Accurate interaction energies from perturbation theory based on Kohn-Sham model

Rafał Podeszwa and Krzysztof Szalewicz

Department of Physics and Astronomy, University of Delaware, Newark, DE 19716

(Dated: January 11, 2022)

The density-functional based symmetry-adapted perturbation theory [SAPT(DFT)] has been applied to the argon, krypton, and benzene dimers. It is shown that—at a small fraction of computational costs—SAPT(DFT) can provide similar accuracies for the interaction energies as high-level wave-function based methods with extrapolations to the complete basis set limits. This accuracy is significantly higher than that of any other DFT or DFT-based approaches proposed to date.

PACS numbers: 34.20.Gj, 31.15.Ew, 31.15.Md, 31.25.-v

The intermolecular forces—sometimes called van der Waals (vdW) interactions or forces—determine the structure and properties of most clusters, liquids, and solids. These forces also govern many life processes, such as the genetic code replication, protein structure and dynamics, and enzymatic actions. Thus, the ability to computationally predict van der Waals forces is significant for the understanding of all these systems. However, although the standard wave-function based electronic structure methods can in principle be used for such predictions, in practice these methods are too time consuming to be applied to most systems of interest in biology, even with extensive use of the current computers capabilities. The density-functional theory (DFT) methods are much less time-consuming, however, the currently existing versions of DFT fail to describe the dispersion interaction, an important part of the van der Waals force. This problem is due to the fact that the dispersion forces result from long-range correlations between electrons, whereas the current exchange-correlation potentials model only short-range correlation effects. Many authors add the asymptotic expansion of the dispersion energy to the DFT interaction energies, which inherently includes some double counting (see Ref. [1] for a discussion of these issues).

Occasionally, for a specific system, one of the variants of DFT can give reasonably good predictions of interaction energies, at least in some regions of a potential energy surface. This fact encouraged some authors to build system-specific potentials fitted to a number of grid points on the potential energy surface computed using a wave-function based method. For example, Boese et al. [2] optimized an ammonia-specific potential by adjusting some parameters in one of the standard functionals. Recently, Lilienfeld et al. [3] proposed to use atom-centered nonlocal effective core potentials with parameters adjusted for specific systems. These methods do not offer physically motivated improvement of the density-functional formalism but rather rely on cancellations of errors. Also, a number of wave-function calculations are needed to optimize the parameters in the functionals, which limits the range of applications to systems that can be treated with the latter methods (unless the parameters can be shown to be transferable).

An approach which uses the specific characteristic of the dispersion interaction has recently been presented by Dion et al. [4]. The method was denoted by the authors as vdW-DF. It adds a nonlocal correlation energy part to existing functionals. This term models the dispersion energy utilizing approximate density response functions. The method predicts interaction energies of the systems investigated in Ref. 4 qualitatively (to within a factor of about 1.5, see below).

Another approach to the calculations of interaction energies for large molecules was developed by Misquitta et al. [5] and independently by Hesselmann and Jansen [6], following ideas of Williams and Chabalowski [7]. This approach is based on symmetry-adapted perturbation theory (SAPT) [8], but utilizes the description of the interacting monomers in terms of Kohn-Sham (KS) orbitals, orbital energies, and frequency-dependent density susceptibility (FDDS) functions. The DFT-based SAPT will be called SAPT(DFT). This method can be shown to be potentially exact for all major components of the interaction energy (asymptotically for exchange interactions) in the sense that these components would be exact if the DFT description of the monomers were exact. Applications to a number of small dimers have shown that SAPT(DFT) provides surprisingly accurate results, sometimes more accurate than the standard SAPT at the currently programmed level [9].

