Important role of screening the electron-hole exchange interaction for the optical properties of molecules near metal surfaces - DTU Orbit (17/04/2019)

Important role of screening the electron-hole exchange interaction for the optical properties of molecules near metal surfaces

Optical experiments on nanostructures such as molecules, one- or two-dimensional materials, are often performed with the nanostructures in close proximity of a substrate or some other polarizable media. In this case, the Bethe-Salpeter equation (BSE) can be used to calculate the optical excitations of the nanostructure by including the effect of the substrate via the screened electron-hole interaction. Here we show, that in such an approach, where the states of the substrate are not explicitly included in the BSE Hamiltonian but only enter through the screened Coulomb interaction, it is important also to screen the electron-hole exchange interaction. For the case of molecules like benzene physisorbed on the metallic Au(111) surface, the screening of the exchange interaction by the substrate redshifts the lowest optical transition by up to 300 meV. Furthermore, the screening of the exchange is essential in order to obtain the correct ordering of the size of quasiparticle and optical energy gap.