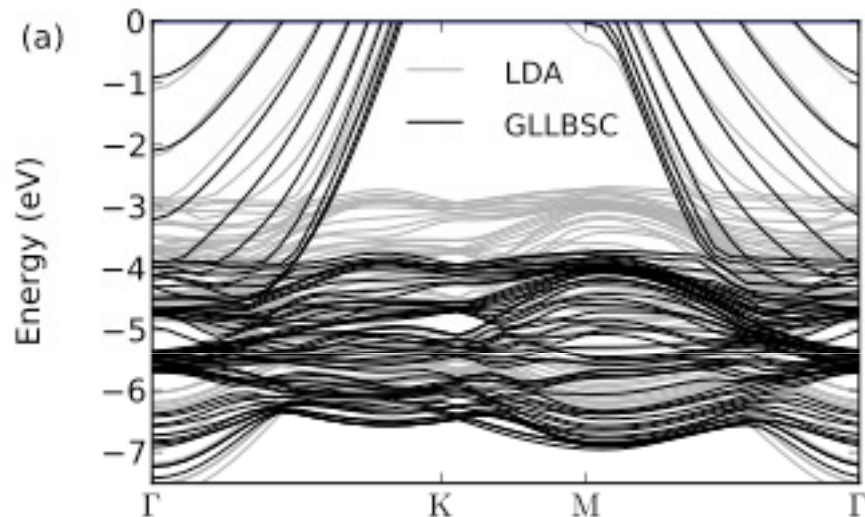
Surface plasmons on Mg(0001)



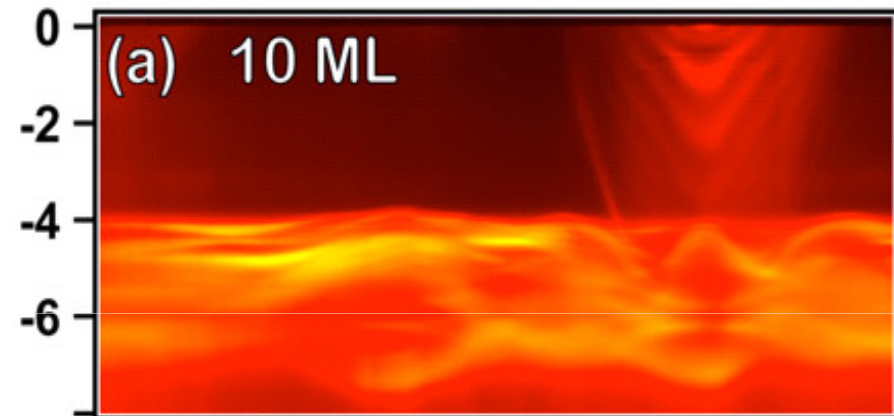
The surface plasmon energy is accurately reproduced at the level of ALDA

Surface plasmons on Ag(111)

Calculated band structure for
10 ML Ag(111) slab



Photoemission experiments on
Ag(111) 10ML film



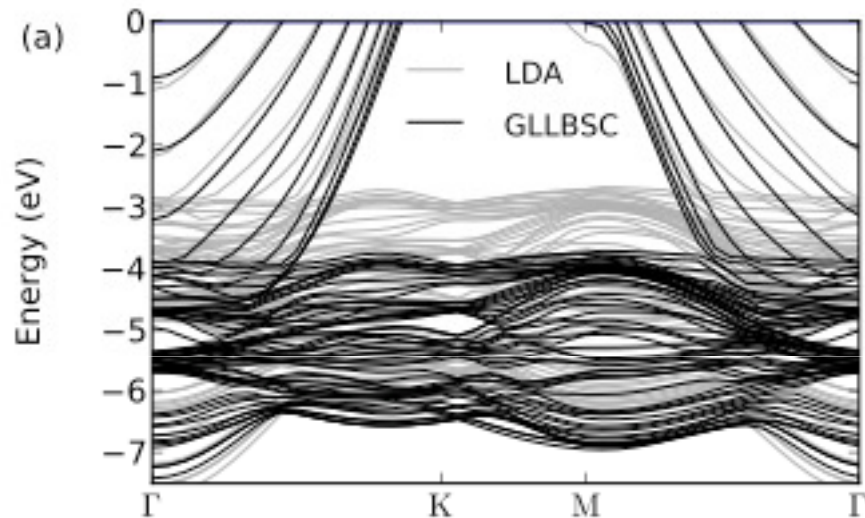
Correct alignment of the Ag d -band is accomplished by using a non-standard exchange-correlation potential (GLLB).

