Satellite structures in photoemission and inelastic scattering

Recent developments using a dynamic exchange-correlation kernel of TDDFT

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Introduction & Motivation

A common ingredient to the simulation of many electronic spectroscopies is the response function $\chi(q,\omega)$, which describes the change in density when an external perturbation is applied to the system. This change is measured experimentally as an excitation of the material. One outstanding feature is that $\chi(q,\omega)$ bridges different approaches in the quantum simulation of materials such as time-dependent density-function theory (TDDFT) and many-body perturbation theory (MBPT), for example in the form of Hedin's equations [1]. However, the usual problem often encountered in quantum simulation also applies to the response function: Not all ingredients are known in a functional form lending itself to practical application. Typically we neglect the exchange-correlation contribution to the response function, which is called the exchange-correlation kernel f_{xc}. Approaches to include f_{xc} have been an intense subject of study but broadly successful solutions to the problem are scarce if compared to the vast amount of successful exchange-correlation potentials in regular density-function theory (DFT). While neglect or a static approximation of $f_{xc}(q,\omega)$ can often give good results, some features such as satellite structures in spectroscopic measurements are often not captured at all or wrongly described. In particular we focus here on satellites in photoemission and plasmon excitations in inelastic x-ray scattering. In this study we describe an approach on how to use a numerically tabulated fxc-kernel including single-particle-hole and two-particle two-hole excitations, which was calculated for the homogeneous electron gas (HEG) [2,3] in both TDDFT and beyond-GW applications. We study the effect of the kernel on the calculation of the dynamic structure factor (inelastic X-ray scattering) and the spectral function (photoemission) of sodium and silicon.

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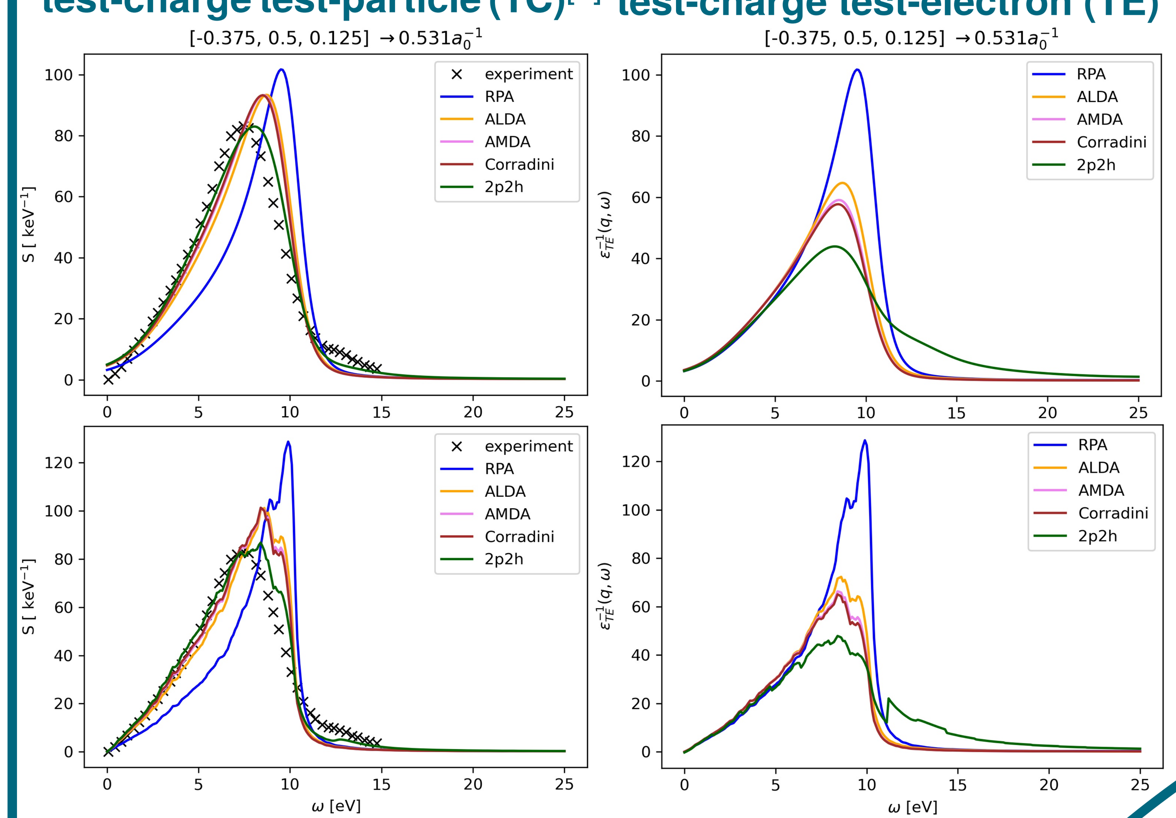
TDDFT

