

Using Wave-function Approaches to Provide Insight into Density-Functional Theory: An Adiabatic Connection Approach

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The adiabatic connection (AC) [1, 2, 3, 4] provides a link between the non-interacting Kohn–Sham (KS) system and physical interacting system via a series of partially interacting systems described by the Hamiltonians and wave-functions

$$H_\lambda[v] = T + \sum_i v(\mathbf{r}_i) + W_\lambda \quad H_\lambda[v]\Psi_\lambda = E_\lambda[v]\Psi_\lambda \quad (1)$$

Where λ is the coupling strength ($\lambda = 0$ for the KS system), T is the kinetic energy operator, the external potential $v(\mathbf{r})$ is adjusted such that the density remains fixed at the physical ($\lambda = 1$) density for all λ values and W_λ is a coupling strength dependent two-electron interaction operator. Following Lieb’s formulation of density-functional theory [5] the energy $E_\lambda[v]$ may be expressed in terms of a convex conjugate functional $F_\lambda[\rho]$, the universal density functional.

$$E_\lambda[v] = \inf_\rho \left(F_\lambda[\rho] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} \right) \quad F_\lambda[\rho] = \sup_v \left(E_\lambda[v] - \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} \right) \quad (2)$$

By choosing a wave-function model, for the calculation of $E_\lambda^{\text{mod}}[v]$ and $\Psi_\lambda^{\text{mod}}$, a hierarchy of universal density functionals $F_\lambda^{\text{mod}}[\rho]$ may be established, which systematically approach the exact universal density functional for each coupling strength λ . In this talk we review our implementation of a scheme to perform the Lieb maximization for $F_\lambda[\rho]$ [6, 7, 8]. The correlation energy of KS-DFT is then recovered by the coupling constant integral

$$E_{c,\lambda}[\rho] = \int_0^\lambda \left\langle \Psi_\lambda \left| \frac{dW_\lambda}{d\lambda} \right| \Psi_\lambda \right\rangle - \left\langle \Psi_0 \left| \frac{dW_\lambda}{d\lambda} \right| \Psi_0 \right\rangle d\lambda \quad (3)$$

The choice of the interaction W_λ specifies the path of the integration and the relevance of this choice to range-separated exchange–correlation functionals will be discussed [9]. Recent efforts and future prospects for utilizing the calculated ACs for the construction of new exchange–correlation functionals for practical calculation will be outlined [10].

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