

Development of multicomponent coupled-cluster theory for treating electron-hole correlation in multiexcitonic systems

Ben Ellis and Ari Chakraborty

Department of Chemistry, Syracuse University

Multicomponent systems are defined as chemical systems that require quantum mechanical description of two or more different types of particles without invoking the Born-Oppenheimer approximation. Examples of physical systems that require multicomponent quantum mechanical formalism include non-Born–Oppenheimer electron-nuclear interaction in molecules, electron-hole interaction in electronically excited nanoparticles, and electron-positron interactions. The central challenge in the theoretical treatment of multicomponent systems is in capturing the many-body correlation effects that exist not only between particles of identical types (electron-electron) but also between particles of different types (electron-nuclear and electron-hole). In this work, the development and implementation of multicomponent coupled-cluster (mcCC) theory¹ for treating particle-particle correlation in multicomponent systems is presented. The developed method provides a size-consistent and size-extensive theory for a balanced treatment of many-particle correlation in a general multicomponent system. The multicomponent CC ansatz presented here is of the form $|\Psi_{cc}\rangle = e^{T_1^I + T_2^I + T_1^{II} + T_2^{II} + T_{11}^{II} + T_{12}^{II} + T_{21}^{II} + T_{22}^{II}} |0^I 0^{II}\rangle$ and is an extension of many-electron CCSD formulation for multicomponent system with type-I (e.g., electrons) and type-II (e.g., protons, positrons, or holes) particles. This work focuses on the three critical aspects of the multicomponent CC ansatz. The first is the form of the T-operators, second is the choice of the ground state reference function $|0^I 0^{II}\rangle$, and the third is related to issues of practical implementation of the method and perturbative approximation to the multicomponent t-amplitudes. The presence of type-II particles requires us to renormalize the traditional electronic normal-ordered Hamiltonian. The analysis of this renormalization on the diagrams for the energy and t-amplitude equations for multicomponent implementation and comparison with EOM-CC and Green's function methods will be presented. The reference state $|0^I 0^{II}\rangle$ in the CC wave function can be obtained either by using two independent single-component Hartree-Fock calculations or by using a single multicomponent Hartree-Fock calculation. A comparison of the two approaches will be presented. The cluster amplitudes in the mcCC wave function were obtained by projecting the mcCC equation on to a direct product space of singly and doubly excited states of type-I and II particles and solving the resulting equations iteratively. The derivation of these equations was achieved by using computer-assisted application of the generalized Wick's theorem and computer-assisted CC source code generation using an integral-driven approach will be presented. The applicability of the developed method was demonstrated by computing ground state energy of positronium hydride (PsH), and exciton and biexciton binding energies in CdSe, CdS, CdTe, and PbSe quantum dots.¹ The results were benchmarked against full configuration interaction method,¹ electron-hole explicitly correlated Hartree-Fock method,² and experimental binding energies.^{3,4} In summary, these results demonstrate that inclusion of connected excitations in type I-II space is critical for capturing electron-hole correlation in multiexcitonic systems.

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