Dynamic structure factor $S(q,\omega)$ of Na

test-charge test-particle (TC)[2] test-charge test-electron (TE)



S(q,ω) of Na has two distinct features:

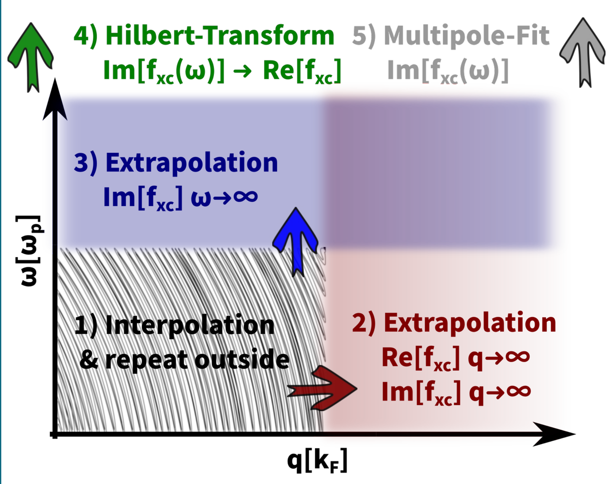
- a plasmon energy at ca. 6eV, which is predicted too large
- a double plasmon peak at 12eV, which is not captured by a static kernel

We now employ the (q,ω)-dependent 2p2h kernel in the calculation of both test-charge test-particle and test-charge test-electron dielectric functions and aim to correct the plasmon position and introduce the double plasmon.
experiment [5]

$$\epsilon_{TC}^{-1}(q,\omega) = 1 + v(q)\chi(q,\omega)$$
$$\epsilon_{TE}^{-1}(q,\omega) = 1 + [v(q) + f_{xc}(q,\omega)]\chi(q,\omega)$$
$$S(q,\omega) = -\frac{\hbar|q|^2\Im[\epsilon^{-1}(q,\omega)]}{4\pi^2 e^2\rho}$$

- Only the ω-dependent f_{xc} recovers the double plasmon resonance of Na
- The outer vertex in ϵ_{TE} is synergistic with the inner vertex in $\chi \Rightarrow$ impact on self-energy in GW?

Working with numerical data for f_{xc}



Representing kernel with anti-resonant pole functions ϕ_1 along real axis:

$$\phi_1(\omega,\eta,\omega_p) = \frac{1}{\omega-\omega_p+i\eta} - \frac{1}{\omega+\omega_p-i\eta} = \frac{2\omega_p - 2i\eta}{\omega^2-(\omega_p-i\eta)^2} \Rightarrow f_{xc}(\omega,\omega_p,i\eta) = \sum_i \phi_i(\omega,\omega_{p_i})$$

