



Intermolecular dispersion energies from coupled exact-exchange Kohn-Sham excitation energies and vectors

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ABSTRACT

The calculation of intermolecular dispersion energies within a time-dependent density-functional theory framework (TDDFT) is reviewed. While the commonly used route to compute dispersion energies is to employ the Casimir-Polder integral transform and thereby describing the dispersion energy as a functional of the response functions of the monomers, this alternative approach leads to a particularly simple form for the long-range interaction between two subsystems in terms of the TDDFT eigenvectors and excitation energies. We present two different schemes to reduce the high computational cost for calculating the excitation energies and vectors of the monomers to be used to compute the dispersion energies via the TDDFT method. This is achieved by a decoupling of the occupied-virtual orbital product basis functions which are associated with single-particle excitations belonging to large and small oscillator strengths. It will be shown that this approach can lead to large speedups of 90% and more compared to a full diagonalisation of the hessian, while the fully coupled dispersion energies can be reproduced with a reasonable accuracy. We also investigate the role of the dispersion energy for the description of σ - and π -stacking interactions and discuss various dispersion energy approximations, including the D3 model by Grimme.

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1. Introduction

The dispersion energy is that part of the intermolecular interaction energy which can not be described in terms of the permanent or induced multipoles of the interacting molecules. Unlike the electrostatic interaction energy, the (second-order contribution to the) dispersion energy is always attractive, yet is more short-ranged than interactions between permanent charges, dipoles and/or quadrupoles. Another difference between the (two-body) dispersion interaction and the first order Coulomb interactions is that dispersion forces are rather isotropic, i.e., they do not depend much on the orientation of the monomers but only on the distances of their electron distributions. Because of this, the dispersion interaction can typically be well approximated by simple pairwise atom-atom force field expressions.

Such models of the dispersion energy are commonly in use in intermolecular force fields [1], semiempirical quantum chemistry methods [2,3] as well as within the framework of density-functional theory (DFT) methods to correct their deficiency of the description of long-range electron correlation effects [4–12] (see

also the review by Riley et al. [13]). In all cases, the dispersion energy is described by its long-range multipole-expanded form, using suitable molecular or atom-atom dispersion coefficients. For short interatomic distances the dispersion energy then needs to be properly damped to resolve the singularity of the expanded form of the interaction. In case of dispersion-corrected DFT methods, this damping approach also needs to be applied in order to avoid the double-counting of electron correlation effects at short distances.

Early dispersion-correction models to DFT methods have used a fixed parametrisation for the different atom-atom coefficients of the long-range expanded form [4–6], thereby neglecting the explicit chemical environment of the atoms, characterised, e.g., by their hybridisation states. Because of this, in the recent years a number of different advanced models for the dispersion energy have been developed which correct this deficiency. The perhaps most widely used method to date is the D3 model by Grimme et al. [11]. Here, the atom-atom dispersion coefficients have been parametrised against polarisabilities from time-dependent density functional theory calculations for various hydride compounds of the atoms to reflect their different hybridisation states. More advanced dispersion corrections also incorporate atomic or molecular densities to improve the description of the classical approaches [7,8,10,9,12], e.g., the exchange-hole dipole moment (XDM) model by Becke and

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Johnson [7,8] or the dispersion correction by Tkatchenko and Scheffler that is based on scaling the dispersion coefficients of free pairs of atoms (that are not exposed to a chemical environment) by the ratios of the effective volume of the atoms in the molecule over the volume of the free atom [10]. The applicability of the Tkatchenko-Scheffler dispersion model could be extended to ionic systems by employing an iterative Hirshfeld partitioning, see Refs. [14,15]. Very recently, Grimme et al. have presented, too, a dispersion energy model which takes into account the dependence of the dispersion coefficients on the molecular density [16]. This model, termed as D4 correction, utilises densities which are determined by semiempirical DFT tight-binding calculations and was shown to improve the description of the interactions of, e.g., charged complexes, see Ref. [16].

The atom-atom dispersion coefficients to be used in pairwise dispersion models can also more rigorously be derived from exact known expressions of the response function of the monomers. One such approach is the local response dispersion (LRD) method by Sato and Nakai [9]. This method uses a local approximation of the response function developed by Dobson and Dinte [17] which is based on a simple model of the density-density response function of the homogeneous electron gas (see also the work by Andersson et al. [18]). Alternatively, approximate expressions for the dispersion energy can also be obtained by using an Unsöld approximation to the response function, see Refs. [19–21]. In Ref. [12] this approach has been refined to derive local frequency-dependent polarisabilities of the monomers to be employed in dispersion energy corrections to DFT functionals. Note that this method, termed as weighted exchange-hole method, is also related to the XDM method by Becke and Johnson [7,8,19–21].

