

Supplement to the paper:
Dispersionless density functional theory

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I. DETAILS OF ELECTRONIC STRUCTURE CALCULATIONS

The SAPT(DFT) and CCSD(T) interaction energies—both for the training set and for the NIB and S22 validation sets—were computed using the aug-cc-pVTZ (aVTZ) basis set [1] supplemented by a $3s3p2d2f$ set of midbond functions (exponents sp : 0.9/0.3/0.1 df : 0.6/0.2) from Ref. [2]. We will denote this basis set as aVTZ+mb. In all calculations, the complete dimer-centered [2] basis set was used. The only exception were the SAPT(DFT) calculations for the adenine-thymine dimers (appearing in one of the validation sets) where we used the monomer-centered “plus” basis set [2]. The reference dipole moments were computed using the CCSD(T) method and the aVTZ basis set. For $\text{H}_2\text{O}-\text{H}_2\text{O}$, we have also included the set of interaction energies computed using the aug-cc-pVDZ plus midbond basis set to decrease the dependence on basis set type used in optimizations. Therefore, there was a total of 33 data points in our training set.

The dlDF interaction energies were always computed in the same basis set as the corresponding CCSD(T)/SAPT(DFT) dispersionless interaction energies of the training and validation sets, except for omitting midbond functions (this omission is well justified since the bond functions have a very small impact on the dispersionless interaction energies as their main role is to improve the dispersion component [2]). Thus, in our approach the parameters of dlDF do not have to compensate for basis set incompleteness. Similarly, the M05-2X, M06-2X, and B97-D interaction energies for the NIB and S22 sets were computed by us using the aVTZ basis set. In *all* supermolecular calculations, the basis set superposition error was removed using the counterpoise (CP) correction [3, 4].

Whereas we have taken the geometries of the NIB complexes from literature [5, 6], we have used as benchmarks the CCSD(T) interaction energies, $E_{\text{int}}^{\text{CCSD(T)}}$, computed by us in the aVTZ+mb basis set. Since the aVTZ+mb basis set gives rather accurate interaction energies, mainly due to the use of bond functions, for several systems our values of $E_{\text{int}}^{\text{CCSD(T)}}$ may be more accurate than the published benchmarks. The benchmark energies for the NIB set are listed in the file `epaps.txt`.

For the S22 validation set, we have use the published energies [7]. Note that Ref. 7 applies the same definition of the interaction energy as we do.

The SAPT(DFT) and CCSD(T) interaction energies were computed using the SAPT2008 [8] and MOLPRO [9] programs, respectively. The dlDF interaction energies were computed using the Gaussian [10] program with a patch (with modified parameters) developed by the authors of Ref. [11]. Starting from the Gaussian03 revision E.01, the M05-2X functional became a part of the distributed version. We have therefore developed a patch to Gaussian allowing calculations of dlDF energies. This patch is available on the web: <http://www.physics.udel.edu/~szalewic/dldf>. See the accompanying documentation for instructions. Similar patches can be easily prepared for other codes containing M05-2X such as Q-Chem or NWChem.

II. DETAILS OF THE DISPERSION FIT

The sum of the dispersion and exchange-dispersion energies, $E_{\text{disp}}^{(2)} + E_{\text{exch-disp}}^{(2)}$, from SAPT(DFT) was fitted by the function

$$D_{\text{as}} = \sum_{a \in \text{A}} \sum_{b \in \text{B}} D_{\text{as}}^{ab}, \quad (1)$$

where the atom-atom contributions D_{as}^{ab} are expressed as

$$D_{as}^{ab} = -\frac{\sqrt{\mathbf{C}_a^6 \mathbf{C}_b^6}}{R_{ab}^6} \cdot f_6(\sqrt{\beta_a \beta_b} R_{ab}) - \frac{\sqrt{\mathbf{C}_a^8 \mathbf{C}_b^8}}{R_{ab}^8} \cdot f_8(\sqrt{\beta_a \beta_b} R_{ab}) - \sqrt{\mathbf{A}_a \mathbf{A}_b} \exp\left(-\sqrt{\beta_a \beta_b} R_{ab}\right) \quad (2)$$

and all the quantities in bold (\mathbf{C}_x^6 , \mathbf{C}_x^8 , β_x , and \mathbf{A}_x) are fitting parameters. The Tang-Toennies damping function $f_n(R)$ is defined as

