Title: Green's function approach to vibrational contributions in X-ray spectroscopy

Andrey Geondzhian, Keith Gilmore
European Synchrotron Radiation Facility, 71 Avenue des Martyrs, 38000 Grenoble, France
andrey.geondzhian@esrf.fr

Resonant inelastic X-ray scattering (RIXS) is a promising technique for obtaining electron-phonon coupling constants [1]. However, the ability to extract these coupling constants throughout the Brillouin zone for crystalline materials remains limited. To address this need, we developed a Green's function formalism to capture electron-phonon contributions to core–level spectroscopes without explicitly solving the full vibronic problem.

Our approach is based on the cumulant expansion of the Green's function and density functional theory (DFT) based dynamical response calculations. We have constructed related vibronic Green's functions for addressing X-ray photoemission spectroscopy (XPS), X-ray absorption spectroscopy (XAS), and RIXS. In the case of the XAS and RIXS, we used the concept of an effective exciton Green's function, which accounts implicitly for particle-hole interference effects that have previously proved challenging [2].

As a first test, we apply our formalism to small molecules, such as acetone, for which there exists high quality experimental data showing clear vibrational features. In all cases -- XPS, XAS and RIXS -- agreement with experiment is very satisfactory. These calculations, based in DFT, contain no free parameters and can be used predictively. The route for extending this work to include non-local vibrational modes (phonons) will be outlined.

While it is typically claimed that RIXS probes electron-phonon coupling in materials, we show that this interpretation cannot reproduce the experimental data. Instead, we find that RIXS quantifies exciton-phonon coupling. The difference between the two values can be significant in the soft X-ray regime when the effect of the core-hole cannot be neglected.

[1] L.J.P. Ament, M. van Veenendaal and J. van den Brink, European Physics Letters 95, 27008 (2011)
[2] Kas, J. J. and Rehr, J. J. and Curtis, J. B., Phys. Rev. B 94 3 035156 (2016)