O. Gritsenko, R. van Leeuwen, E. van Lenthe, and E. J. Baerends,
Phys. Rev. A **51**, 1944 (1995)

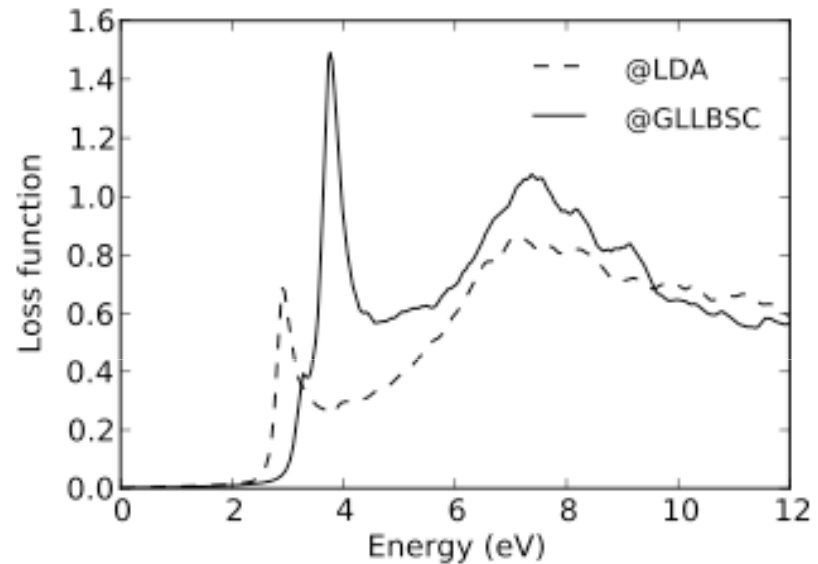
M. Kuisma, J. Ojanen, J. Enkovaara, and T. T. Rantala,
Phys. Rev. B **82**, 115106 (2010)

Surface plasmons on Ag(111)

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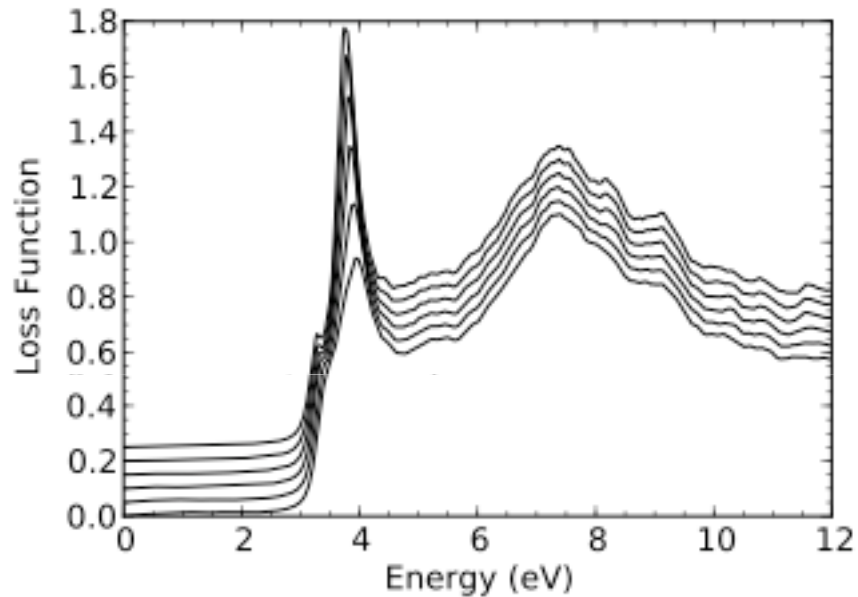
Calculated electron energy
loss spectrum



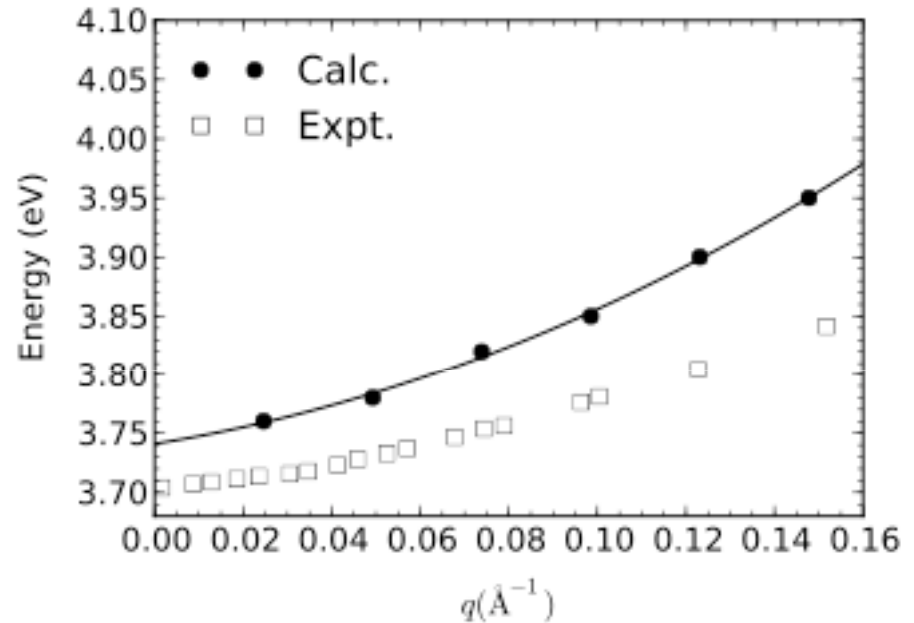
- ❑ Too high position of Ag d -band leads to overscreening of the plasmon.
- ❑ The problem is (almost) solved by the GLLB potential

Surface plasmons on Ag(111)

Calculated EELS spectra at different q vectors.



