# DISPERSION ENERGY IN DENSITY-FUNCTIONAL THEORY 

by

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# DISPERSION ENERGY IN DENSITY-FUNCTIONAL THEORY 

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#### Abstract

Density Functional Theory (DFT), in various local and semilocal approximations, cannot completely describe long-range correlations between the electrons responsible for dispersion interactions. A large number of methods have been designed to correct DFT for the missing dispersion effects (DFT + D methods). These methods add a fraction of true dispersion energy to DFT methods assuming that a part of it has already been recovered by DFT. We estimate the amount of dispersion recovered by different popular DFT methods and show that what appears to be recovered dispersion energy does not possess the physical character expected of dispersion interactions. Moreover, a large part of it originates from those terms of the DFT interaction energy that do not have any physical mechanism to capture such effects. The technique used to estimate the recovered dispersion will help for future developments of DFT methods as it points out the shortcomings of the dispersionless parts of the DFT interaction energy as well. A new method for calculating dispersion interactions is also developed using a modified polarizability density from nonlocal correlation methods. The performance of the new method is tested on a set of dimers at various intermonomer separations. The new method outperforms all nonlocal correlation functionals and reduces the average error on the test set by at least a factor of 2 . Finally, a path for the future development of nonlocal correlation methods is provided by comparing polarizability densities from nonlocal correlation functionals to the accurate one provided by time-dependent DFT.


## Chapter 1 INTRODUCTION

The dispersion interactions are quantum mechanical in nature and are absent from classical picture of atoms. These interactions result from the long-range correlation between electron motions. Symmetry-adapted perturbation theory (SAPT) [1, $2,3,4]$ identifies dispersion as a pure intermonomer correlation effect. SAPT is a wave-function-based (WF-based) method which clearly defines dispersion up to all orders in the intermolecular interaction potential, but its accurate calculation requires usage of high-electron excitations, which leads to a high computational cost. This limitation is same for all WF-based methods that account for dispersion interactions, for example, the coupled-cluster method with single, double and noniterative triple excitations $[\operatorname{CCSD}(T)]$. The computational cost of WF-based methods scales so steeply (for example, it scales as $O\left(N^{7}\right)$ for SAPT and $\operatorname{CCSD}(\mathrm{T})$ where $N$ is the number of electrons involved) that we cannot perform such calculations for systems with more than a couple dozen atoms. Therefore, the development of accurate methods with an affordable computational cost is an essential requirement for understanding the properties of materials through first principles.

Density functional theory (DFT) is an attempt to calculate all observables of a system from its electron density. The advantage of this approach is that one needs to find a function of only three coordinates (electron density) instead of a 3 N -dimensional function which represents a solution of Schrödinger's equation for a system of $N$ electrons. The computational cost of DFT scales as $N^{4}$ (if the so-called exact or HartreeFock (HF) exchange is included), which is same as that of the HF method, but it accounts for many properties much more accurately than the HF method.

The subtle many-electron effects of an electronic system, including dispersion interactions, are put together in the so-called exchange-correlation energy term defined in the Kohn-Sham (KS) implementation of DFT [5]. The exact exchange-correlation energy expression, unfortunately, remains unknown, so several approximate methods have been developed to calculate it. The standard approaches either work within the local density approximation (LDA) [5, 6, 7, 8, 9, 10] or various semilocal approximations known under the name of generalized gradient approximations (GGAs) [11, 12, 13].

In Chapter 2, we criticise the popular assumption about DFT methods that they recover a part of the dispersion interactions in the physically important region of the van der Waals minimum and of shorter separations $[14,15,16,17]$. The semilocal DFT methods cannot retrieve the long-range correlation of electron motions (dispersion interactions) due to the tiny size of their exchange-correlation hole [18], a quantity related to the electron pair-correlation function which will be defined precisely later. This deficiency is such a serious problem that a large number of methods have been designed to correct DFT by addition of a dispersion correction, the so-called DFT + D methods. The dispersion corrections can be obtained using atom-atom dispersion functions $[15,16,19,20,21]$, the many-body dispersion (MBD) model [22, 17], the exchange-hole dipole model (XDM) [23, 24], and nonlocal correlation functionals (vdW-DF1/2, VV09/10, DADE) [25, 26, 27, 28, 29]. A critical ingredient in this addition of the dispersion energy is the use of damping mechanisms to taper off the dispersion energy at close range based on the assumption that DFT should start recovering dispersion energy when the monomers are sufficiently close. Nonlocal correlation functionals have implicit damping procedure built in to their physical formulation, while all other methods mentioned above use explicit damping functions. An assessment whether DFT methods recover dispersion energies is not straightforward since there are no explicit dispersion energy terms in these methods. Thus, we can estimate this quantity for a given DFT method only in some indirect way. To this end, we calculated the benchmark interaction energy using $\operatorname{CCSD}(\mathrm{T})$, and the benchmark dispersion energy using SAPT. The dispersionless part of the interaction energy is then
computed by taking the difference of the $\operatorname{CCSD}(\mathrm{T})$ interaction and SAPT dispersion energy. If dispersion were the only deficiency of DFT, then subtraction of the dispersionless energy from the DFT interaction energy (we call this difference $E_{\text {extra }}$ ) would give us the dispersion energy recovered by a given DFT method. We performed DFT calculations for the $\mathrm{Ar}-\mathrm{Li}^{+}$and the argon-proton systems establishing that DFT has errors unrelated to dispersion interactions which could be several times larger than the contribution of the dispersion energy to the interaction energy. Thus, $E_{\text {extra }}$ contains the dispersion energy recovered by a given DFT method, if any, as well as errors of the dispersionless part of the DFT interaction energy. We show that the behavior of $E_{\text {extra }}$ is remarkably different from the one expected of the dispersion energy, since its value continues to increase beyond the true dispersion energy when monomers are brought very close and it has significant values, amounting up to $50 \%$ of the dispersion energy, even when the monomers are separated more than the van der Waals minimum distance, where there is unlikely to be any overlap of the exchange-correlation holes. We also confirmed that $E_{\text {extra }}$ needs a significant contribution from the interaction energy terms other than the exchange-correlation term. The former terms do not have any physical mechanism to capture the electron correlation. Additionally, we refuted the notion that for intermediate range exchange could contribute to the dispersion energy, since exchange makes a positive contribution to the interaction energy in this region for most of the investigated functionals. Even the cutting-edge DFT functional SCAN [30], which satisfies seventeen exact physical constraints, is shown to have both density-driven and functional-driven errors, and therefore even such constraints are not sufficient. Other functionals have in general still more problems. Therefore, DFT +D methods which adjust their correction to $E_{\text {extra }}$ using damping are correcting DFT for errors unrelated to dispersion in disagreement with their claimed justification that the purpose of damping is to avoid a double counting of dispersion interactions at separations relevant for intermolecular interactions. Thus, a physically sound improvement of DFT is possible if we improve the dispersionless part of the interaction energy along with improving the dispersion corrections. A DFT approximation which works without
cancelling errors for different types of interactions is more likely to work for all kind of systems and for all kind of properties.

