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Density Functional Tight Binding: Contributions from the American Chemical Society Symposium

The enormous success of density functional theory (DFT), starting in the 1990s was driven by the development of gradient corrected exchange and correlations functionals, combined with considerable advantages in efficient computer programs for the solution of the Kohn−Sham (KS) equations. This opened a new field of applications for computational chemistry and promised the treatment of large molecular and solid state systems with up to hundreds of atoms at high accuracy. Simultaneously, it seemed to devalue semiempirical (SE) approaches, which, based on Hartree−Fock (HF) theory, depend on a quite involved parametrization process. Although being the workhorse of quantum chemistry for many years, the promises of DFT made the use of SE methods, which always had to care about accuracy and transferability, suspicious or even dispensable. This was reflected, e.g., in the symposium “Semi-Empirical Methods: Is There a Future?“, at the 21lth National Meeting of the American Chemical Society (New Orleans, LA, March 24-28, 1996).

The last 10 years, however, have led to a clearer and perhaps more balanced picture of strengths and weaknesses of DFT. On the one hand, actual gradient corrected density functionals show clear limitations, e.g., in the description of VdW complexes, charge transfer excitations, or isomerization reactions, owing to the approximate character of the XC functionals. Current attempts to overcome these difficulties seem to sacrifice the computational efficiency, closing the gap to the more involved perturbation approaches (e.g., MP2 or local MP2).

Second, recent years have witnessed an explosion in the number of new density functionals, ranging from “ab initio” type approaches to very empirical ones, containing a large number of parameters fitted to experimental data. These functionals have different strengths and weaknesses for the various molecular systems, getting the community used to the pragmatic idea that different methods may have to be applied for different problems. This, however, is also the working principle behind more approximate, SE methods. They are to some degree expert systems that require a basic knowledge about their strengths, limitations, and applicability to certain chemical environments.

Third, there are many problems beyond the capabilities of ab initio or density functional theory methods. This is particularly true for large biomolecules, adsorption studies of molecules on surfaces, molecular dynamics studies on nanosecond time scales and taking account of environmental conditions, investigations of molecules or clusters with hundreds or thousands of conformations, computer aided drug and materials design, or investigations of the properties of nanostructures. Here, approximated methods can lead to valuable insights not accessible with more sophisticated methods even when the quantitative accuracy is limited. Therefore, there is an urgent need for methods, which fill the space between ab initio/DFT and empirical force field methods.

The density functional tight binding (DFTB) method is an alternative to the quantum chemical SE methods. It can be understood as an approximate DFT scheme, having the computational speed of the traditional semiempirical quantum chemical methods (like MNDO, AM1, and PM3) but without having a large number of empirical parameters. It is derived from DFT, thereby inheriting its strengths but also weaknesses. Instead of approximating and parameterising Fock−Matrix elements, an effective one-electron KS-like Hamiltonian is derived from DFT calculations. On the other hand, DFTB is in close connection to the so-called tight-binding methods, which are very popular in solid state physics. DFTB can be seen as a tight binding method, parametrized from DFT. Tight binding methods are usually based on a LCAO representation of the Hamilton matrix. These matrix elements are usually treated as empirical parameters, which often makes it difficult to find an accurate and transferable set of numbers. This problem is avoided within DFTB by calculating the matrix elements explicitly within DFT. Furthermore, DFTB was augmented by a self-consistency treatment based on atomic charges in the so-called self-consistent charge density-functional tight-binding (SCC-DFTB) method. Because the wave functions in DFTB are well defined as Kohn−Sham-like orbitals, one can easily derive expressions for any property in the same way as within a “full” DFT scheme. This has been demonstrated in recent years in applications for a large number of systems and properties, as there are, for example, vibrational spectra of molecules and solids, optical properties of molecules and clusters within a DFTB adapted time-dependent DFT (TD-DFT) approach, nonadiabatic molecular dynamics simulations to model pump−probe processes, calculations of hyperfine coupling constants for radicals and magnetic properties of clusters with a spin-polarized extension of DFTB, calculations of scanning probe (STM) images of surfaces, calculation of nuclear magnetic shielding tensors in molecules and fullerenes, and the calculation of

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electronic transport properties within the nonequilibrium Green's function technique, to mention only some of the applications and methodological extensions of the DFTB method.

DFTB may be a good complement to the quantum chemical SE methods. Its strength is the transparent derivation, inclusion of electron correlation on the DFT-GGA level and a parametrization process, which is based on a few molecules per pair of atom types. This leads to a robust method that predicts molecular geometries quite reliably. The SE methods, on the other hand, emphasize molecular heats of formation in the parametrization process, which may guide the further development of DFTB. The flexibility of the DFTB model to accommodate various chemical environments with good accuracy may not have been exploited completely in the current version. Improvements in heats of formation and parametrization of more elements across the periodic tables may be the main challenges in the next years.

This issue contains contributions from the symposium "DFTB, An Approximate DFT Method: Theory and Applications" at the 232nd National Meeting of the American Chemical Society, showing the present status of the DFTB method and its applications. Selected abstracts and presentations from the Symposium may be found at www.dftb.org, "Events."

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