

DFT Problems

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DFT Problems

Despite the many successes of DFT, there are some areas where the current functionals are known to perform poorly.

- Weak interactions due to dispersion forces (part of van der Waals type interactions) arise from electron correlation in wave function methods, but this is poorly described by current DFT methods.

Rare gas atoms should show a slight attraction, but most functionals display a purely repulsive energy curve, and those that do predict an attraction underestimate the effect and the variation between systems. Furthermore, none have the correct R^{-6} limiting behavior in the long distance limit, although very recent developments appear to provide quite accurate results with only a single parameter. In some approaches, an empirical attraction term is added that improves the performance, but this is clearly an *ad hoc* repair. Owing to the general overestimation of bond strengths, LSDA does predict an attraction between rare gas atoms, but significantly overestimates the magnitude. Hydrogen bonding, however, is mainly electrostatic and is reasonably well accounted for by many DFT functionals.

- Loosely bound electrons, such as anions arising from systems with relatively low electron affinities, represent a problem for exchange–correlation functionals that do not include self-interaction corrections or correct for the incorrect long-range behavior of the exchange–correlation potential. Since loosely bound electrons by definition have most of the associated density far from the nuclei, this may cause the self-interaction error to be larger than the actual binding energy, and thus lead erroneously to an unbound electron. In actual calculations using a limited basis set, this may not be obvious, since the outer electron is confined by the most diffuse basis function. A positive HOMO energy, however, is a clear warning sign, and extending the basis set with many diffuse functions in such cases may cause the outer electron to drift away from the atom. This means that only systems with high electron affinities have a well-defined basis set limiting value. Nevertheless, a medium-sized basis set with a single set of diffuse functions will in many cases give a reasonable estimate of the experimental electron affinity. The basis set confines the outer electron to be in the correct physical space, and the exchange–correlation functional gives a reasonable estimate of the energy of this density. It should be noted that the relatively good performance is in essence due to a correct physical description, rather than a correct theoretical methodology.

- For chemically bonded systems, analysis similar to the H₂ system suggest that bonds involving:

- two-centre two-electrons (e.g. normal covalent bonds),
- two-centre four-electrons (e.g. steric repulsion between closed shell systems), and
- three-centre three-electrons (e.g. radical abstraction) should be reasonably

described by gradient-corrected methods.

- . Systems involving:
 - two-centre one-electron (e.g. radical cations),
 - two-centre three-electrons (e.g. radical anions), and
 - three-centre four electrons (e.g. atom transfer transition structures)are, however, predicted to be too stable. The dissociation of charged odd-electron systems is a problem for most DFT methods, with the dissociation energy profile displaying an artificial barrier and an incorrect dissociation energy, often in error by as much as 100kJ/mol. Transition structures are similarly predicted to be too stable (barriers are underestimated) by functionals that do not include exact exchange. Since Hartree–Fock overestimates activation barriers, hybrid methods involving exact exchange, however, often give reasonable barriers.

- The absence of a wave function makes a direct description of excited states with the same symmetry as the ground state problematic. Excited states must be orthogonal to the ground state, which is easy to enforce if the spatial or spin symmetry differ, but difficult to ensure for excited states having the same spatial and spin symmetry. Excited state properties, however, can be calculated by time-dependent DFT (linear response) methods, since the excited state is never needed explicitly.

Such calculations can give for example excitation energies and transition moments, as well as gradients of the excited surface, which allows excited states to be optimized.

- The accuracy of excitation energies is typically ~ 0.5 eV for valence states, but Rydberg states, where the electron is excited into a diffuse orbital, can be in error by several eV. This problem has the same physical reason as the anion problem above, and can be solved by using corrections for the asymptotic behavior of the exchange–correlation potential. Such *Asymptotic Corrected* (AC) functionals display much improved predictions for response properties.

- The exchange–correlation functional is inherently local, depending only on the density and possibly its derivatives at a given point, and this causes DFT methods to be inherently unsuitable for describing charge transfer systems, where an electron is transferred over a large distance. Such systems are predicted to have excitation energies that are too low by several eV.

- Relative energies of states with different spin multiplicity are often poorly described. In HF theory, the energy difference between a singlet and triplet state with the same orbital occupancy is given by an exchange integral. In DFT, this must be described by the exchange–correlation functional, which only depends on the electron density. If the two spin states arise from the same electron configuration the two electron densities are very similar, and this makes the results sensitive to the details of the exchange–correlation functional. These problems are especially problematic for transition metal systems, where several low-energy spin states are often possible, and many of these cannot be described by a single determinant. Pure DFT methods

favors low spin states while HF favors high spin states, and hybrid methods with a suitable parameterized amount of exact exchange perform better. These problem can perhaps be improved by adding current density terms to the DFT formalism but this is not yet a commonly used procedure since it requires that the orbitals be allowed to become complex.

- Individual spatial components of a spin multiplet may have different energies, even in the absence of a magnetic field. The boron atom, for example, has the electron configuration $1s^2 2s^2 2p^1$, and the single p-electron can be in either a p^{-1} , p^0 or p^{+1} orbital. These should all have the same energy, but since the density associated with the p_0 orbital is different from that of a $p_{\pm 1}$ orbital, their energies as a result differ by ~ 25 kJ/mol. This is clearly non-physical, but can be significantly improved by introducing current density terms