In Chapter 3, we develop a new method for calculating the dispersion energy based on the local polarizability density. This new method, called damped asymptotic dispersion energy (DADE), uses the modified polarizability density from van der Waals density functionals (vdW-DF) [25, 26] in an expression for the dispersion energy obtained under the assumption that the polarizability tensor is local and isotropic. This expression was introduced by Anderson, Langreth, and Lundqvist (ALL) [31] and independently by Dobson and Dinte [32]. The value of the ALL expression is, in general, infinite and a physical cutoff was used to avoid singularities. We used a generalized Tang-Toennies damping function to regularize it. The three parameters of the damping function and the one parameter of the polarizability density were roughly adjusted to get good results for the argon dimer. The method was tested on a set of dimers used in Ref. [33] in addition to $\mathrm{Ar}_{2}$ and $\mathrm{Ar}-\mathrm{HF}$ dimers. The calculations were done for the complete range of intermonomer separations, from the repulsive wall to the asymptotic region of the interaction energy curve. The mean absolute percentage error (MAPE) of dispersion energies relative to SAPT(DFT) (SAPT based on DFT description of monomers) $[34,35,36,37]$ ) values was found to be 2.3 times smaller than that in the case of vdW-DF2. DADE does not have unphysical damping at medium and short ranges, therefore, it should be used with those DFT functionals which give interaction energies close to the dispersionless contributions. We found that when DADE is added to the interaction energy from a dispersionless density functional (dlDF) [20], it predicts interaction energies better than vdW-DF2.

In Chapter 4, we evalulate essentially all methods used in DFT for calculating the dispersion correction by comparing their results with those obtained by SAPT(DFT) for the test set used in Chapter 3. The tested methods include atom-atom functions based on an asymptotic expansion for the dispersion energy ( $\mathrm{D}_{\mathrm{as}}[20,21]$, D3 [16, 19]), methods based on models of atoms in molecules (XDM [23, 24] and MBD [22, 17]), and the methods involving nonlocal correlations (VV09 [27], VV10 [28],
vdW-DF1 [25], vdW-DF2 [26], and DADE [29]). The performances of methods in different regions of monomer separations indicate the quality of the van der Waals dispersion coefficients related to the methods as well as the role of damping functions. It is found that atom-atom functions perform best with the average of MAPEs about $10 \%$, and DADE is quite close to these methods with a $12 \%$ value of this quantity. All other nonlocal methods perform much worse with the average of MAPEs ranging from $24 \%$ to $49 \%$. The performance of DADE gives such a huge improvement over the other nonlocal functionals (VV09 [27], VV10 [28], vdW-DF1 [25], vdW-DF2 [26]) that it should replace them in the future DFT calculations which use such functionals.

In Chapter 5, we compare the dipole-dipole polarizability densities from vdWDF2 [26], VV09/10 [27, 28], and DADE [29] with the one obtained from time-dependent DFT (TD-DFT). The polarizability density computed using vdW-DF2 agrees with TDDFT more closely than VV09/10. DADE is closest to TD-DFT, and also the differences with vdW-DF2 are small. TD-DFT is known to give accurate polarizabilities and that is the reason for its use in $\mathrm{SAPT}(\mathrm{DFT})$. Therefore, this comparison tests the physical soundness of the tested methods and identifies regions of polarizability which need improvement. The best agreement of DADE with TD-DFT is in line with its performance described in Chapters 3 and 4. One way to improve DADE is to enhance its agreement with TD-DFT at the dipole-dipole level. Another possibility is to improve the DADE polarizability density such that it could reproduce TD-DFT polarizability including quadrupole and higher order multipole effects. To get still closer to the exact method, we need to go beyond the local and isotropic character of the polarizability.

### 1.1 Density Functional Theory

Atoms, molecules, clusters, and solids are composed of mutually interacting electrons and nuclei. Since nuclei are very massive compared to electrons, they move relatively slowly so that we can separate their motion from the motion of electrons, i.e., we can solve Schrödinger's wave equation for electrons taking the nuclear coordinates as parameters. This approximation is known as the Born-Oppenheimer approximation.

The Hamiltonian for electrons in this approximation can be written in atomic units as [38]

$$
\begin{equation*}
\hat{H}=\hat{T}+\hat{\mathscr{W}}+\hat{V}_{\mathrm{ext}}=-\sum_{j=1}^{N} \frac{1}{2} \nabla_{j}^{2}+\frac{1}{2} \sum_{i \neq j} \frac{1}{\left|\boldsymbol{r}_{i}-\boldsymbol{r}_{j}\right|}-\sum_{j, J} \frac{Z_{J}}{\left|\boldsymbol{r}_{j}-\boldsymbol{R}_{J}\right|}, \tag{1.1}
\end{equation*}
$$

where $\hat{T}$ is kinetic energy operator, $\hat{\mathscr{W}}$ is electron-electron repulsion energy, and $\hat{V}_{\text {ext }}$ is the potential energy representing the interaction of electrons with nuclei. $Z_{J}$ and $\boldsymbol{R}_{J}$ represent the charge and position of the $J$ th nucleus, respectively and values of $i, j$ run over all electrons. The external potential can be written as $\hat{V}_{\mathrm{ext}}=\sum_{i} v_{\mathrm{ext}}\left(\boldsymbol{r}_{i}\right)$ where $v_{\text {ext }}\left(\boldsymbol{r}_{i}\right)=-\sum_{J} \frac{Z_{J}}{\left|\boldsymbol{r}_{i}-\boldsymbol{R}_{J}\right|}$ is the total external potential for the $i$ th electron. The electron-density operator is defined as $\hat{n}(\boldsymbol{r})=\sum_{i} \delta\left(\boldsymbol{r}-\boldsymbol{r}_{i}\right)$, which allows us to write $\hat{V}_{\mathrm{ext}}=\int d^{3} \boldsymbol{r} v(\boldsymbol{r}) \hat{n}(\boldsymbol{r})$.

The time independent Schrödinger wave equation for the systems discussed is

$$
\begin{equation*}
\hat{H} \Psi_{j}\left(\boldsymbol{x}_{1}, \boldsymbol{x}_{2}, \boldsymbol{x}_{3}, \ldots, \boldsymbol{x}_{N}\right)=E_{j} \Psi_{j}\left(\boldsymbol{x}_{1}, \boldsymbol{x}_{2}, \boldsymbol{x}_{3}, \ldots, \boldsymbol{x}_{N}\right) \tag{1.2}
\end{equation*}
$$

where $\Psi_{j}$ is the wave function of the $j$ th eigenstate of $\hat{H}$ with energy $E_{j}$ and $\boldsymbol{x}_{i} \equiv\left(\boldsymbol{r}_{i}, \sigma_{i}\right)$ specifies both position and spin coordinates of the $i$ th electron. All the information about the system is contained in the wave function of the system and its observables are obtained by calculating the expectation value of the corresponding operators. However, the exact solution of the Schrödinger's wave equation can only be obtained in very simple cases and, therefore, several approximate methods [for example Hartree-Fock (HF) theory, SAPT, and CCSD(T)] have been developed.