The regular SAPT method involves expansions in powers of the intermonomer interaction operator $V$ and the intramonomer correlation operator $W$, the so-called Moller-Plesset (MP) potential. The terms proportional to powers of $W$ describe the effects of intramonomer electron correlation on the interaction energy. Similarly as in the electronic-structure many-body perturbation theory (MBPT) or coupled-cluster (CC) methods, these terms are expensive to compute, with CPU times scaling as a high power of system size $N$—the seventh power if the complete currently programmed set of SAPT components is included. This scaling is the same as for MBPT in the fourth order (MP4) or CC including single, double, and noniterated triple excitations (CCSD(T)). In SAPT(DFT), no terms of this type
appear, as the intramonomer correlation effects are accounted for by DFT. Therefore, SAPT(DFT) scales as only \(N^3\), i.e., a SAPT(DFT) calculation is generally orders of magnitude faster than a regular SAPT calculation at the complete currently programmed level. This computational advantage is further significantly increased by the superior basis set convergence of SAPT(DFT) compared to the wave-function based electron correlation methods. The latter methods converge slowly due to the necessity of reproducing the intramonomer electron-electron cusps by expansions in products of one-electron functions. Such expansions do not appear in DFT. In SAPT(DFT), the orbital-product expansions are present in the expressions for the dispersion energy, however, it has been shown \(\text{[10, 11]}\) that this component (similarly as the SAPT dispersion energy of zeroth order in \(W\)) can be saturated in reasonably small basis sets provided that “midbond” functions are used, i.e., basis functions are placed at a point between the two monomers. It appears that, in many cases, polarized triple-zeta (TZ) quality bases give SAPT(DFT) interaction energy components converged to a similar number of digits as the regular SAPT components in polarized quadruple-zeta (QZ) bases. This results in a difference in the basis set size of about a factor of two, a ratio of \(2^4\) in computer time at the MP4 or CCSD(T) level. Our current implementation of SAPT(DFT) is using an interface to the time-dependent DFT (TD-DFT) part CADPAC \(\text{[12]}\) to compute FDDS’s, which is the time-limiting step of the calculations. An optimized TD-DFT program now under development should decrease time requirements of this step by at least one order of magnitude. This will make the largest calculations described here comparable to the supermolecular DFT calculations in the same basis. Thus, the SAPT(DFT) method is not prohibitively expensive, as stated by the authors of Ref. \(\text{[13]}\) and it has already been applied to systems containing about 40 atoms and 200 electrons \(\text{[12]}\).

We present here the first application of SAPT(DFT) to relatively large interacting monomers. In order to compare with the vdW-DF method, we have chosen the same systems as investigated in Ref. \(\text{[13]}\): Ar\(_2\), Kr\(_2\), and the benzene dimer. We have used the following Cartesian basis sets: \text{aug-cc-pV5Z} \(\text{[14]}\) for Ar\(_2\) (with \(g\) and \(h\) functions removed due to restrictions of CADPAC), \text{aug-cc-pVTZ} \(\text{[14]}\) for Kr\(_2\), and a polarized double-zeta size basis with polarization coefficients optimized on dispersion energy \(\text{[15]}\) for benzene. In all cases, we used a set of midbond functions consisting of \(s\) and \(p\) functions with exponents 0.9, 0.3, 0.1, and \(d\) and \(f\) functions with exponents 0.6 and 0.2, placed at the center of mass of each dimer. We used the monomer-centered “plus” form of basis sets \(\text{[15]}\) for the argon (including \(d\) functions on the interacting partner) and benzene dimers, and the full dimer-centered form Kr\(_2\). For the benzene dimer, we considered the parallel “sandwich” configuration, and the monomer geometry was taken from Ref. \(\text{[17]}\). We employed PBE0 \(\text{[18]}\) DFT functional with the asymptotic correction \(\text{[19]}\) for all the systems. In addition, the B97-2 \(\text{[19]}\) functional was applied at near minimum geometries for all dimers and at all points for the argon dimer. Effects of the third and higher orders in \(V\) have been neglected. In TD-DFT, we have used the standard PBE0 or B97-2 kernels for argon and krypton, and the LDA kernel for benzene. The use of the LDA kernel provides a considerable speedup of calculations. To check the accuracy of this approximation, we performed a single-point calculation using the PBE0 kernel for the benzene dimer. The error in the dispersion energy was smaller than 1%.

Figure 1 presents the interaction potential for the argon dimer. The benchmark results are the empirical potential of Aziz \(\text{[20]}\) and the CCSD(T) potential with extrapolation to the complete basis set (CBS) limit by Patkowski et al. \(\text{[20]}\). The two curves are almost indistinguishable, showing the very high level of agreement between \textit{ab initio} theory and experiment for this system. The SAPT(DFT) calculations are very close to the benchmarks, within about 2 cm\(^{-1}\) or 2% at the minimum geometry. In contrast, the vdW-DF method gives a curve which is about 1.5 times too deep, and the minimum position is shifted by 0.2 Å.