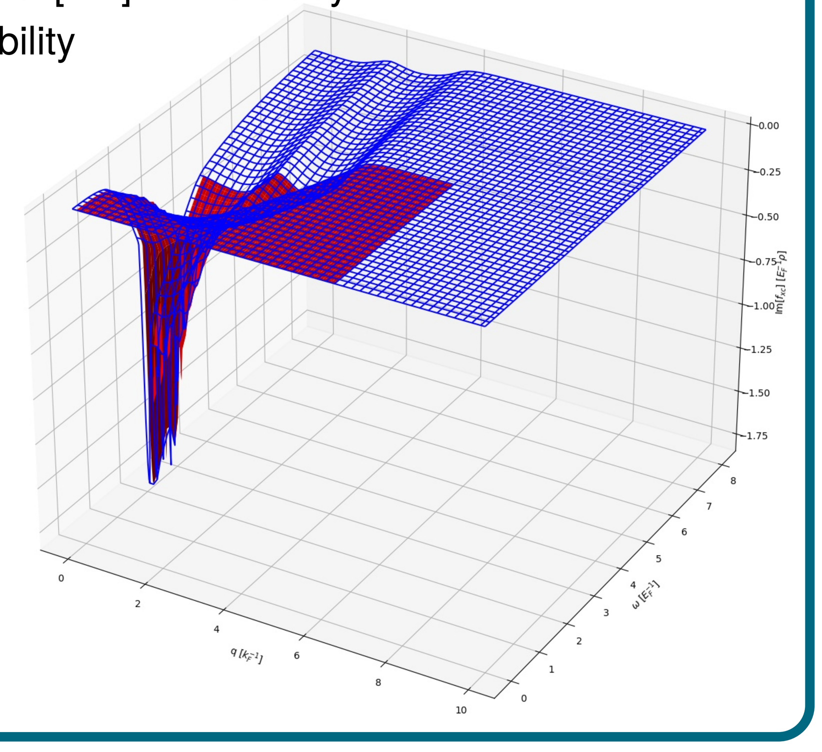
ϕ_1 is defined for a variable $z = \omega + i\eta\,\mathrm{sgn}(\omega)$ and parameter ω_p. Writing down $\phi_1(z,\omega_p)$, the *analytic continuation* becomes apparent:

along real axis ($\eta \neq 0$): $$\phi_1(z,\omega_p) = \frac{1}{\omega+i\eta\,\mathrm{sgn}(\omega)-\omega_p} - \frac{1}{\omega+i\eta\,\mathrm{sgn}(\omega)+\omega_p} = \frac{1}{z-\omega_p} - \frac{1}{z+\omega_p} = \frac{2\omega_p}{z^2-\omega_p^2}$$

on imag. axis ($z = 0 + i\omega$): $$\phi_1(0+i\omega,\omega_p) = \frac{2\omega_p}{(i\omega)^2-\omega_p^2} = \boxed{\frac{2\omega_p}{\omega^2-\omega_p^2}}$$

- Connector approach permits to import kernel for suitable density [8,9]
  - The pole representation is much more versatile than pure data
  - Possibility of evaluation in the entire complex plane
  - Implemented for 2p2h-kernel [2-4] in this study
  - Increased transferability

$f_{xc}(\omega,q,r_s)$



Linear Response χ

The linear response function of TDDFT χ describes the change in the density ρ when the external potential changes. χ_0 is the independent-particle response function, which does the same for V_{eff}.

$$\delta\rho(1) = \chi(12)\delta V_{ext}(2)$$
$$\delta\rho(1) = \chi_0(12)\delta V_{eff}[\rho](2) \Rightarrow \chi_0^{-1}(12) = \frac{\delta V_{eff}(2)}{\delta\rho(1)}$$

By relating the two equations we obtain the Dyson equation for χ, which requires as an ingredient the functional derivative of v_{xc} w.r.t. the density. We call this quantity f_{xc}, the exchange-correlation kernel.

$$\delta V_{eff}(2) = \delta V_{ext}(2) + \delta V_H(2) + \delta V_{xc}(2) \Rightarrow \frac{\delta V_{eff}(2)}{\delta\rho(1)} = \frac{\delta V_{ext}(2)}{\delta\rho(1)} + \frac{\delta V_H(2)}{\delta\rho(1)} + \frac{\delta V_{xc}(2)}{\delta\rho(1)}$$
$$= \chi_0^{-1}(12) = \chi^{-1}(12) + v(12) + f_{xc}(12)$$

χ can alternatively be expressed in terms of Green's functions: $\chi(12) = -iG(12)G(21^+)$

$$\boxed{\Rightarrow \chi(12) = \chi_0(12) + \chi_0(12)[v(12) + f_{xc}(12)]\chi(12)}$$

In the modeling of spectroscopies such as photoemission we are interested in the spectral function A(ω). An ingredient to calculate it is the screened Coulomb interaction W. For spectroscopies such as IXS or EELS we are interested in the dielectric function ϵ.