Surface plasmon dispersion

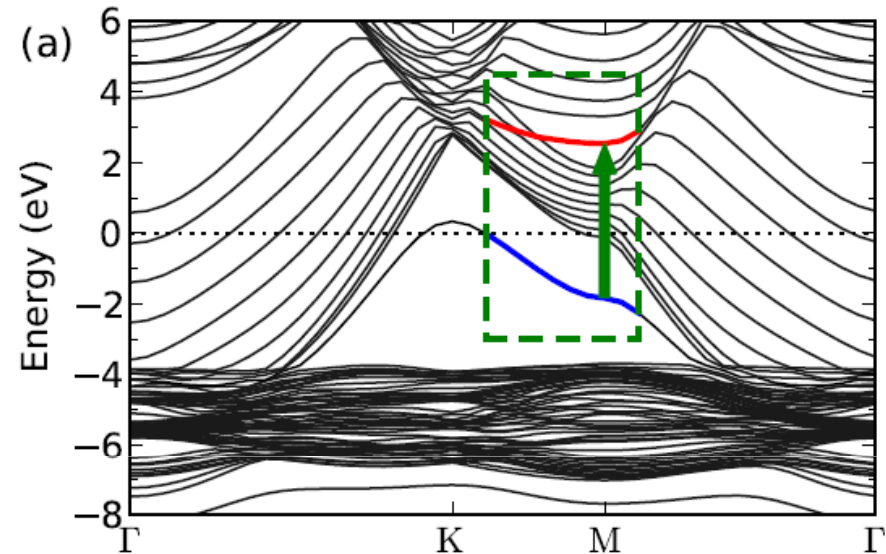
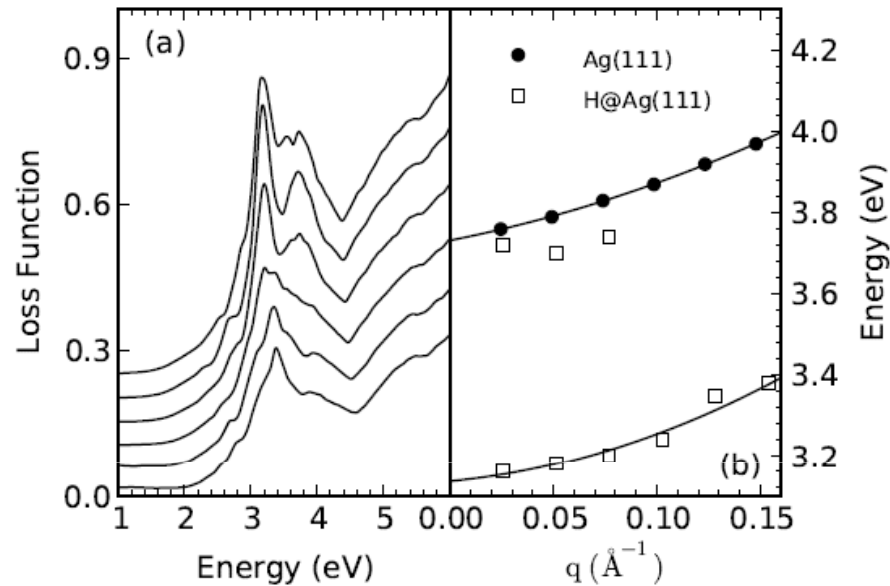


Agreement with experiments within 0.1 eV.

How can we tune the surface plasmon?

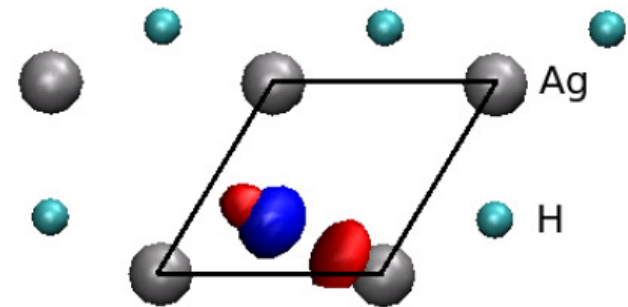
- Nanostructuring of the surface
- Nano clusters of various shapes
- Doping in the bulk to change electron density
- Chemical functionalization/doping of the surface itself

Influence of adsorbed hydrogen



Low energy peak in EELS spectrum.

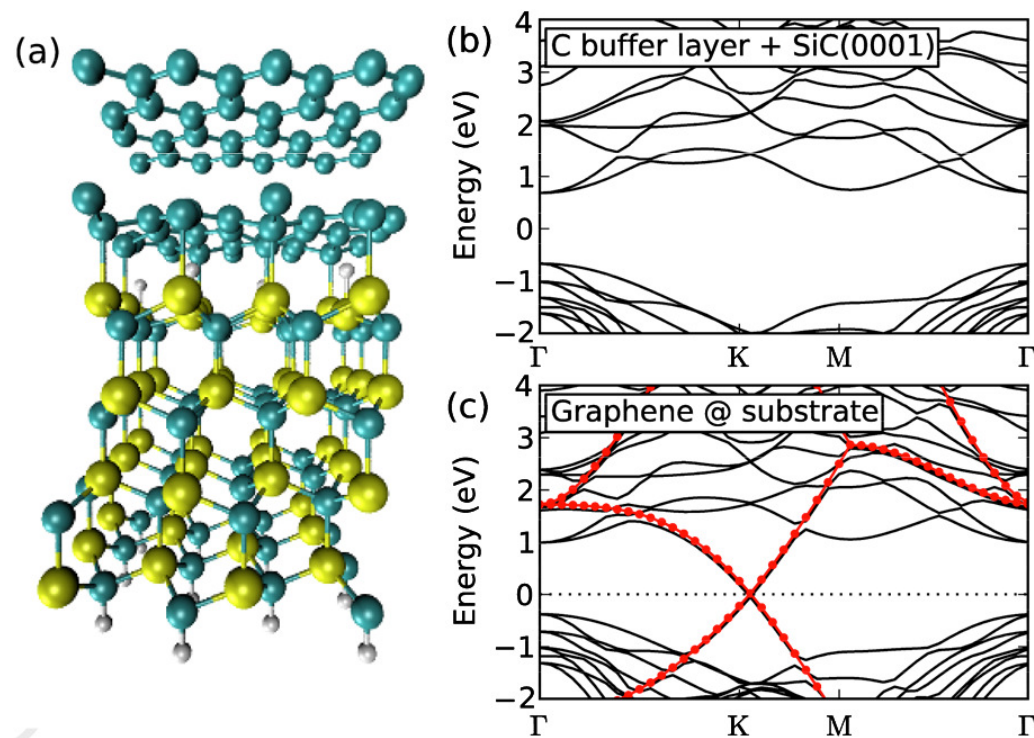
This peak is due to interband transitions from occupied H states (blue) to empty Ag d -states (red).



