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Exchange-correlation energies from pairing matrix fluctuations and the particle-particle Random Phase Approximation[1]

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Despite their unmatched success for many applications, commonly used local, semi-local and hybrid density functionals still face challenges when it comes to describing long-range interactions, static correlation and electron delocalization. Density functionals of both the occupied and virtual orbitals are able to address these problems. The particle-hole Random Phase Approximation (ph-RPA), for instance, has recently known a revival as a density functional approximation, justified by the adiabatic-connection-fluctuation-dissipation (ACFD) theorem. We formulate an adiabatic connection for the correlation energy in terms of pairing matrix fluctuations, similar in form to the ACFD theorem. With numerical examples of the particle-particle Random Phase Approximation (pp-RPA), the lowest-order approximation to the pairing matrix fluctuation, we illustrate the potential of density functional approximations based on this adiabatic connection. The pp-RPA is size-extensive, self-interaction free, fully anti-symmetric, describes the strong static correlation limit in H_2 and eliminates delocalization errors in H_2^+ and other single-bond systems. It gives good non-bonded interaction energies – competitive with the ph-RPA – with the correct R^{-6} asymptotic decay as a function of the separation R, much better atomization energies than the ph-RPA, and reaction energies of similar quality. The adiabatic connection in terms of pairing matrix fluctuations thus paves the way for promising new density functional approximations.

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