Alternatively, the ground state energy of the system, according to the RayleighRitz principle, can be found by minimizing the expectation value of the Hamiltonian with respect to the wave function [39], i.e.,

$$
\begin{align*}
E_{0} & =\min _{\Psi}\langle\Psi| \hat{H}|\Psi\rangle=\min _{\Psi}\langle\Psi| \hat{T}+\hat{\mathscr{W}}+\hat{V}_{\text {ext }}|\Psi\rangle \\
& =\min _{\Psi}\left[\langle\Psi| \hat{\mathscr{F}}|\Psi\rangle+\langle\Psi| \hat{V}_{\text {ext }}|\Psi\rangle\right], \tag{1.3}
\end{align*}
$$

where $\langle\Psi| \hat{\mathscr{F}}|\Psi\rangle=\langle\Psi| \hat{T}+\hat{\mathscr{W}}|\Psi\rangle$ and $\Psi$ must be a normalized antisymmetric function satisfying appropriate boundary conditions for the considered system. The groundstate single-particle density of the system is given as

$$
\begin{equation*}
n_{0}(\boldsymbol{r})=N \sum_{\sigma} \int d^{3} \boldsymbol{r}_{2} \cdots \int d^{3} \boldsymbol{r}_{N}\left|\Psi_{0}\left(\boldsymbol{r}, \sigma_{1}, \boldsymbol{x}_{2}, \boldsymbol{x}_{3}, \ldots, \boldsymbol{x}_{N}\right)\right|^{2}, \tag{1.4}
\end{equation*}
$$

where $\Psi_{0}$ is the ground-state wave function and the integral of the density is the total number of electrons in the system, i.e., $\int d^{3} \boldsymbol{r} n_{0}(\boldsymbol{r})=N$.

The basic idea of DFT is that we can completely describe the system if we know its ground state density $n_{0}(\boldsymbol{r})$. In a system of $N$ electrons, $\hat{T}$ and $\hat{\mathscr{W}}$ are fixed and hence the wave function is a functional of the external potential $\hat{V}_{\text {ext }}$. Thus, the ground state density is a functional of the external potential, i.e., $n_{0}[v](\boldsymbol{r})$, where we used square brackets to denote the functional dependence.

The Hohenberg-Kohn theorem [6] states that the ground state density of a finite system of electrons uniquely determines the local external field (such as the field of nuclei) up to a constant. Thus, the external potential is a functional of the ground density, $v\left[n_{0}\right](\boldsymbol{r})$. Note that this theorem is in general applicable to any finite number of particles with a given particle-particle interaction. We will later use it for a system of noninteracting particles [38]. Hence the Hamiltonian of the system is a functional of the electron density, $\hat{H}\left[n_{0}\right]$. Consequently, via Schrödinger's wave equation, the wave function of the system is a functional of the ground state density $\left(\Psi_{j}\left[n_{0}\right](\boldsymbol{r})\right)$ and so is the energy of the system $\left(E_{j}\left[n_{0}\right]\right)[38]$.

The variational principle in terms of the density becomes

$$
\begin{equation*}
E_{0}=\min _{n(\boldsymbol{r})}\left\{\mathscr{F}[n]+E_{\text {ext }}[n]\right\}, \tag{1.5}
\end{equation*}
$$

where $\mathscr{F}[n]=\langle\Psi[n]| \hat{T}+\hat{\mathscr{W}}|\Psi[n]\rangle, E_{\text {ext }}[n]=\langle\Psi[n]| \hat{V}_{\text {ext }}|\Psi[n]\rangle=\int d^{3} \boldsymbol{r} v_{\text {ext }}(\boldsymbol{r}) n(\boldsymbol{r})$, and we used short-hand notation $n(\boldsymbol{r})$ for $n_{0}(\boldsymbol{r})$. To get the stationary condition, we need to equate the functional derivative of Eq. (1.5) to zero. If $f$ is a functional of density
$n(\boldsymbol{r}), f=f[n]$, then its functional derivative with respect to $n(\boldsymbol{r}), \frac{\delta f[n]}{\delta n(\boldsymbol{r})}$, is defined by [39]

$$
\begin{equation*}
\lim _{\eta \rightarrow 0} \frac{f[n+\eta \delta n]-f[n]}{\eta}=\int d^{3} \boldsymbol{r} \frac{\delta f[n]}{\delta n(\boldsymbol{r})} \delta n(\boldsymbol{r}), \tag{1.6}
\end{equation*}
$$

where $\eta$ is a positive number and $\delta n(\boldsymbol{r})$ is a density variation. The minimum condition of the variational principle of Eq. (1.5), with the constraint that $\int d^{3} \boldsymbol{r} n(\boldsymbol{r})=N$, can be replaced by the following condition on the functional derivative [38, 39]

$$
\begin{equation*}
\frac{\delta}{\delta n(\boldsymbol{r})}\left[\mathscr{F}[n]+E_{\text {ext }}[n]-\mu \int d^{3} \boldsymbol{r} n(\boldsymbol{r})\right]=\frac{\delta \mathscr{F}[n]}{\delta n(\boldsymbol{r})}+v_{\mathrm{ext}}(\boldsymbol{r})-\mu=0 \tag{1.7}
\end{equation*}
$$

where $\mu$ is a Lagrange multiplier ensuring that $\int d^{3} \boldsymbol{r} n(\boldsymbol{r})=N$. The density $n(\boldsymbol{r})$ which satisfies this equation is the ground state electron density and the sum of $\mathscr{F}[n]$ and $E_{\text {ext }}[n]$ with that value of density gives precisely the ground state energy of the system as indicated by Eq. (1.5). One could find the ground state density without solving the Schrödinger wave equation corresponding to the system if one knew the functional $\mathscr{F}[n]$. However, this functional is not known.

Kohn and Sham in 1965 [5] proposed an approximate solution to this problem by considering the so-called non-interacting system, i.e., a system analogous to the physical system but with electron-electron interactions turned off. The Hamiltonian of this non-interacting system is written as $[38,39]$

$$
\begin{equation*}
\hat{H}_{s}=\hat{T}+\hat{V}_{s}=\sum_{j=1}^{N}\left[-\frac{1}{2} \nabla_{j}^{2}+v_{s}\left(\boldsymbol{r}_{j}\right)\right] \tag{1.8}
\end{equation*}
$$

where $\hat{V}_{s}=\sum_{j} v_{s}\left(\boldsymbol{r}_{j}\right)$ is the so-called effective Kohn-Sham(KS) potential, which we will define shortly. The Hohenberg-Kohn theorem applies to this system as well and, hence, a unique one-to-one correspondence exists between its external potential and the ground-state density. Since $\hat{H}_{s}$ is a sum of one-electron Hamiltonians, the solution of the Schrödinger's equation for the KS system is a product of one electron functions (orbitals), and if the antisymmetry condition is taken into account, it is a Slater determinant built of these orbitals.

