Singlet–Triplet Energy Gaps for Diradicals from Particle–Particle Random Phase Approximation YANG YANG, DEGAO PENG, Duke Univ, ERNEST DAVIDSON, University of Washington, WEITAO YANG, Duke Univ — The particle–particle random phase approximation (pp-RPA) has been applied to the calculation of vertical and adiabatic singlet–triplet energy gaps for a variety of categories of diradicals, including diatomic diradicals, carbene-like diradicals, disjoint diradicals, four-π-electron diradicals, and benzynes are calculated. Except for some excitations in four-π-electron diradicals, where four-electron correlation may play an important role, the singlet–triplet gaps are generally well predicted by pp-RPA. With a relatively low O(r4) scaling, the pp-RPA with DFT references outperforms spin-flip configuration interaction singles. It is similar to or better than the (variational) fractional-spin method. For small diradicals such as diatomic and carbene-like ones, the error of pp-RPA is slightly larger than noncollinear spin-flip time-dependent density functional theory (NC-SF-TDDFT) with LDA or PBE functional. However, for disjoint diradicals and benzynes, the pp-RPA performs much better and is comparable to NC-SF-TDDFT with long-range corrected ωPBEh functional and spin-flip configuration interaction singles with perturbative doubles (SF-CIS(D)). In particular, with a correct asymptotic behavior and being almost free from static correlation error, the pp-RPA with DFT references can well describe the challenging ground state and charge transfer excitations of disjoint diradicals in which almost all other DFT-based methods fail. Therefore, the pp-RPA could be a promising theoretical method for general diradical problems.

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