

Exact Hohenberg-Kohn Functional for a Lattice System

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Standard local and semi-local functionals in ground-state density functional theory are known for their shortcomings in describing correct charge transfer, dissociation energies of molecular ions, band gaps of materials, and barriers of chemical reactions [1,2]. One major reason for these shortcomings is the delocalization error of commonly used approximations of the exchange-correlation functional. Approximated functionals violate the derivative discontinuity of the exact potential and hence, underestimate ground-state energies for fractional particle numbers, as in the stretched limit of molecules [2,3]. Some of these shortcomings are partially resolved by ensemble density functional theory [4], logarithmically diverging enhancement factors in GGA functionals [5], or the particle-particle random-phase approximation [6]. To understand the failures of approximate functionals, to gain insight into the behavior of the exact functional, and to devise new approximations, we investigate the exact solution of the many-body Schrödinger equation in Fock space for a lattice system with a soft-Coulomb interaction term. Using quadratic optimization with quadratic constraints, or alternatively exact diagonalization, we explicitly construct the *exact* Hohenberg-Kohn functional and the mapping from densities to wavefunctions [7]. The exact functional exhibits softened *intra-system derivative discontinuities* in the low-density limit that resemble the inter-system derivative discontinuity widely discussed in the density functional community [3]. Besides the energy expectation value also the CI-coefficients of the wavefunction can be regarded as functional of the density. We show that also the CI-coefficients exhibit a softened intra-system derivative discontinuity which directly affects expectation values of general operators. Using exact many-body densities, we compute exact Kohn-Sham potentials by inverting the Kohn-Sham equations. The exact potentials exhibit clear steps and peaks and we observe the same softened intra-system derivative discontinuity in the low-density limit. We discuss how such effects can be incorporated on top of simple exchange-correlation functionals. The description of many physical phenomena linked to charge-transfer processes (both in the static and dynamical regimes) require a proper account of those "intra-system derivative discontinuities". The present work provides a new avenue to a quantitative description of such effects within an efficient density-functional scheme.

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