Graphene plasmonics

Graphene supports π -plasmons with propagation length $\sim\mu\text{m}$ and velocity $\sim 10^6$ m/s. Upon doping 2D metallic plasmons are introduced.

What is the influence of substrate on the graphene plasmon?



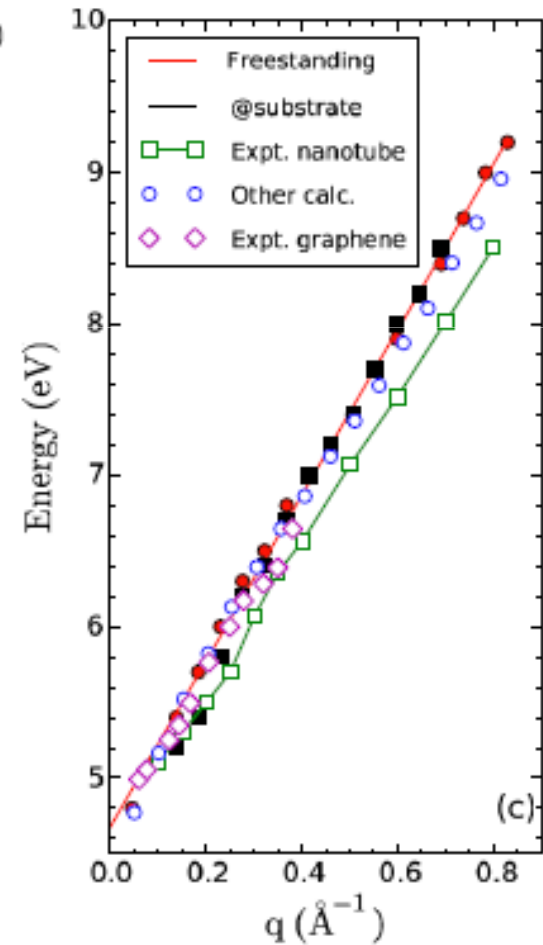
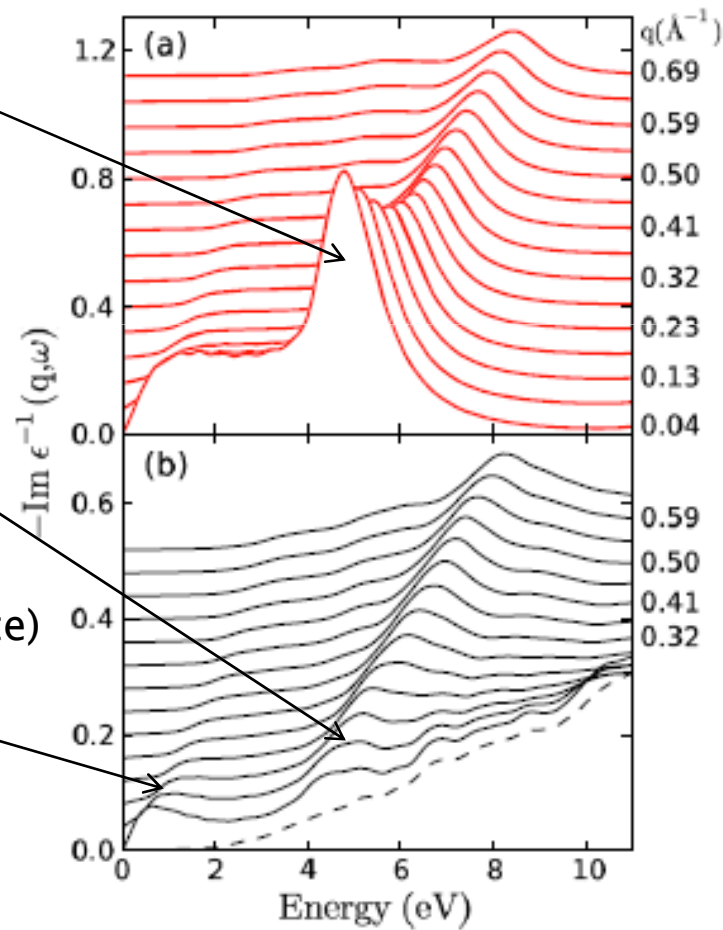
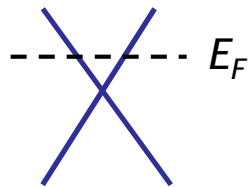
Graphene plasmonics