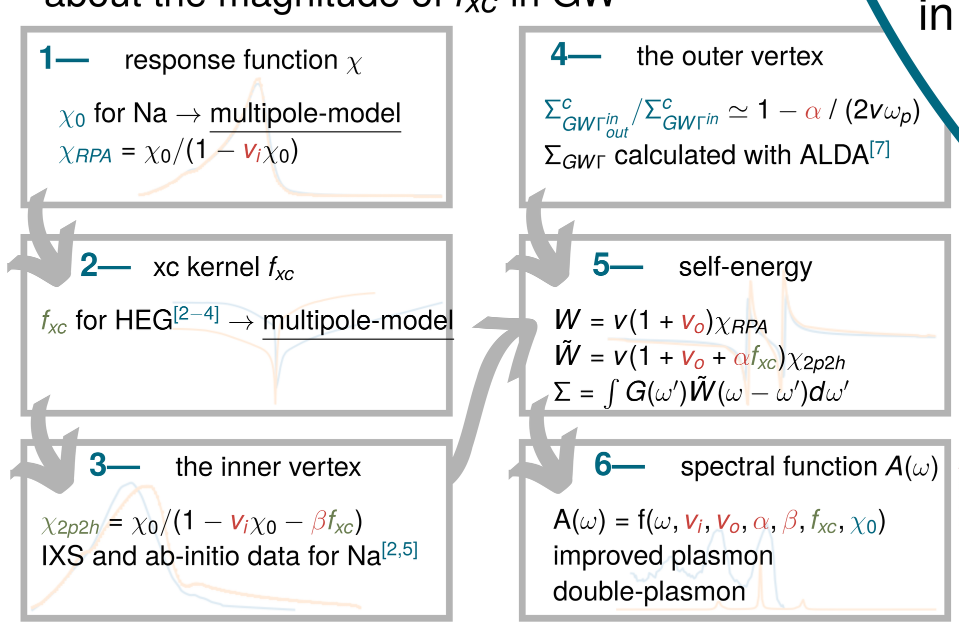
$$\epsilon^{-1}(12) = 1 + v(12)\chi(12)$$
$$W(12) = \epsilon^{-1}(12)v(12)$$

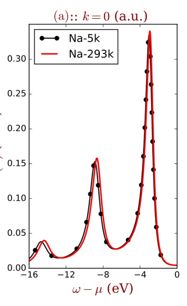
We typically neglect the contribution of f_{xc} to either quantities and as such are missing important physics.

