



On the best partitioning of the density functional energy

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Abstract

This essay discusses special features for two different ways of partitioning the density functional energy expression. The contribution, which is part of the special issue for Pratim Chattaraj, was stimulated by a thought-provoking suggestion by him at a recent conference.

Keywords Essay: density functional energy expression · Coordinate scaling · Constrained search

It is a pleasure to contribute this essay as part of the special issue for Pratim Chattaraj.

In density functional calculations, the ground-state electronic energy E is traditionally partitioned as $E = V_{en}[n] + T_s[n] + U[n] + E_{xc}[n]$, where n is the ground-state electron density, V_{en} is the electron-nuclear attraction energy, T_s is the Kohn–Sham non-interacting kinetic energy, U is the classical Hartree energy, and E_{xc} is the exchange–correlation energy. Alternatively, one could partition E as $E = V_{en}[n] + T[n] + V_{ee}[n]$, where T and V_{ee} are, respectively, the true physical interacting kinetic and electron–electron repulsion energies.

Most often, T_s is computed from the optimum orbitals of the Kohn–Sham equations. However, for large complex molecular systems, there has been encouraging progress in approximating T_s directly as an orbital-free functional of n , and a lecture was given at the recent American Chemical Society meeting in New Orleans (March, 2018), where these orbital-free advances were summarized.

During the discussion session, after the lecture, Pratim made an interesting and thought-provoking suggestion, whose essence I now recall: “Since T is the true kinetic energy, perhaps we should work on approximating an orbital-free T instead of T_s .” The response was that with the use of T_s , we can directly take advantage of the known successful

approximations to E_{xc} . Moreover, it is easy to make an approximation to T_s that satisfies its fundamental coordinate scaling requirement, which is that T_s scales homogeneously (as the square of the scale factor) when the coordinates of n are scaled uniformly. The required scaling of T is more complicated because $T = T_s + T_c$, where T_c is the positive kinetic contribution to the correlation energy.

Another consideration is the fact that $T_s < T$, and, independent of other factors, it is generally easier to approximate a smaller quantity than a larger one. Along these lines, the magnitude of E_{xc} is less than the magnitude of $V_{ee} - U$, which is approximated when one uses T .

However, there is something enchanting about the possible use of the full T . Namely, the total energy, E (total), is of course given simply and elegantly by E (total) = $-T[n]$ at the minimizing geometry. It is certainly worthwhile to think about this beautiful virial relation.

In closing, note that the constrained-search approach explains why $T_s[n]$ scales homogeneously and why $T_s[n]$ is less than $T[n]$. Specifically, observe that $T_s[n]$ is the kinetic energy of the wavefunction that yields n and simultaneously minimizes just the kinetic energy expectation value, while $T[n]$ is the kinetic energy of the wavefunction that yields n and minimizes the expectation value of the sum of the kinetic and electron–electron repulsion operators.

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