Electron Energy Loss Spectrum

π -plasmon in free standing graphene

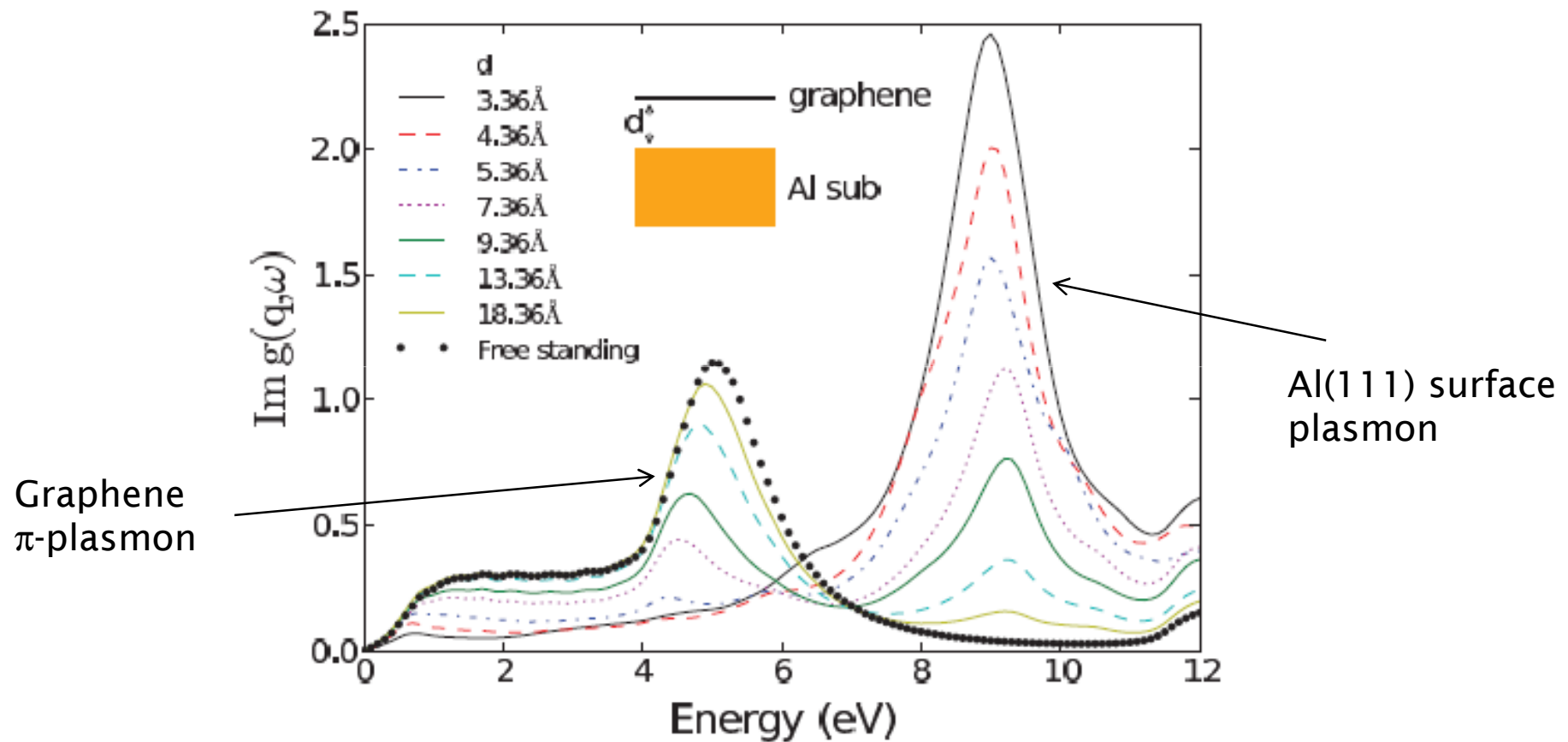
Strong damping of π -plasmon by e-h pairs in SiC substrate

Metallic sheet plasmon (natural doping by substrate)



Graphene plasmonics

Electron Energy Loss Spectrum – graphene@Al(111)



The graphene π -plasmon couples strongly to the metallic surface plasmon.

