

# Core and Valence Photoelectron Spectroscopy Using a Scalable Molecular GW Implementation

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Fast and accurate simulation enables the analysis and interpretation of complex structural and dynamical features contained in photoelectron spectroscopies. The GW approximation is prominent among the theoretical methods used for such simulations due to its relatively low computational cost and good accuracy profile. The GW approximation has been used with considerable success over the last three decades and has a widespread reputation as an accurate and efficient method for the prediction of band structures in solids. In recent years, there has been growing interest in the GW method for molecular and finite systems, and many molecular GW implementations exist nowadays. Although the GW approximation can only be used to simulate charged excitations, the quasiparticle energies obtained have been widely used for subsequent Bethe-Salpeter equation (BSE) calculations to obtain information about neutral excitations, especially charged-transfer ones.

Here, we will show that a molecular GW implementation based on the contour-deformation technique, can be efficiently paired with the MINRES linear equation solver and with the density fitting technique to reduce the overall scaling of the approach. We use this implementation to predict core-level binding energies in water clusters of up to a few hundred atoms, with results in very good agreement to those obtained from the Green's-function coupled-cluster (GFCC) method. Finally, we will also show that the GW approximation can be used for the accurate prediction of valence ionization spectra of hydrated 3d transition metal complexes by using clusters with up to 60 water molecules. Special emphasis will be placed on the Cu<sup>2+</sup> aqua complex, where structural dynamics plays an important role.

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