beyond-GW

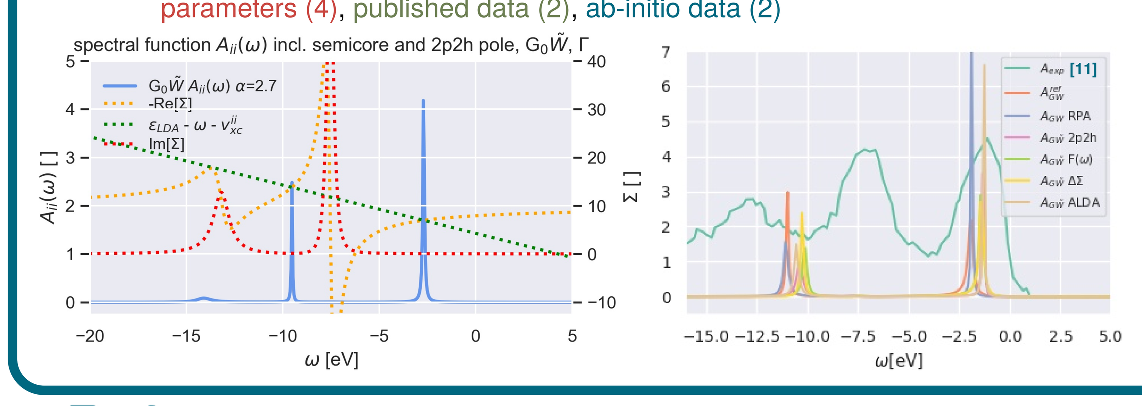
Analytic model for Na

- We look at photoemission satellites
- The GW spectral function has a (wrong) satellite (*plasmaron*), which is an artefact of an intersection of the $\Re[\Sigma]$ [6]
- A first pure analytic model showed that inner and outer vertex are synergistic
- A refined model with ab-initio helped learn about the magnitude of f_{xc} in GW





parameters (4), published data (2), ab-initio data (2)

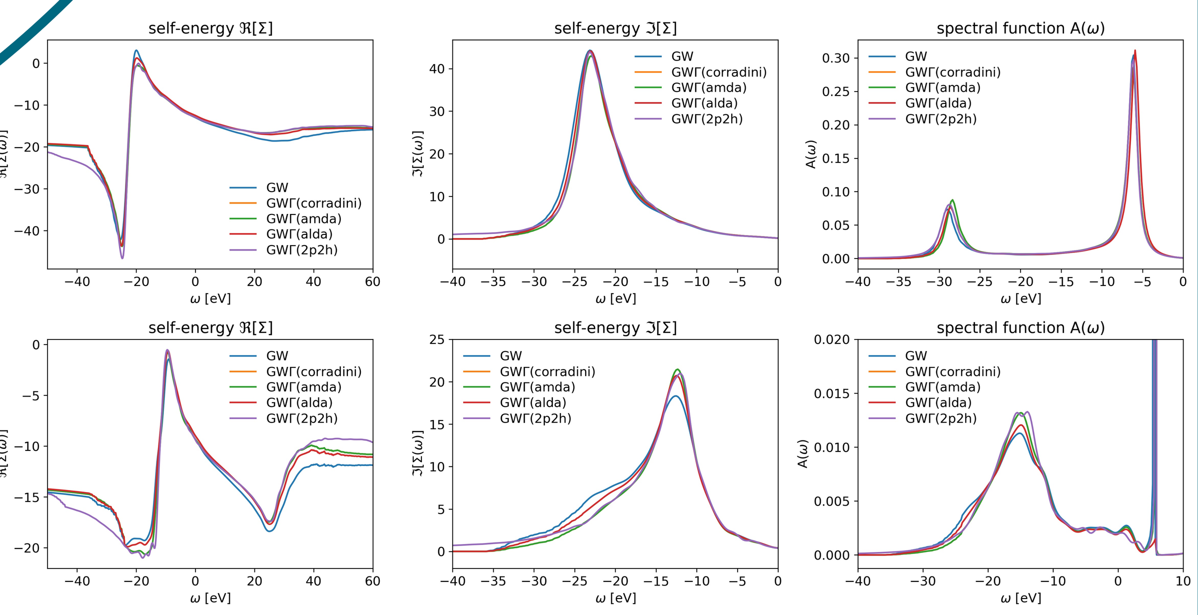


- In principle the approach can correct the GW satellite and create a double plasmon
- The magnitude of f_{xc} determines if in a fully ab-initio implementation we will have the correction

beyond-GW

Photoemission of Si

- We have implemented the multipole-expansion from above in the dp-code
- The state-of-the-art for the description of plasmon satellites in silicon is the cumulant expansion [6]
- We calculate the GWΓ spectral functions including the inner and outer vertex to avoid the cumulant approach



Work in Progress

- $\Re[\Sigma]$ modified in problematic region and $\Im[\Sigma]$ shifted to lower energies
- plasmon slightly improved but double plasmon not visible

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