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Constrained-DFT method for energy level alignment of metal-molecule interfaces AMAURY DE MELO SOUZA, Trinity College Dublin, CHAITANYA DAS PEMMARAJU, Lawrence Berkeley National Laboratory, IVAN RUNGGER, STEFANO SANVITO, Trinity College Dublin — The electron transport properties of molecular junctions depend strongly on the alignment of the molecule's ionization potential (IP) and electron affinity (EA) with respect to the metal Fermi energy. It has been demonstrated experimentally[1] and theoretically **J. Neaton et al., Phys. Rev. Lett. 97, 216405 (2006).** that the IP and the EA of molecules change when they are absorbed on a polarizable substrate, due to the formation of an image charge in the surface when an electron is either removed or added to the molecule. While within the GW approximation such a renormalization can be described, the energy levels of standard density functional theory (DFT) fail to capture it. However, DFT total energy differences between charged and neutral systems can usually describe IP and EA of molecules rather well. Here we therefore apply constrained DFT (CDFT) to calculate charge transfer energies between molecules and a metallic substrate in the weak coupling limit. We present CDFT results for the IP and EA of a benzene molecule as function of molecule-surface separation, and find good agreement with GW calculations. Within the CDFT approach we also evaluate the image plane height as function of separation.

[1]M. T. Greiner et al., Nature Mater. **11**, 76 (2011)

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