Natural Orbital Functional Theory of the Molecular Electronic Structure

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The one-particle reduced density matrix (1-RDM) functional theory, was proposed a few decades ago [1]. One major advantage of such density matrix formulation is that the kinetic energy is explicitly defined and does not require the construction of a functional. Hence, the electron correlation functional remains as the only unknown energy functional. Since, the electron correlation is a known functional of the two-particle reduced density matrix (2-RDM), a reconstruction functional of the 2-RDM in terms of 1-RDM solves the problem on formal grounds, but poses the problem of its N-representability, not solved yet. Here we will present an explicit recontruction of the 2-RDM in terms of the spectral expansion of the 1-RDM using the cumulant expansion [3] which leads to the Piris Natural Orbital Functional (PNOF) [4]. The PNOF is based on an explicit ansatz of the two-particle cumulant $\lambda(\Delta,\Pi)$ satisfying the D-, Q- and G-necessary positivity conditions for the 2-RDM [5]. Appropriate forms of matrices $\Delta(\{n_p\})$ and $\Pi(\{n_p\})$ lead to different implementations of the PNOF [6].

In this presentation, special emphasis will be put on the spin conserving NOF theory [7]. Some examples of strongly correlated systems, where electron density functionals yield pathological failures, are shown to illustrate the capability of the NOF theory. In particular, our NOF implementation yields a remarkably accurate description of the homolitic dissociation of a number of selected diatomic molecules. It is also found that the method describes correctly their dissociation limit yielding an integer number of electrons on the dissociated atoms. Compounds with full or partial diradical character have been also considered. We have found that PNOF shows a reliable description of these species, and yields the correct trends in their occupation numbers as compared highly correlated with wave-function methods such as CASSCF. The calculations presented here have been carried out with our implementation, the PNOFID code [8], based on a recently proposed algorithm [9] which yields the natural orbitals by an iterative diagonalization of a generalized pseudo-Fockian matrix.

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