Each orbital in the Slater determinant satisfies the single-particle Schrödinger equation called KS equation

$$
\begin{equation*}
\left[-\frac{1}{2} \nabla^{2}+v_{\mathrm{s}}(\boldsymbol{r})\right] \psi_{j}(\boldsymbol{x})=\varepsilon_{j} \psi_{j}(\boldsymbol{x}) \tag{1.9}
\end{equation*}
$$

where $\psi_{j}$ is a spin-orbital. The corresponding electron density is

$$
\begin{equation*}
n(\boldsymbol{r})=\sum_{s, j=1}^{N_{\text {occ }}}\left|\psi_{j}(\boldsymbol{x})\right|^{2} \tag{1.10}
\end{equation*}
$$

where $N_{\text {occ }}$ represents number of occupied orbitals and $s$ in the sum represents the summation over spin. The kinetic energy is then obtained using the orbitals as

$$
\begin{equation*}
T_{\mathrm{s}}[n]=-\frac{1}{2} \sum_{s, j}\left\langle\psi_{j}\right| \nabla^{2}\left|\psi_{j}\right\rangle \tag{1.11}
\end{equation*}
$$

Therefore, the kinetic energy becomes an explicit functional of the orbitals and an implicit functional of the density of the system. The total energy of the non-interacting system is

$$
\begin{equation*}
E_{\mathrm{s}}[n]=T_{\mathrm{s}}[n]+\int d^{3} \boldsymbol{r} n(\boldsymbol{r}) v_{\mathrm{s}}(\boldsymbol{r}) \tag{1.12}
\end{equation*}
$$

The variational principle for the KS system becomes

$$
\begin{equation*}
\frac{\delta}{\delta n}\left[T_{\mathrm{s}}[n]+\int d^{3} \boldsymbol{r} v_{\mathrm{s}}(\boldsymbol{r}) n(\boldsymbol{r})-\mu \int d^{3} \boldsymbol{r} n(\boldsymbol{r})\right]=\frac{\delta T_{\mathrm{s}}[n]}{\delta n}+v_{\mathrm{s}}-\mu=0 \tag{1.13}
\end{equation*}
$$

where again the Lagrange multiplier $\mu$ ensures that number of particles in the system is $N$. The total energy of the KS system can also be written in terms of single orbital energies as $E_{\mathrm{s}}[n]=\sum_{j=1}^{N_{\text {occ }}} \varepsilon_{j}$. Now one can write $\mathscr{F}[n]$ for the fully interacting system as

$$
\begin{align*}
\mathscr{F}[n] & =T[n]+\mathscr{W}[n] \\
& =T_{\mathrm{s}}[n]+E_{\mathrm{H}}[n]+T[n]-T_{\mathrm{s}}[n]+\mathscr{W}[n]-E_{\mathrm{H}}[n] \\
& =T_{\mathrm{s}}[n]+E_{\mathrm{H}}[n]+E_{\mathrm{xc}}, \tag{1.14}
\end{align*}
$$

where $E_{\mathrm{H}}[n]=\frac{1}{2} \iint d^{3} \boldsymbol{r} d^{3} \boldsymbol{r}^{\prime} \frac{n(\boldsymbol{r}) n\left(\boldsymbol{r}^{\prime}\right)}{\left|\boldsymbol{r}-\boldsymbol{r}^{\prime}\right|}$ is the so-called Hartree energy, and defining in this way the exchange-correlation energy $E_{\mathrm{xc}}=T[n]-T_{\mathrm{s}}[n]+\mathscr{W}[n]-E_{\mathrm{H}}[n]$. Thus, $E_{\mathrm{xc}}[n]$
has both a kinetic component and a component arising from the electron-electron interaction. It is a very clever decomposition which uses the density and orbitals of the KS system to calculate a large part of $\mathscr{F}[n] . E_{\text {xc }}$ turns out to be small as compared to $T_{\mathrm{s}}[n]+E_{\mathrm{H}}[n]$, so even if it is approximated in a crude way, the resulting method may work reasonably well. However, although $E_{\mathrm{xc}}$ is a tiny part of the total energy of atoms and molecules, it may contribute $100 \%$ to the binding and atomization energies [40]. The dispersion energy, being a correlation effect, is a part of $E_{\mathrm{xc}}$ in KS DFT. The total energy of the interacting system can be written as

$$
\begin{equation*}
E[n]=T[n]+\mathscr{W}[n]+E_{\text {ext }}[n]=T_{\mathrm{s}}[n]+E_{\mathrm{H}}[n]+E_{\mathrm{xc}}[n]+E_{\text {ext }}[n] . \tag{1.15}
\end{equation*}
$$

Now using Eq. (1.15) in Eq. (1.7) we get [38, 39]

$$
\begin{equation*}
\frac{\delta T_{\mathrm{s}}[n]}{\delta n(\boldsymbol{r})}+\frac{\delta E_{\mathrm{H}}[n]}{\delta n(\boldsymbol{r})}+\frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\boldsymbol{r})}+v_{\mathrm{ext}}(\boldsymbol{r})-\mu=0 \tag{1.16}
\end{equation*}
$$

If we compare Eq. (1.16) with Eq. (1.13) we get the effective KS potential

$$
\begin{equation*}
v_{\mathrm{s}}(\boldsymbol{r})=\frac{\delta E_{\mathrm{H}}[n]}{\delta n}+\frac{\delta E_{\mathrm{xc}}[n]}{\delta n}+v_{\mathrm{ext}}(\boldsymbol{r})=v_{\mathrm{H}}(\boldsymbol{r})+v_{\mathrm{xc}}(\boldsymbol{r})+v_{\mathrm{ext}}(\boldsymbol{r}), \tag{1.17}
\end{equation*}
$$

