Exchange-Correlation and Electronic Excitation Energies from Pairing Matrix Fluctuations and the Particle-Particle Random Phase Approximation

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We have developed an adiabatic connection to formulate the ground-state exchange-correlation energy in terms of pairing matrix linear fluctuations, opening new a channel for density functional approximations. This resulting method has many highly desirable properties. It has minimal delocalization error with a nearly linear energy behavior for systems with fractional charges, describes van der Waals interactions similarly and thermodynamic properties significantly better than the conventional RPA, and eliminates static correlation error for single bond systems. It is the first known functional with closed-form dependence on orbitals, which captures the energy derivative discontinuity in strongly correlated systems. We also adopted pp-RPA to approximate the pairing matrix fluctuation and then determine excitation energies by the differences of two-electron addition/removal energies. This approach captures many types of interesting excitations: single and double excitations are described accurately, Rydberg excitations are in good agreement with experimental data and CT excitations display correct $1/R$ dependence.