Our results for the krypton dimer are displayed in Fig. 2. For this system, the benchmark curve is given by the empirical fit of Dham et al. \(\text{[22]}\). The CCSD(T) curve computed by Slavíček et al. \(\text{[23]}\) represents the best literature non-relativistic theoretical result and is in fact at the limit of what the \textit{ab initio} methods are capable of achieving at the present time. The SAPT(DFT) curve agrees with the benchmark slightly better than the CCSD(T) one, and much better than the curve produced by the vdW-DF method \(\text{[4]}\). The latter curve is about a factor

![FIG. 1: (Color online). Interaction energy of the argon dimer. SAPT(DFT)—this work. CCSD(T)/CBS—Ref. \text{[20]}. Benchmark—Aziz, Ref. \text{[21]}. vdW-DF—Ref. \text{[4]}.](image-url)
of 1.4 too deep and has the minimum position shifted by about 0.2 Å.

Finally, the benzene dimer results are presented in Fig. 3. For this system, there is no highly reliable benchmark available. The best ab initio calculations for a number of monomer separations are those by Tsuzuki et al. [17] at the CCSD(T) level. The values displayed were termed “Model II” and included the MP2 energies computed in a polarized DZ-quality basis augmented with a single diffuse polarization set [aug(d,p)-6-311G**] and the ΔCCSD(T) = CCSD(T)-MP2 component computed in a DZ basis polarized only on carbons. Below

we will quote the MP2 and ΔCCSD(T) values in parentheses. Model II gives −1.62 (−2.85, 1.24) kcal/mol at 3.8 Å. The authors computed also an extrapolated interaction energy (“Model III”, only at 3.8 Å) by performing a CBS extrapolation at the MP2 level and scaling the ΔCCSD(T) component, which gave −1.48 (−3.28, 1.80) kcal/mol. Accurate calculations for the benzene dimer were also performed by Sinnokrot et al. [24], but only at a single point, R = 3.7 Å. These authors computed the MP2 energies in bases up to aug-cc-pVQZ and ΔCCSD(T) in aug-cc-pVDZ, which gives −1.54 (−3.37, 1.83) kcal/mol. If one extrapolates the MP2 TZ-QZ results of Ref. 24 using the X−3 extrapolation scheme, one obtains the value of −3.45 kcal/mol, not much different from the best calculated result. Sinnokrot et al. computed the MP2 energy using also the so-called MP2-R12 explicitly correlated basis and their recommended interaction energy is −1.81 (−3.64, 1.83) kcal/mol. The fairly large discrepancy between the extrapolated and MP2-R12 results could be due to an insufficient convergence of the resolution of identity applied in the MP2-R12 approach in the [spdf/spd] bases. Based on these considerations, one has to assume that the uncertainty of the CCSD(T) curve in Fig. 3 is about ±0.2 kcal/mol.

Figure 3 shows that the agreement of SAPT(DFT) with the CCSD(T) results is very good, in particular taking into account the uncertainty of the latter. In fact, in view of this uncertainty, the SAPT(DFT) results provide an independent set of the best current estimates of the exact interaction energies for the benzene dimer. The vdW-DF curve is deeper by about a factor of 1.4 and the minimum is shifted by about 0.2 Å. Figure 3 includes also the MP2 results from Ref. 17, the DFT results of Lilienfeld et al. from Ref. 3 and the MP2 results of Sinnokrot et al. [24] which were used to calibrate the Lilienfeld et al. DFT functional. The differences between the two MP2 curves are consistent with the sizes of the basis set effects discussed above. For the benzene dimer, the MP2 level of theory is not adequate and therefore the results of Lilienfeld et al. [3] are very far from the CCSD(T) benchmark. If these authors had chosen to fit their functional

This development will bring some important biophysical applications within reach of computational physics (e.g., interactions involving DNA bases, small polypeptides, and sugars).