where $v_{\mathrm{H}}(\boldsymbol{r})=\frac{\delta E_{\mathrm{H}}[n]}{\delta n}=\int d^{3} \boldsymbol{r}^{\prime} \frac{n\left(\boldsymbol{r}^{\prime}\right)}{\left|\boldsymbol{r}-\boldsymbol{r}^{\prime}\right|}$ is the Hartree potential and $v_{\mathrm{xc}}(\boldsymbol{r})=\frac{\delta E_{\mathrm{xc}}[n]}{\delta n}$ is the exchange-correlation potential. Thus, we could calculate the energy of a fully interacting system using the ground-state density and the orbitals of a noninteracting (KS) system if we knew the exchange-correlation potential. If we knew the exact $v_{\mathrm{xc}}(\boldsymbol{r})$, the DFT results would be exact. While the exact $v_{\mathrm{xc}}(\boldsymbol{r})$ is not known, several approximations for it has been developed. The approximations which represent $E_{\mathrm{xc}}$ as a functional depending only on the density are called local-density approximations (LDAs) $[6,5,7,8,9,10]$, while those which involve also gradients of the density are called generalized gradient approximations (GGAs) [11, 41, 42, 43]. Note that both LDAs and GGAs contain the Hartree term which is actually nonlocal, but $E_{\mathrm{xc}}$ is always local, i.e., it is an integral of the exchange-correlation energy density $\varepsilon_{\mathrm{xc}}(\boldsymbol{r})$ [ that $\left.E_{\mathrm{xc}}=\int d \boldsymbol{r} n(\boldsymbol{r}) \varepsilon_{\mathrm{xc}}(\boldsymbol{r})\right]$ which depends on the density at a point $\boldsymbol{r}(\mathrm{LDA})$ and both the density and its derivative (GGA). One of the common weakness of all local and
semilocal methods is their inability to take into account long-range correlation effects and hence the dispersion interactions.

Let us derive a wave function based expression for the exchange-correlation energy using the adiabatic-connection approach [44, 45, 46]. In this approach the electron-electron repulsion operator is multiplied by a positive parameter $\lambda \in[0,1]$ to control its strength. Keeping the density of the system fixed at its physical value for the fully interacting system, $\lambda$ is varied so that if $\lambda=0$ we get the Kohn-Sham system and if $\lambda=1$ we have the actual physical system of fully interacting electrons. The Hamiltonian for the system at $\lambda$ is

$$
\begin{equation*}
\hat{H}^{\lambda}=\hat{T}+\hat{V}_{\mathrm{ext}}^{\lambda}+\lambda \hat{\mathscr{W}} \tag{1.18}
\end{equation*}
$$

where $\hat{V}_{\text {ext }}^{\lambda}=\sum_{i} v_{\text {ext }}^{\lambda}\left(\boldsymbol{r}_{i}\right)=\int d^{3} \boldsymbol{r} v_{\text {ext }}^{\lambda}(\boldsymbol{r}) \hat{n}(\boldsymbol{r})$. [Note that $\hat{V}_{\text {ext }}^{\lambda}$ has to be properly adjusted to keep $n(\boldsymbol{r})$ unchanged]. If $\Psi^{\lambda}$ is the ground-state wave function of the system then $n(\boldsymbol{r})=\left\langle\Psi^{\lambda}\right| \hat{n}\left|\Psi^{\lambda}\right\rangle$ and $E_{0}^{\lambda}=\left\langle\Psi^{\lambda}\right| \hat{H}^{\lambda}\left|\Psi^{\lambda}\right\rangle$ are its ground-state density and energy, respectively. The energy of the fully interacting system of electrons can be written as

$$
\begin{equation*}
E_{0}^{\lambda=1}=E_{0}^{\lambda=0}+\int_{0}^{1} d \lambda \frac{d E_{0}^{\lambda}}{d \lambda}=E_{0}^{\lambda=0}+\int_{0}^{1} d \lambda\left[\left\langle\Psi^{\lambda}\right| \frac{d \hat{V}_{\mathrm{ext}}^{\lambda}}{d \lambda}\left|\Psi^{\lambda}\right\rangle+\left\langle\Psi^{\lambda}\right| \hat{\mathscr{W}}\left|\Psi^{\lambda}\right\rangle\right], \tag{1.19}
\end{equation*}
$$

where we have used the Hellman-Feynman theorem which gives $\frac{d E_{0}^{\lambda}}{d \lambda}=\left\langle\Psi^{\lambda}\right| \frac{d \hat{H}^{\lambda}}{d \lambda}\left|\Psi^{\lambda}\right\rangle$. Now consider

$$
\begin{align*}
\int_{0}^{1} d \lambda\left\langle\Psi^{\lambda}\right| \frac{d \hat{V}_{\text {ext }}^{\lambda}}{d \lambda}\left|\Psi^{\lambda}\right\rangle & =\int_{0}^{1} d \lambda\left\langle\Psi^{\lambda}\right| \frac{d\left[\int d^{3} \boldsymbol{r} v_{\text {ext }}^{\lambda}(\boldsymbol{r}) \hat{n}(\boldsymbol{r})\right]}{d \lambda}\left|\Psi^{\lambda}\right\rangle \\
& =\int d^{3} \boldsymbol{r} n(\boldsymbol{r}) \int_{0}^{1} d \lambda \frac{d v_{\text {ext }}^{\lambda}(\boldsymbol{r})}{d \lambda} \\
& =\int d^{3} \boldsymbol{r} n(\boldsymbol{r})\left[v_{\text {ext }}^{\lambda=1}(\boldsymbol{r})-v_{\text {ext }}^{\lambda=0}(\boldsymbol{r})\right] \tag{1.20}
\end{align*}
$$

It should be noticed that $E_{0}^{\lambda=0}=E_{s}$ is the ground-state energy of the KS system, $v_{\text {ext }}^{\lambda=0}=v_{\mathrm{s}}$ is the effective KS potential, $v_{\text {ext }}^{\lambda=1}=v_{\text {ext }}$ is the external potential for the fully
interacting system, and $E_{0}^{\lambda=1}=E_{0}$ is the ground-state energy of the fully interacting system. Using this information and inserting Eq. (1.20) in Eq. (1.19) we get

$$
\begin{align*}
E_{0} & =E_{\mathrm{s}}-\int d^{3} \boldsymbol{r} n(\boldsymbol{r}) v_{\mathrm{s}}(\boldsymbol{r})+\int d^{3} \boldsymbol{r} n(\boldsymbol{r}) v_{\mathrm{ext}}(\boldsymbol{r})+\int_{0}^{1} d \lambda\left\langle\Psi^{\lambda}\right| \hat{\mathscr{W}}\left|\Psi^{\lambda}\right\rangle \\
& =T_{\mathrm{s}}+E_{\mathrm{ext}}+\int_{0}^{1} d \lambda\left\langle\Psi^{\lambda}\right| \hat{\mathscr{W}}\left|\Psi^{\lambda}\right\rangle \tag{1.21}
\end{align*}
$$

where we used the fact that $T_{\mathrm{s}}=E_{\mathrm{s}}-\int d^{3} \boldsymbol{r} n(\boldsymbol{r}) v_{\mathrm{s}}(\boldsymbol{r})$. Now comparing Eq. (1.15) and Eq. (1.21), we get

$$
\begin{equation*}
E_{\mathrm{xc}}[n]=\int_{0}^{1} d \lambda\left\langle\Psi^{\lambda}\right| \hat{\mathscr{W}}\left|\Psi^{\lambda}\right\rangle-E_{\mathrm{H}}[n] . \tag{1.22}
\end{equation*}
$$

This is the formal expression for the exchange-correlation energy. The contrbution of the electron-electron repulsion is evident here while the kinetic component is hidden in the integration over the parameter $\lambda$.

