Electronic Structure and Processes from Two-Electron Reduced Density Matrices

David A. Mazziotti
Department of Chemistry
James Franck Institute
929 E. 57th St.
The University of Chicago
Chicago, IL 60637 USA

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). Computing the 2-RDM of an *N*-electron quantum system requires that the two electrons represent the *N* electrons through constraints known as *N*-representability conditions. Three approaches to the direct calculation of the 2-RDM will be discussed: (i) the variational 2-RDM method [1], (ii) the parametric 2-RDM method [2,3], and (iii) the solution of the contracted (CSE), or anti-Hermitian contracted (ACSE), Schrödinger equation [4,5]. First, the variational 2-RDM method minimizes the energy as a functional of the 2-RDM constrained by *N*-representability conditions. Because the *N*-representability conditions are not based on perturbative arguments, strong electron correlation can be accurately approximated with a cost that scales polynomially with system size. Second, the parametric 2-RDM method, a variant of the variational method, improves upon the accuracy of the coupled cluster singles-doubles at a computational cost that scales like configuration interaction singles-doubles. It is particularly useful in treating problems with moderate multi-reference correlation as in single-bond dissociation and diradicals. Third, the ACSE method solves for the 2-RDM through a cumulant-based reconstruction of the 3-RDM from the 2-RDM. The ACSE enables the computation of strongly correlated ground- and excited-state energies at a cost that grows quadratically with the number of active orbitals. Applications of the 2-RDM methods will be made to the description of conical intersections, polyaromatic hydrocarbons, and bioluminescence. Additionally, RDM theory can also be employed to perform measurement-driven reconstruction of quantum processes [6]. In quantum process reconstruction we extract Information about many-particle systems from experimental data in the form of 1- or 2-RDMs.

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