Graphene plasmonics

Model for non-local coupling of plasmons

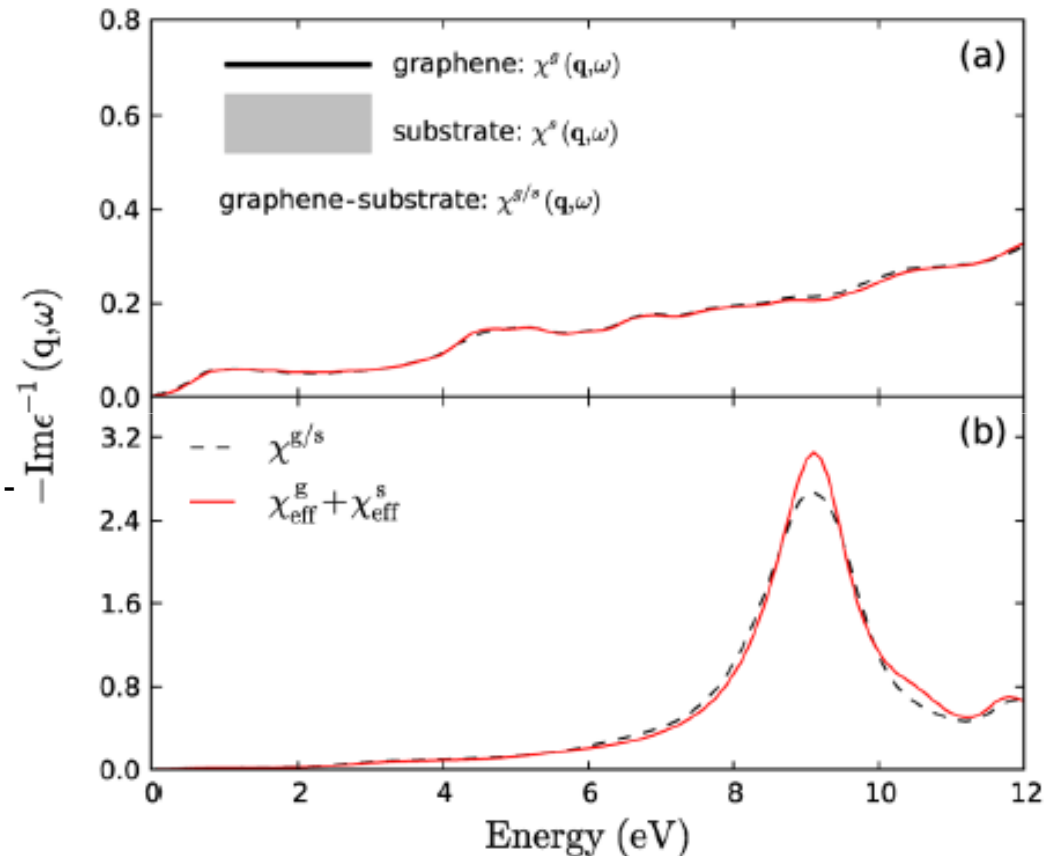
Defining the coupled individual density responses:

$$\delta n^g = \chi^g [\delta V_{ext} + V_c \delta n^s]$$

$$\delta n^s = \chi^s [\delta V_{ext} + V_c \delta n^g]$$

We obtain a model for the purely non-local response

$$\chi_{eff}^g = \frac{\delta n^g}{\delta V_{eff}} = \frac{\chi^g [1 + V_c \chi^s]}{1 - \chi^g V_c \chi^s V_c}$$



The results are nearly identical to the calculation of the full system

Plasmon outlook

- ❑ Tailoring surface plasmons on noble and simple metal surfaces by chemical functionalization/doping
- ❑ Atomic-scale understanding of the relation between metal-molecule interaction and plasmon energy (chemical sensing)
- ❑ Approaching plasmonics: Microscopic dielectric function + Maxwell equations
- ❑ Introduce “material dimension” in plasmonics research

Total energies from RPA

The adiabatic connection and fluctuation-dissipation theorem gives the correlation energy in terms of the response function:

$$E_c = -\frac{1}{2\pi} \int_0^1 d\lambda \int_0^\infty d\omega \text{Tr} [v\chi^\lambda(i\omega) - v\chi^0(i\omega)]$$

From TDDFT we have

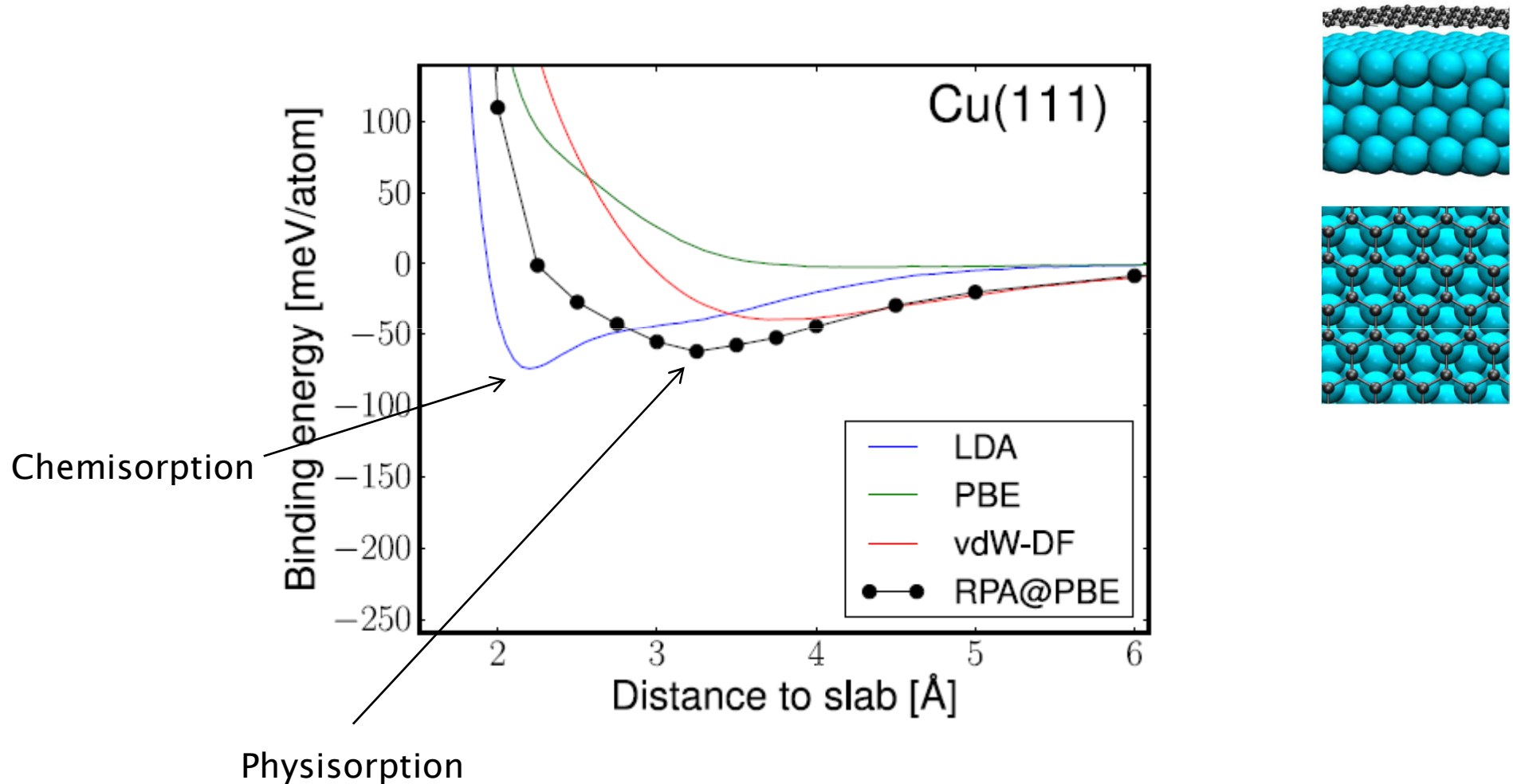
$$\chi^\lambda(\omega) = \chi^0(\omega) + \chi^0(\omega) f_{Hxc}^\lambda(\omega) \chi^\lambda(\omega)$$

