Many-electron Correlation from Two Electron-Reduced Density Matrices

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Because electrons are indistinguishable with pairwise interactions, the energy of any many-electron molecule can be written as a functional of a two-electron quantity—the two-electron reduced density matrix (2-RDM). While many successful approaches exist to recover correlation effects, most are not tractable in the limit of strong correlation in large molecular systems or materials. The 2-RDM methods can treat strongly correlated electrons at a computational scaling that grows non-exponentially with system size. Computing the 2-RDM of an $N$-electron quantum system requires that we constrain it to represent $N$ electrons through constraints known as $N$-representability conditions. Three different approaches to the direct calculation of the 2-RDM have recently been developed: (1) the variational 2-RDM method [1,2] in which $N$-representability conditions are imposed explicitly by semidefinite programming, (2) the parametric 2-RDM method [3] in which $N$-representability conditions are imposed implicitly by parameterization, and (3) the anti-Hermitian contracted Schrödinger equation (CSE) method [4] in which the ACSE in combination with cumulant reconstruction of the 3-RDM is solved for the 2-RDM. In this lecture we will discuss recent advances in 2-RDM methods including applications to studying metal-to-insulator transitions [1], conical intersections [4], polyaromatic hydrocarbons [2], and firefly bioluminescence [5].