The authors are grateful to Bogunil Jeziorski for reading the manuscript and for valuable advice. This research was supported by a grant from ARO.

| TABLE II: Interaction energy components (in kcal/mol) for the benzene dimer at the parallel “sandwich” geometry obtained with SAPT(DFT) compared to those obtained with the regular SAPT and a modified aug-cc-pVDZ basis in Ref. [26]. |
| --- |
| Calculation |静电能 |诱导能 |交换-诱导能 |交换-诱导能 |总能 |
| PBE0/3.8 Å | −0.28 | 4.94 | 1.46 | 0.64 | 1.48 |
| PBE0/3.7 Å | −1.24 | 6.44 | 7.47 | 0.94 |
| SAPT/3.7 Å | −0.14 | 0.02 |

*aSee Ref. [27] for the SAPT components included at each level.*

[1] X. Wu, M. C. Vargas, S. Nayak, V. L. Lotrich, and G. Scotes, J. Chem. Phys. 115, 8748 (2001).
[2] A. D. Boese, A. Chandra, J. M. L. Martin, and D. Marx, J. Chem. Phys. 119, 5965 (2003).
[3] O. A. von Lilienfeld, I. Tavernelli, U. Rothlisberger, and D. Sebastiani, Phys. Rev. Lett. 93, 153004 (2004).
[4] M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, and B. I. Lundqvist, Phys. Rev. Lett. 92, 246401 (2004).
[5] A. J. Misquitta and K. Szalewicz, Chem. Phys. Lett. 357, 301 (2002).
[6] A. J. Misquitta, B. Jeziorski, and K. Szalewicz, Phys. Rev. Lett. 91, 033201 (2003).
[7] A. Hesselmann and G. Jansen, Chem. Phys. Lett. 357, 464 (2002); 362, 319 (2002); 367, 778 (2003).
[8] H. L. Williams and C. F. Chabalowski, J. Phys. Chem. A 105, 646 (2001).
[9] B. Jeziorski, R. Moszynski, and K. Szalewicz, Chem. Rev. 94, 1887 (1994).
[10] A. J. Misquitta and K. Szalewicz, submitted to J. Chem. Phys.
[11] A. J. Misquitta, R. Podeszwa, B. Jeziorski, and K. Szalewicz, manuscript in preparation.
[12] CADPAC: The Cambridge Analytic Derivatives Package Issue 6, Cambridge, 1995. A suite of quantum chemistry programs developed by R. D. Amos with contributions from I. L. Alberts et al.
[13] R. Podeszwa and K. Szalewicz, work in progress.
[14] D. Woon and J. T.H. Dunning, J. Chem. Phys. 98, 1358 (1993).
[15] R. Bukowski, K. Szalewicz, and C. Chabalowski, J. Phys. Chem. A 103, 7322 (1999).
[16] H. L. Williams, E. M. Mas, K. Szalewicz, and B. Jeziorski, J. Phys. Chem. 103, 7374 (1995).
[17] S. Tsuzuki, K. Honda, M. Mikami, and K. Tanabe, J. Am. Chem. Soc. 124, 104 (2002).
[18] C. Adamo, M. Cossi, and V. Barone, J. Mol. Struct. (Theochem) 493, 245 (1999).
[19] P. J. Wilson, T. J. Bradley, and D. J. Tozer, J. Chem. Phys. 115, 9233 (2001).
[20] K. Patkowski, G. Murdachaew, C.-M. Fou, and K. Szalewicz, Mol. Phys., in press.
[21] R. A. Aziz, J. Chem. Phys. 99, 4518 (1993).
[22] A. K. Dham, A. R. Allnatt, W. J. Meath, and R. A. Aziz, Mol. Phys. 67, 1291 (1989).
[23] P. Slavût, R. Katus, P. Paška, I. Odárková, P. Hobza, and A. Malijevský, J. Chem. Phys. 119, 2102 (2003).
[24] M. O. Sinnokrot, E. F. Valeev, and C. D. Sherrill, J. Am. Chem. Soc. 124, 10887 (2002).
[25] S. Tsuzuki and H. P. Lüthi, J. Chem. Phys. 114, 3949 (2001).
[26] M. O. Sinnokrot and C. D. Sherrill, J. Am. Chem. Soc. 126, 7690 (2004).