There exist, however, a number of cases which cannot be described by atom-pairwise dispersion energy models. Firstly, the interaction between two atoms *A* and *B* may be screened by an additional polarizable centre *C* so that the bare interaction of the two atoms is altered. This many-body effect is described, e.g., by the Axilrod-Teller interaction energy term that describes the interaction between three atoms [22]. This three-body correction term has been evaluated, e.g., for large supramolecular complexes in Ref. [23] and it has been found that it yields a rather small yet non-negligible contribution to the interaction energy in these cases. A many-body dispersion correction model has also been developed by Tkatchenko et al. that was shown to yield strong improvements in the description of the interaction energy of large molecular complexes compared to DFT employing only an atom pairwise dispersion energy model [24]. This model has been further refined by Gould et al. by employing a fractional ions scheme which was shown to improve the description of dispersion interactions of more difficult nanosystems [15].

The second case that can not be described by atom-pairwise models and that, in fact, is generally difficult to model via simple force field expressions, is the interaction between molecules that possess a (nearly) degenerate and strongly delocalised electronic structure [25]. In such systems the lowest excitation energy would be almost zero, so that the density response of the molecule would almost exclusively be described by the lowest transition. Examples where such effects need to be taken into account are, e.g., metals or highly conjugated π -aromatic systems like graphene or (extended) fullerene molecules [26–29]. Note also that asymptotically the dispersion interaction between such systems will decay more slowly with respect to the distance than for the interactions between large-gap systems [26,28,30,31]. For example, the interaction energy between two parallel oriented graphene sheets decays as R^{-3} with the distance [26].

It is clear, therefore, that an accurate description of dispersion interactions that respects all of the aforementioned situations

can only be achieved with the aid of quantum chemical electron correlation methods of an adequate level. Generally there exist two different approaches to describe intermolecular interactions with quantum chemical methods. The first one is the supermolecular method in which the interaction energy is calculated by subtracting the monomer energies from the dimer energy. This method, however, does not separate the dispersion energy from the rest of the interaction energy contributions, so that further techniques involving orbital localisations need to be applied in order to extract the dispersion interaction [32,33].

The second common approach to describe intermolecular interactions is the symmetry-adapted perturbation theory (SAPT) method which was developed by Jeziorski and co workers [34–36]. Here, the interaction energy between two molecules is calculated directly as a sum of physically distinct terms, including the dispersion energy. To take intramonomer electron correlation effects into account, various variants of the SAPT method have been developed that are based on different approximations of the monomer wave functions. The most accurate SAPT approaches describe intramonomer correlation effects by using a many-body perturbation or coupled-cluster expansion of the wave function [37–43]. These methods, however, exhibit a strong scaling dependency on the molecular size and can only be applied to very small dimers. Compared to this, the SAPT method based on DFT monomer properties, termed DFT-SAPT method [44–52], was shown to yield very accurate dispersion [47,48] and other interaction energy terms [44,45] at a much lower computational cost compared to the many-body SAPT approaches.

To achieve this high performance, density-fitting techniques are implemented in the DFT-SAPT method with which products of two orbital functions are reduced to a linear expansion of auxiliary basis functions [50,51,53]. It was shown that this approach leads to a reduction of the computational cost of the dispersion energy by two orders of magnitude compared to the canonical method that would require steps in the calculation which scale as \mathcal{N}^6 with the molecular size \mathcal{N} . The dispersion energy can then be calculated using the Casimir-Polder integral transform [54] (Eq. (1)) using monomer response functions represented in the reduced auxiliary basis set [48,50,55]. The latter can easily be computed at given imaginary frequencies by solving the Dyson equation to the density-density response propagator [55,56]. However, the response function of a molecular system can alternatively also be computed by a sum-over-states expression employing the excitation energies and vectors of the system [57–59] (Eq. (3)). While this would require the knowledge of the complete eigenvalue and -vector spectrum of the electronic hessian, the formula for calculating the dispersion energy can then be transformed into a very simple and interpretable form [59,47], see below.

In this work we will review this alternative approach for calculating dispersion interaction energies employing the excitation energies and vectors of the monomers computed using time-dependent density functional theory (TDDFT) methods. We then introduce computational schemes which allow to drastically reduce the computational cost. This is achieved by a decoupling of basis functions that represent the hessian matrix using the uncoupled oscillator strengths associated with the occupied-virtual orbital products as a criteria. In the second part of this work we will then apply the methods for analysing the dispersion interactions between parallel and linear shaped alkane and alkene dimers. It will be shown that the commonly used uncoupled or single-pole approximations are unable to reproduce the π - π stacking interactions of extended conjugated systems due to the breakdown of the second-order expansion of the response function for low-gap systems. Compared to this, it is shown that the D3 dispersion model by Grimme [11] can describe the dependence of the

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