For $f_{xc} = 0$, one obtains the RPA result:

$$E_c^{RPA} = \int_0^\infty \frac{d\omega}{2\pi} \text{Tr} [\ln(1 - v\chi^0(i\omega)) + v\chi^0(i\omega)]$$

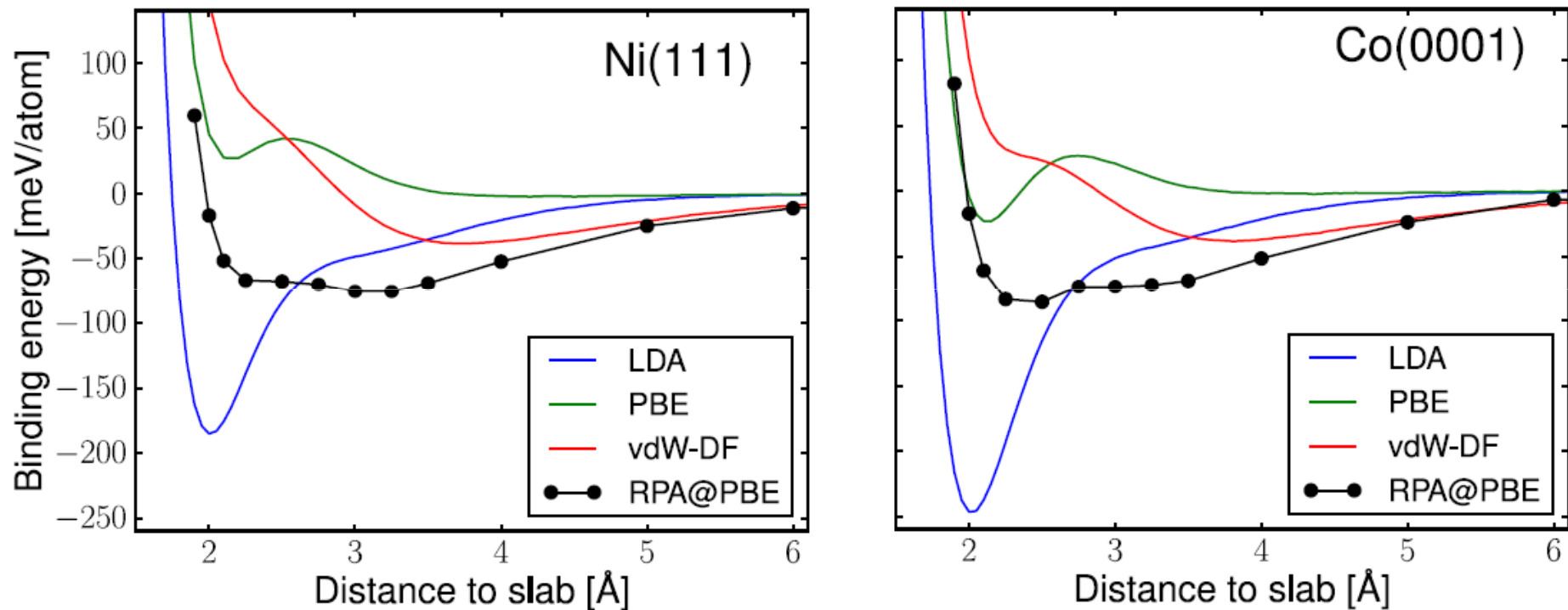
Total energies from RPA

RPA potential energy surfaces – graphene@Cu(111)



