Towards simple density-functional approximations from accurate *ab initio* theory

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The exchange–correlation energy can be expressed in terms of the well known adiabatic connection formula [1, 2]

$$E_{\text{xc}}[\rho] = \int_0^1 \langle \Psi_\lambda | W | \Psi_\lambda \rangle - J[\rho] \ \ \mathrm{d}\lambda$$

where W is the electron-electron interaction operator, $J[\rho]$ the Coulomb energy and Ψ_λ is a ground state wave function constrained to yield the physical electronic density ρ for all coupling strengths λ between 0 (the Kohn–Sham system) and 1 (the physical system). A brief overview of one approach to calculate the integrand in this formula, using the Lieb variation principle [3–5], will be presented in this talk.

Whilst modelling this integrand can lead to expressions for the exchange–correlation energy [6–8] two key problems afflict the results of this approach: (i) typical non-linear interpolations violate size-consistency and (ii) many models require expensive *ab initio* information for accurate parameterisation. The latter problem reflects the nature of the adiabatic integrand above, expressed in terms of an expectation value over the electron-electron interaction operator. However, most practical density-functional approximations are simple models built from local or semi-local quantities such as $\rho(\mathbf{r})$ and $\nabla\rho(\mathbf{r})$. This leads to something of a language barrier when attempting to compare the inherently non-local adiabatic connection integrand with simple density functionals.

It has been suggested that these issues can be overcome if the adiabatic connection integrand is reduced to the form of an energy density (see for example Ref. [9]). In a specific choice of gauge a coupling constant averaged energy density $\bar{w}_{\text{xc}}(\mathbf{r})$ can be derived with the property

$$E_{\text{xc}}[\rho] = \int \bar{w}_{\text{xc}}(\mathbf{r})\rho(\mathbf{r})\mathrm{d}\mathbf{r}$$

In this talk I will outline how $\bar{w}_{\text{xc}}(\mathbf{r})$ can be calculated accurately from *ab initio* theory and how it may be divided into exchange and correlation contributions. Based on calculations of this quantity for atomic and molecular systems I will discuss future prospects for building improved (semi-) local exchange–correlation functionals.

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