A physically appealing way to compare various approximations for $E_{\mathrm{xc}}$ is to examine the so-called exchange-correlation hole. It is related to the pair correlation function defined as [47]

$$
\begin{equation*}
g\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}\right)=\frac{1}{n(\boldsymbol{r}) n\left(\boldsymbol{r}^{\prime}\right)}\left\langle\Psi_{0}\right| \sum_{i \neq j} \delta\left(\boldsymbol{r}-\boldsymbol{r}_{i}\right) \delta\left(\boldsymbol{r}^{\prime}-\boldsymbol{r}_{j}\right)\left|\Psi_{0}\right\rangle . \tag{1.23}
\end{equation*}
$$

The pair correlation function $g\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}\right)$ is the normalized probability of finding an electron at $\boldsymbol{r}$ while there is another electron at $\boldsymbol{r}^{\prime}$. Now if we represent the electron-electron repulsion operator in the form

$$
\begin{equation*}
\hat{\mathscr{W}}=\frac{1}{2} \sum_{i \neq j} \frac{1}{\left|\boldsymbol{r}_{i}-\boldsymbol{r}_{j}\right|}=\frac{1}{2} \iint d^{3} \boldsymbol{r} d^{3} \boldsymbol{r}^{\prime} \sum_{i \neq j} \frac{\delta\left(\boldsymbol{r}-\boldsymbol{r}_{i}\right) \delta\left(\boldsymbol{r}^{\prime}-\boldsymbol{r}_{j}\right)}{\left|\boldsymbol{r}-\boldsymbol{r}^{\prime}\right|}, \tag{1.24}
\end{equation*}
$$

the expectation value of this operator can be written as

$$
\begin{align*}
\left\langle\Psi_{0}\right| \hat{\mathscr{W}}\left|\Psi_{0}\right\rangle & =\frac{1}{2} \iint d^{3} \boldsymbol{r} d^{3} \boldsymbol{r}^{\prime} \sum_{i \neq j} \frac{\left\langle\Psi_{0}\right| \delta\left(\boldsymbol{r}-\boldsymbol{r}_{i}\right) \delta\left(\boldsymbol{r}^{\prime}-\boldsymbol{r}_{j}\right)\left|\Psi_{0}\right\rangle}{\left|\boldsymbol{r}-\boldsymbol{r}^{\prime}\right|}  \tag{1.25}\\
& =\frac{1}{2} \iint d^{3} \boldsymbol{r} d^{3} \boldsymbol{r}^{\prime} \frac{n(\boldsymbol{r}) n\left(\boldsymbol{r}^{\prime}\right) g\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}\right)}{\left|\boldsymbol{r}-\boldsymbol{r}^{\prime}\right|} \tag{1.26}
\end{align*}
$$

where in the last equation we used the definition of the pair correlation function from Eq. (1.23). Using the definition for the pair-correlation function given in Eq. (1.23)
and expectation value of the electron-electron repulsion operator given in Eq. (1.26) we can write the exchange-correlation energy as

$$
\begin{equation*}
E_{\mathrm{xc}}[n]=\frac{1}{2} \iint d^{3} \boldsymbol{r} d^{3} \boldsymbol{r}^{\prime} \int_{0}^{1} d \lambda \frac{n(\boldsymbol{r}) n\left(\boldsymbol{r}^{\prime}\right)\left[g^{\lambda}\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}\right)-1\right]}{\left|\boldsymbol{r}-\boldsymbol{r}^{\prime}\right|}, \tag{1.27}
\end{equation*}
$$

where $g^{\lambda}\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}\right)$ is the pair-correlation function for the system in which electron-electron interaction is scaled by $\lambda$. This expression can be written in terms of the average exchange-correlation hole function. The (regular) exchange-correlation hole function is defined as

$$
\begin{equation*}
n_{\mathrm{xc}}^{\lambda}\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}\right)=n\left(\boldsymbol{r}^{\prime}\right)\left[g^{\lambda}\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}\right)-1\right] . \tag{1.28}
\end{equation*}
$$

The average exchange-correlation hole function $n_{\mathrm{xc}}\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}\right)$ of the system is defined as [48]

$$
\begin{equation*}
n_{\mathrm{xc}}\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}\right)=\int_{0}^{1} d \lambda n_{\mathrm{xc}}^{\lambda}\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}\right)=\int_{0}^{1} d \lambda n\left(\boldsymbol{r}^{\prime}\right)\left[g^{\lambda}\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}\right)-1\right] . \tag{1.29}
\end{equation*}
$$

This function represents the reduction in the probability of finding an electron at $\boldsymbol{r}^{\prime}$ in the presence of another electron at $\boldsymbol{r}$. This reduction occurs due to the Pauli exclusion principle (this effect applies only to electrons of the same spin) and the Coulomb repulsion [40]. The exchange-correlation energy can now be written in terms of $n_{\mathrm{xc}}\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}\right)$ as

$$
\begin{equation*}
E_{\mathrm{xc}}[n]=\frac{1}{2} \iint d^{3} \boldsymbol{r} d^{3} \boldsymbol{r}^{\prime} \frac{n(\boldsymbol{r}) n_{\mathrm{xc}}\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}\right)}{\left|\boldsymbol{r}-\boldsymbol{r}^{\prime}\right|} \tag{1.30}
\end{equation*}
$$

Thus, the exchange-correlation energy is the Coulomb interaction between the electrondensity and the exchange-correlation hole surrounding it. The exchange-correlation hole satisfies a sum rule $\int d^{3} \boldsymbol{r}^{\prime} n_{\mathrm{xc}}\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}\right)=-1$. It played a major role in the development of DFT approximations. It was obvious for a long time that the way to improve the LDA is to use an expansion in terms of density gradients. This gives the so-called gradient-expansion approximation (GEA) [6, 5, 49] which, however, gives less accurate energies than the LDA and violates some of the sum rules. This problem has been cured by analyzing the exchange-correlation hole and introducing a cutoff to make the hole more physical. The resulting approximations are called generalized gradient approximations (GGAs) [50, 51].

### 1.2 Symmetry-Adapted Perturbation Theory

In a cluster of atoms or molecules the intermolecular interactions are a few orders of magnitude weaker than the intramolecular interactions. Therefore, intermolecular interactions can be treated through perturbation theory. The fermionic nature of electrons requires using properly antisymmetrized wave functions for the system. The perturbation theory which uses antisymmetric wave functions is known as symmetry-adapted perturbation theory (SAPT) $[1,2,3,4]$. The starting point for the perturbation theory would be the solution of Schrödinger equation for monomers, but except for very simple systems this equation cannot be solved exactly. Hence even at the monomer level, we have to use some approximate method. Thus, perturbation theory is an obvious choice for monomers as well, and SAPT becomes a double perturbation theory. This approach resolves intermolecular interactions into several terms and provides physical insight into these components by associating each one with a particular physical phenomenon. The Hamiltonian of the dimer is

$$
\begin{equation*}
\hat{H}=\hat{F}+\hat{V}+\hat{W} \tag{1.31}
\end{equation*}
$$

where $\hat{F}=\hat{F}_{A}+\hat{F}_{B}$ is the sum of Fock operators for the monomers, $\hat{W}=\hat{W}_{A}+\hat{W}_{B}$ is the sum of Møller-Plesset fluctuation operators coming from the difference between Fock operator of each monomer with the actual Hamiltonian of that monomer, and $\hat{V}$ is the intermonomer interaction operator which represents the Coulomb interaction between particles of the two monomers.

