Linked-cluster formulation of screened electron-hole interaction from explicitly-correlated geminal functions without using unoccupied states

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Electron-hole or quasiparticle representation plays a central role in describing electronic excitations in many-electron systems. For charge-neutral excitation, the electron-hole interaction kernel is the quantity of interest for calculating important excitation properties such as optical gap, optical spectra, electron-hole recombination and electron-hole binding energies. The electron-hole interaction kernel can be formally derived from the density-density correlation function using both Green's function and TDDFT formalism. The accurate determination of the electron-hole interaction kernel remains a significant challenge for precise calculations of optical properties in the GW+BSE formalism. From the TDDFT perspective, the electron-hole interaction kernel has been viewed as a path to systematic development of frequency-dependent exchange-correlation functionals. Traditional approaches, such as MBPT formalism, use unoccupied states (which are defined with respect to Fermi vacuum) to construct the electron-hole interaction kernel. However, the inclusion of unoccupied states has long been recognized as the leading computational bottleneck that limits the application of this approach for larger finite systems. In this work, we present an alternative derivation that avoids using unoccupied states to construct the electron-hole interaction kernel. The central idea of our approach is to use explicitly correlated geminal functions for treating electron-electron correlation for both ground and excited state wave functions. Using this ansatz, we demonstrate with diagrammatic techniques that the frequency-dependent electron-hole interaction kernel can be expressed only in terms of connected closed-loop diagrams. We show that the cancelation of disconnected diagrams is a consequence of linked-cluster theorem in real-space representation. Our results also demonstrate that the renormalized operators appearing in the real-space representation are equivalent to infinite-order summations of particle-hole diagrams in the occupation-number representation. The electron-hole interaction kernel derived in this work was used to calculate excitation energies in atoms, molecules, clusters and quantum dots and the results for these systems will be presented. The results will also be compared to other methods including CIS, TDHF, TDDFT, EOM-CCSD, and GW+BSE. The numerical results highlight the effectiveness of the developed method for overcoming the computational barrier of accurately determining the electron-hole interaction kernel to applications of large finite systems such as quantum dots and nanorods.

References:

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