Strategies for the Development of New Density Functionals for the Exchange-Correlation Energy

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In condensed matter physics and quantum chemistry, there is a continuing need for the development of more accurate approximations to the exchange-correlation energy E_{xc} as a functional of the electron density $n(\mathbf{r})$ or spin densities. The qualitative physics of exchange and correlation is easily understood, and a constrained search definition shows that $E_{\mathrm{xc}}[n]$ depends upon nothing more than quantum mechanics and Coulomb's law. Although systematic constructions of $E_{\mathrm{xc}}[n]$ are possible, nonsystematic (or creative) ones are more common and often more practical. Nonsystematic constructions can be non-empirical (based upon exact constraints on E_{xc} which are reviewed here) or empirical (fitted to important ground-state physical properties which are also reviewed), or both together. The functionals may depend upon the density either explicitly or implicitly (e.g., functionals that depend explicitly on the Kohn-Shanm orbitals). Most functionals that exist or are under development fall on various rungs of a "Jacob's Ladder", in which higher rungs invoke more complicated ingredients to be used to find the exchange-correlation energy density at position $\mathbf{r}$. The first rung is the local density approximation, which uses only $n(\mathbf{r})$, and the second is the generalized gradient approximation (GGA), which uses $n(\mathbf{r})$ and grad $n(\mathbf{r})$. These two lowest rungs are probably now developed as far as they can be. The third rung is the meta-GGA, which uses $n(\mathbf{r})$, $\nabla n(\mathbf{r})$, $\nabla^2 n(\mathbf{r})$, and the orbital kinetic energy density $\tau(\mathbf{r})$. The fourth rung uses as well all or part of the exact exchange energy or exchange energy density, and the fifth rung uses not only the occupied but also the unoccupied Kohn-Sham orbitals, as in random-phase-approximation-like functionals.