The Derivative Discontinuity from H₂ to the Anderson Model

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Exchange-Correlation Functionals

Here we show the performance of many different exchange-correlation functionals. Individual errors are shown for all the molecules in the G3 set as well as a standard set of hydrogen-transfer barriers. The errors for infinitely stretched H₂ and H₂⁺ are massive. This is a manifestation of the derivative discontinuity.

Fractional Nuclei: a tool for theoreticians

We have seen that the energy of two protons with one and two electrons is a massive challenge for all DFT methods. What about the density? Of course there is no problem as the density is constrained by symmetry. Now consider removing that symmetry by smoothly changing the nuclear charge on one of the protons. This is the H₂⁺, molecule. HF is exact. At infinite separation we can see discontinuous behaviour of the density, and also the decolocalisation error of BLYP.

The gap of the 1D-Hubbard model

The 1D-Hubbard model contains the interesting physics of strong correlation. If we consider the 2-site Hubbard model with occupation from 0 to 4, of course the U → ∞ limit corresponds exactly to infinitely stretched hydrogen systems. In the following τ=1, We investigate the large U limit to see how many-body methods perform. The Hubbard model nicely encapsulates the need to describe both H₂ and H₂⁺, with the same method to correctly describe the gap at half-filling (2 electrons). Here, the recent spin-PIPA method from Yang and coworkers which has been shown to give the flat-plane also begins to correctly describe the gap of the 2-site Hubbard model. It is correct in the U → ∞ limit. We can see the failure of methods such as MP2 which diverges for degenerate situations such as H₂ and dRPA which corrects that error but only at the cost of an error in H₂⁺.

Anderson Model: occupation of the impurity site

We consider an Anderson model with several non-interacting sites with one impurity which has an electron-electron interaction term U compared to the hopping term t and an onsite chemical potential, μ. As we vary the chemical potential we see the occupation of the impurity site change. This change in the large U limit is very discontinuous.

References