The use of $\hat{V}$ and $\hat{W}$ as perturbations leads to an expansion for interaction energy $E_{\text {int }}$ as

$$
\begin{equation*}
E_{\text {int }}=\sum_{n=1}^{\infty} \sum_{j=0}^{\infty}\left(E_{\mathrm{RS}}^{(n j)}+E_{\text {exch }}^{(n j)}\right) \tag{1.32}
\end{equation*}
$$

where the superscripts $n$ and $j$ denote the orders in $\hat{V}$ and $\hat{W}$ respectively. The corrections $E_{\mathrm{RS}}^{(n j)}$ are defined in the Rayleigh-Schrödinger perturbation theory, while
$E_{\text {exch }}^{(n j)}$ are called the exchange corrections and result from the antisymmetrization of the dimer wave function. The second-order dispersion energy given by SAPT is [3]

$$
\begin{equation*}
E_{\mathrm{disp}}^{(2)}=\sum_{k \neq 0} \sum_{l \neq 0} \frac{\left.\left|\left\langle\Phi_{0}^{A} \Phi_{0}^{B}\right| \hat{V}\right| \Phi_{k}^{A} \Phi_{l}^{B}\right\rangle\left.\right|^{2}}{E_{0}^{A}+E_{0}^{B}-E_{k}^{A}-E_{l}^{B}}, \tag{1.33}
\end{equation*}
$$

where $\hat{V}$ is intermonomer interaction operator and $\Phi_{i}^{X}$ and $E_{i}^{X}$ are the exact wave function and energy for the $i$ th state of monomer $X$. This second-order dispersion energy fully includes the charge overlap effects, i.e., is valid for all intermonomer separations. This definition shows that the dispersion energy is a pure intermolecular correlation effect. The second-order dispersion energy can be written in terms of the density-density response function (called also the frequency-dependent density susceptibility (FDDS)) as $[52,34,35]$

$$
\begin{equation*}
E_{\mathrm{disp}}^{(2)}=-\frac{1}{2 \pi} \int_{0}^{\infty} d u \iiint \int d \boldsymbol{r}_{1} d \boldsymbol{r}_{2} d \boldsymbol{r}_{1}^{\prime} d \boldsymbol{r}_{2}^{\prime} \frac{\chi_{A}\left(\boldsymbol{r}_{1}, \boldsymbol{r}_{1}^{\prime}, \mathrm{i} u\right) \chi_{B}\left(\boldsymbol{r}_{2}, \boldsymbol{r}_{2}^{\prime}\right), \mathrm{i} u}{\left|\boldsymbol{r}_{1}-\boldsymbol{r}_{2}\right|\left|\boldsymbol{r}_{1}^{\prime}-\boldsymbol{r}_{2}^{\prime}\right|}, \tag{1.34}
\end{equation*}
$$

where $\chi_{A}$ and $\chi_{B}$ are response functions (FDDS's) of monomer $A$ and $B$ and $u$ is the imaginary frequency. The response functions are purely monomer properties. Thus, the second-order dispersion energy has been expressed here in terms of monomer properties. Note that sometimes the symbol $\alpha$ is used instead of $\chi$ in this context, with $\alpha\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}, \mathrm{i} u\right)=-\chi\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}, \mathrm{i} u\right)$. Eq. (1.34) is often called the generalized Casimir-Polder expression. The second-order dispersion energy can also be written as

$$
\begin{equation*}
E_{\text {disp }}^{(2)}=\left\langle\Phi_{0}\right| V\left|\Phi_{\text {disp }}^{(1)}\right\rangle, \tag{1.35}
\end{equation*}
$$

where $\left|\Phi_{0}\right\rangle=\left|\Phi_{0}^{A} \Phi_{0}^{B}\right\rangle$ and $\Phi_{\text {disp }}^{(1)}$ is the first-order dispersion wave function of the system, given by

$$
\begin{equation*}
\left|\Phi_{\mathrm{disp}}^{(1)}\right\rangle=\sum_{k \neq 0, l \neq 0} \frac{\left|\Phi_{k}^{A} \Phi_{l}^{B}\right\rangle\left\langle\Phi_{k}^{A} \Phi_{l}^{B}\right| V\left|\Phi_{0}^{A} \Phi_{0}^{B}\right\rangle}{E_{0}^{A}+E_{0}^{B}-E_{k}^{A}-E_{l}^{B}} . \tag{1.36}
\end{equation*}
$$

The antisymmetrization of $\Phi_{\text {disp }}^{(1)}$ gives the second-order exchange-dispersion energy which can be written as

$$
\begin{equation*}
E_{\text {exch-disp }}^{(2)}=-\left\langle\Phi_{0}\right|(V-\bar{V})\left(P_{1}-\bar{P}_{1}\right)\left|\Phi_{\text {disp }}^{(1)}\right\rangle, \tag{1.37}
\end{equation*}
$$

where $\bar{V}=\left\langle\Phi_{0}\right| V\left|\Phi_{0}\right\rangle$ and $\bar{P}_{1}=\left\langle\Phi_{0}\right| P_{1}\left|\Phi_{0}\right\rangle$ with the antisymmetrization limited to single pair exchanges of electrons between the monomers denoted by $P_{1}$.

It should be mentioned that $\operatorname{CCSD}(\mathrm{T})$ is a very accurate method for many electron systems and captures all kinds of interactions, but it does not give explicit value for dispersion interactions. Hence, we used $\operatorname{CCSD}(\mathrm{T})$ results as benchmark interaction energy and SAPT results for benchmark dispersion energy.

## Chapter 2

## DO SEMILOCAL DENSITY-FUNCTIONAL APPROXIMATIONS RECOVER DISPERSION ENERGIES AT SMALL INTERMONOMER SEPARATIONS?

The methods that add dispersion energies to interaction energies computed using density functional theory (DFT), known as DFT + D methods, taper off the dispersion energies at distances near van der Waals minima and smaller based on an assumption that DFT starts to reproduce the dispersion energies there. We show that this assumption is not correct as the alleged contribution behaves unphysically and originates to a large extent from non-exchange-correlation terms. Thus, dispersion functions correct DFT in this region for deficiencies unrelated to dispersion interactions.