$$f_n(R) = 1 - \exp(-R) \sum_{i=0}^n \frac{R^i}{i!}. \quad (3)$$

The training set used to determine the fitted parameters in Eq. (2) consisted of the 23 dimers: Ar-Ar, Ar-HF, C₂H₂-ClF, C₂H₄-C₂H₄, C₂H₄-Ar, C₂H₄-F₂, CH₄-CH₄, H₂O-H₂O, H₂S-H₂S, HCl-HCl, HCl-H₂S, HCONH₂-HCONH₂, HCOOH-HCOOH, He-He, He-Ar, HF-HF, N₂-HF, Ne-Ne, NH₃-NH₃, NH₃-ClF, NH₃-H₂O, pyrazine-pyrazine, and benzene-benzene (sandwich configuration). For each dimer, 10 different radial geometries corresponding to the same angular configuration were considered: the near-radial-minimum geometry (usually taken from the NIB or S22 bases), two geometries with the center-of-mass (COM) separation smaller (by up to about 0.5Å) than at the minimum, and seven geometries with the COM separation larger than at the minimum (up to the largest separation of 10Å). For the helium dimer, two additional geometries with smaller COM separation were added, bringing the total number of training geometries to 232.

The fitting procedure was carried out in two steps. First, the asymptotic constants C_x^6 and C_x^8 were fitted to the long-range part of the training set (that is, to a 115-geometry subset containing five largest-COM-separation configurations for each dimer), assuming no damping and no spherical (A_x -dependent) term. To preserve reasonable asymptotics, the values of C_x^6 and C_x^8 obtained in this way were then frozen and the parameters β_x and A_x were optimized on the full 232-geometry set. The weights inversely proportional to the square of the benchmark (dispersion plus exchange dispersion) energy were used throughout the fitting process to promote uniform relative accuracy.

The values of the C_x^6 , C_x^8 , β_x , and A_x obtained in our fit for the 10 elements present in the NIB and S22 bases are shown in the table below. The C_x^6 and C_x^8 constants are given in the units J·nm⁶·mol⁻¹ and J·nm⁸·mol⁻¹, respectively. To obtain the values of C_x^6 and C_x^8 in atomic units, the values in the table need to be multiplied by 17.345 254 95 and 6194.102 092, respectively. The values of β_x and A_x are given in bohr⁻¹ and kcal/mol, respectively.

TABLE I: Parameters of the dispersion energy expression D_{as} for different elements (see text for units).

| Element | C^6 | C^8 | β | A |
|---------|--------|--------|---------|-----------|
| H | 0.1726 | 0.0000 | 2.8580 | 0.0000 |
| He | 0.0832 | 0.0037 | 1.8336 | 241.2709 |
| C | 1.1501 | 0.2505 | 1.1128 | 380.0429 |
| N | 0.9918 | 0.2522 | 1.7952 | 0.0000 |
| O | 0.6463 | 0.2222 | 1.7221 | 0.0000 |
| F | 0.4109 | 0.0589 | 1.2906 | 426.1620 |
| Ne | 0.3159 | 0.0272 | 1.8120 | 1151.9872 |
| S | 5.8531 | 3.9314 | 1.6678 | 6599.1341 |
| Cl | 5.2305 | 1.1213 | 1.7074 | 4251.0224 |
| Ar | 3.0751 | 0.6296 | 1.2277 | 1412.7698 |

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- [1] R. A. Kendall, T. H. Dunning, and R. J. Harrison, *J. Chem. Phys.* **96**, 6796 (1992).
- [2] H. L. Williams, E. M. Mas, K. Szalewicz, and B. Jeziorski, *J. Chem. Phys.* **103**, 7374 (1995).
- [3] S. F. Boys and F. Bernardi, *Mol. Phys.* **19**, 553 (1970).
- [4] K. Szalewicz and B. Jeziorski, *J. Chem. Phys.* **104**, 1198 (1998).
- [5] Y. Zhao and D. G. Truhlar, *J. Chem. Theo. Comp.* **1**, 415 (2005).
- [6] Y. Zhao and D. G. Truhlar, *J. Phys. Chem. A* **109**, 5656 (2005).
- [7] P. Jurecka, J. Sponer, J. Cerny, and P. Hobza, *Phys. Chem. Chem. Phys.* **8**, 1985 (2006).
- [8] R. Bukowski *et al.*, *SAPT2008: An ab initio program for many-body symmetry-adapted perturbation theory calculations of intermolecular interaction energies* (2008), URL <http://www.physics.udel.edu/~szalewic/SAPT>.
- [9] H.-J. Werner *et al.*, *Molpro, version 2006.1* (2006), see <http://www.molpro.net>.
- [10] M. J. Frisch *et al.*, *Gaussian 03, Revision C.02*, Gaussian, Inc., Wallingford, CT, 2004.
- [11] Y. Zhao, N. E. Schultz, and D. G. Truhlar, *J. Chem. Theo. Comp.* **2**, 364 (2006).