Variational Fitting Methods for Electronic Structure Calculations

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We review the basics and the evolution of a powerful and widely applicable general approach to the systematic reduction of computational burden in many-electron calculations. Variational fitting of charge densities (either total or partial) has the great advantage, for quantum mechanical calculations, that it respects the stationary property which is at the heart of the success of the basis set expansion methods ubiquitous in computational chemistry and materials physics. The key point is easy. In a finite system, independent of whether the fitted charge distribution is constrained to contain the proper amount of charge, variational fitting guarantees that the quantum mechanical total energy retains the stationary property. Thus, many-electron quantum mechanics with variational fitting of a charge density in an incomplete charge-fitting basis set behaves similarly as the exact quantum mechanical energy does when evaluated with an incomplete basis set to fit wavefunctions or spin-orbitals. Periodically bounded systems are a bit more subtle but the essential stationarity is preserved. This preservation of an exact property is quite distinct from truncation of the resolution of the identity in a basis. Variational fitting has proven to have benefits far beyond the original objective of making a Gaussian-orbital basis calculation of an early density functional computationally feasible. We review many of those developments briefly, with guidance to the pertinent literature.

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