Total energies from RPA

RPA potential energy surfaces – graphene@Ni(111)/Co(0001)

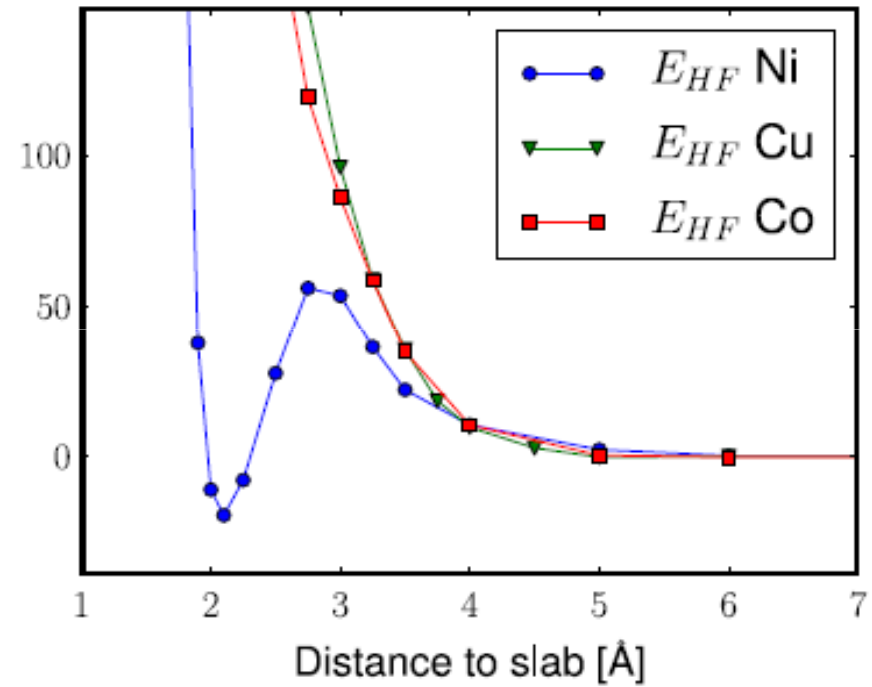
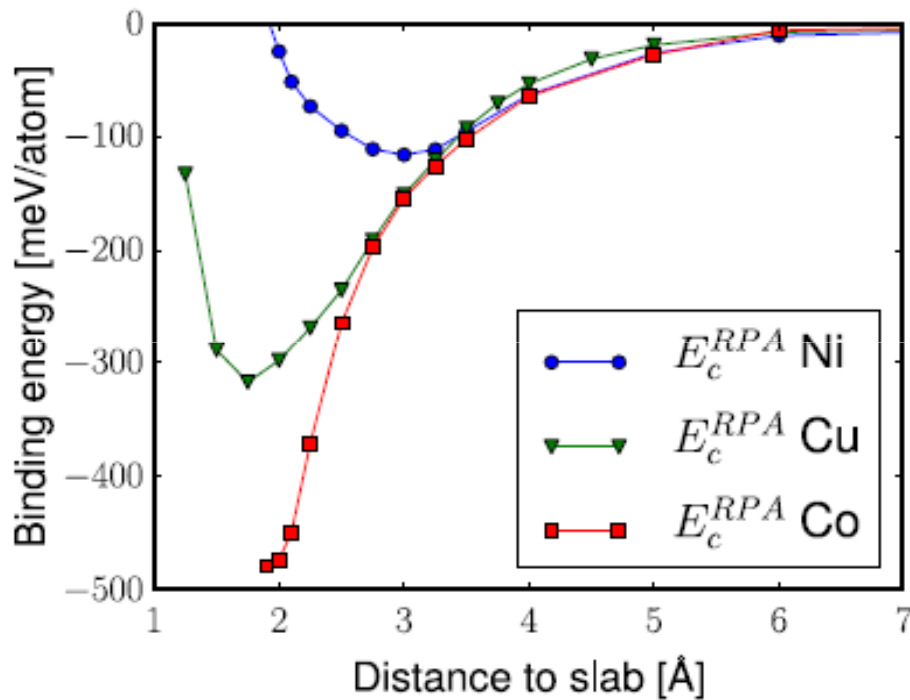


Semi-local and vdW functionals account well for *either* dispersive or covalent interactions

RPA seems to capture both effects

Total energies from RPA

RPA potential energy surfaces – graphene@Ni(111)/Co(0001)



The binding mechanisms are rather different for the three metals

For Ni(111), the chemisorption minimum is due to exchange, while for Cu and Co the binding is due to correlation

Outlook: RPA total energies

- ❑ RPA does not in general improve the description of covalent bonds, but performs much better than semi-local functionals when vdW interactions are important and better than vdW approximations when covalent bonds are important
- ❑ RPA becomes prohibitively expensive for large systems. Approximations could be introduced for
 - The sum over high lying unoccupied bands in the response functions
 - Better extrapolation schemes (beyond $(E_{cut})^{-1.5}$ scaling)
- ❑ Large self-correlation error. The RPA correlation energy of the H atom is -0.57 eV!
- ❑ Cancel the self-correlation error by
 - Many-body perturbation theory - Second order (screened) exchange
 - TDDFT - $f_{xc} \neq 0$.

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