Nonorthogonal configuration interaction: pitfalls and prospects

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Nonorthogonal configuration interaction, NOCI, is a CI approach in which each electronic configuration, or group of configurations, is expressed in terms of its own (optimized) orbitals. Conceptually, NOCI is attractive since, along with accounting for electron correlation and orbital relaxation, it also gives short wavefunction expansions and allows for a clear chemical interpretation.

In recent years we have developed, implemented and applied a new NOCI scheme that is especially suited for the study of electronic excitations that involve multiple molecules or molecular fragments[1]. In this approach, the wavefunction for an ensemble of molecules/fragments is written as a CI expansion in terms of antisymmetrised products of molecular wavefunctions. In practice, the molecular wavefunctions are commonly of CASSCF or RASSCF type, but other molecular wavefunctions can also be used.

We have applied this NOCI approach using the GronOR package[2] for the study of energy and excitation transfer processes, amongst which singlet fission, a molecular process that appears to be a promising way to enhance the efficiency of organic photovoltaics.

In this presentation a number of computational and conceptual aspects of NOCI will be discussed, along with a few practical examples from recent studies.

1. T. P. Straatsma, R. Broer, S. S. Faraji, and R. W. A. Havenith, Annual Reports in Computational Chemistry 14, 77 (2018).
2. R. Broer, S. S. Faraji, C. de Graaf, R. W. A. Havenith, T. P. Straatsma, L. E. Aguilar Suarez, M. A. Izquierdo Morelos, R. K. Kathir, and M. K. Wibowo, "GronOR non-orthogonal configuration interaction, http://gronor.org," (2018).