

Density Matrix Functional Theory for Molecules and Solids

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Density-matrix functional theory has enjoyed increasing popularity in recent years. For the one-body reduced density matrix, the theory rests on a Hohenberg-Kohn-type theorem which was formulated by Gilbert [1]. Employing some well-known reduced-density-matrix functionals [2] for the exchange-correlation energy, we minimize the total energy with the appropriate constraints ensuring N-representability of the density matrix and conservation of the total particle number. Atoms and molecules, periodic bulk insulators, and the electron gas are studied in this way. For molecules, we find that some of the more advanced functionals, such as the BBC3 functional [2], perform as well as MP2, with a much lower numerical cost. This is demonstrated by an extensive comparison using the so-called G2 set of molecules, see Fig 1 below.

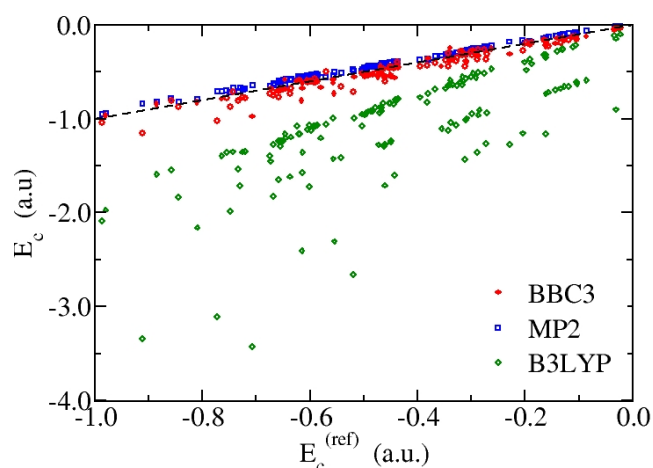


Figure 1: Correlation energies calculated for the G2 set of molecules using various methods (i) the density-matrix functional BBC3, (ii) the density functional B3LYP and (iii) Møller-Plesset-2 (MP2) theory versus a highly accurate quantum chemistry reference calculation E_c^{ref} using CCSD(T).

For insulators we propose a novel method to calculate the fundamental gap Δ [3]. This quantity is defined as the difference between the ionization potential and the electron affinity. Given a system with integer particle number N_0 , the fundamental gap can be expressed rigorously as the discontinuity which the chemical potential μ exhibits at the integer N_0 , i.e., $\Delta = \mu(N_0 + \eta) - \mu(N_0 - \eta)$ with a positive infinitesimal η . We demonstrate [3] that this discontinuity, when evaluated within density-matrix functional theory, represents an excellent measure of the gap, far superior to LDA or GGA calculations. Studying the electron gas [4], we finally propose a novel functional [5], which performs well in two extreme limits: For the dissociation of closed-shell molecules into open-shell fragments, and for the electron gas.

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