Evaluating the contribution of continuum electronic states to van der Waals dispersion interactions

Mohammad Reza Karimpour, Peter Szabo, Dmitry Fedorov, Alexandre Tkatchenko

University of Luxembourg
reza.karimpour@uni.lu

High level calculations have demonstrated that in the case of hydrogen atom around one-third of the atomic polarizability arises from the quantum mechanical fluctuations of atomic electrons into the continuum electronic states. Consequently, there would be a considerable contribution from continuum electronic states to van der Waals (vdW) dispersion interaction between atoms. This contribution is typically neglected due to the lack of continuum states in atomic models, e.g. quantum drude oscillators [1], which are widely used for evaluating vdW dispersion interactions between atoms in preceding studies [2, 3, 4]. In the present work, we model atomic systems with simple one-dimensional potentials possessing both bound and continuum electronic states. Then for two of such modeled atoms, we calculate vdW dispersion interaction from second-order perturbation theory. The results from our analytical and numerical investigations demonstrate considerable contributions from continuum states to vdW interaction between atoms. We also show that the results for hydrogen atoms are recoverable from the models in our work under certain conditions for interacting atoms.

References

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