In the standard Kohn-Sham (KS) implementation of density functional theory (DFT), all electron correlation effects are included in the exchange-correlation energy. The existing semilocal functionals fail to describe interactions which involve regions separated by several angstroms or more due to problems with long-range correlations of electronic motion [53]. The semilocal generalized gradient approximations (GGA's) cannot describe such correlations due to the limited range of the exchange-correlation hole, of the order of $1 \AA$ [18]. One can say that these methods are myopic with the range of vision of about $1 \AA$. An important question is at what separations inter-region correlation effects are (partly) reproduced by GGA's. Since dispersion interactions result from long-range electron correlations and can be precisely defined as functions of intermolecular separations, $R$, these interactions provide an excellent case study to answer this question.

As an example, consider the interaction energy of $\mathrm{Ar}_{2}$, shown in Fig. 2.1, calculated using various DFT methods, as well as the Hartree-Fock (HF) method and


Figure 2.1: Performance of various DFT methods for $\mathrm{Ar}_{2}$ : B3LYP [54], SCAN [30], TPSS [55], PBE0 [42, 56], PBE [42], rPW86-PBE [43, 42] as used in Ref. [28], PW91 [57, 58, 59], revPBE-PW92 [60, 58] as used in Ref. [25], and LDA in the Perdew-Wang parametrization [58]. CCSD(T), SAPT, and HF interaction energies are also shown, as well as the dispersion energy, $E_{\text {dispx }}$. For details of calculations, see Appendix B.
symmetry-adapted perturbation theory (SAPT) [1, 2, 3, 4]. The benchmark interaction energies are from the coupled cluster method with single, double, and noniterative triple excitations $[\operatorname{CCSD}(\mathrm{T})]$. We have also plotted the dispersion energy

$$
\begin{equation*}
E_{\mathrm{dispx}}=E_{\mathrm{disp}}^{(2)}+E_{\text {exch-disp }}^{(2)}+E_{\mathrm{disp}}^{(3)}+E_{\text {exch-disp }}^{(3)} \tag{2.1}
\end{equation*}
$$

where $E_{\text {disp }}^{(i)}\left(E_{\text {exch-disp }}^{(i)}\right)$ are the $i$ th-order SAPT dispersion (exchange-dispersion) energies. These results, as well all other results here, were obtained with extrapolations to
the complete basis set limit. All DFT methods included in Fig. 2.1 fail to recover the interaction energy essentially at all separations, most prominently in the asymptotic region where they decay too fast (exponentially rather than as an inverse power of $R$ ), which clearly can be attributed to the missing dispersion energy. For $R$ roughly in the range 3-5 $\AA$, most DFT interaction energies still differ dramatically from accurate values, but in a few cases the predictions are reasonable. The latter is sometimes interpreted as a partial recovery of the dispersion interactions [14, 15, 16, 17], although the size of the exchange-correlation hole is still small compared to this range of $R$ 's. Finally, for $R$ smaller than about $3 \AA$, DFT interaction energies start to agree with the benchmark. However, this is mainly because $E_{\text {dispx }}$ becomes a small fraction of the total interaction energy, only $12 \%$ in magnitude at $R=1.5 \AA$.

Most methods displayed in Fig. 2.1 can be brought to agreement with CCSD(T) by adding a negative correction, which, at very large $R$, is simply the dispersion energy. At shorter $R$, the dispersion energy has to be tapered, differently for each DFT method. This observation led to a family of methods supplementing DFT interaction energies by a "dispersion" correction referred to as DFT+D type methods $[61,14,15,62,63,16$, $19,17]$. These methods became enormously popular and perform reasonably well, see, e.g., Ref. [64] showing that some DFT+D methods reproduce benchmark interaction energy curves with a median unsigned percentage error of only $4-5 \%$. Only SAPT based on DFT [SAPT(DFT)][36, 37] performed better, with an error of $2 \%$.

In DFT + D, to taper the magnitude of dispersion energy in the region of van der Waals (vdW) minimum and at smaller $R$, one uses switching functions fitted to the total interaction energies computed using accurate wave function methods on a set of dimers. They are called in literature "damping functions", but are substantially different from the conventional damping functions used to account for the chargeoverlap effects neglected in the asymptotic expansions [65, 66, 67, 68, 3]. This is shown in Fig. 2.2 on an example of a popular dispersion correction, called D3BJ [16, 19, 24]. The correction without switching is shown as D3(no-switching). The changes of D3(no-switching) values due to switching are quite significant at all $R$. For example,


Figure 2.2: The dispersion corrections D3BJ [multiplied by $R^{6}$ ] for $\mathrm{Ar}_{2}$ corresponding to various DFT functionals compared to $E_{\text {disp }}^{(2)}+E_{\text {exch-disp }}^{(2)}$ and to the dispersion energy from the asymptotic expansion, $E_{\text {disp,as }}^{(2)}$. The latter quantities were computed using SAPT(DFT) to be at the same level of theory as D3, see Appendix B.
$\mathrm{D} 3 \mathrm{BJ}(\mathrm{PBE})$ is reduced in magnitude by a factor of almost 2 at the vdW minimum, $R_{\mathrm{vdW}}=3.76 \AA$, as compared to D3(no-switching). This reduction is strikingly different from the physical damping of the asymptotic dispersion energy, $E_{\text {disp,as }}^{(2)}$, as shown by the ratio of this quantity to $E_{\text {disp }}^{(2)}$ amounting to about 1.06. The D3BJ switching is also too large to account for the exchange-dispersion effects, included in the curve $E_{\text {disp }}^{(2)}+E_{\text {exch-disp }}^{(2)}$. This curve defines an upper limit for the physical damping of the
asymptotic expansion, the damping which accounts for the exchange and charge-overlap effects and thus removes the singularities of $1 / R^{n}$ terms. The significant additional amount of damping displayed by the D3BJ curves is therefore unphysical. One may notice that for $R>4 \AA$, several dispersion functions, in particular D3BJ(revPBE), are "antidamped". This is an artifact of D3BJ, for explanations see Appendix B.

The standard explanation for the extent of switching off of asymptotic dispersion energies in DFT +D is that this has to be done to avoid double counting since DFT methods start to recover dispersion effects at small $R[14,15,16,17]$, i.e., the conjecture of such recovery is fundamental in the construction of DFT + D. It implicitly assumes that errors of DFT result almost exclusively from the dispersion component which is certainaly true for large $R$ in dispersion-dominated dimers where the DFT interaction energy is exponentially small. However, at smaller separations, the errors not related to dispersion can be large. To demonstrate this behavior, we show in Fig. 2.3 the ratio of interaction energies from different DFT methods to the $\operatorname{CCSD}(\mathrm{T})$ interaction energies as well as the ratio $E_{\text {dispx }} / E_{\text {int }}^{\mathrm{CCSD}(\mathrm{T})}$ for $\mathrm{Ar}-\mathrm{Li}^{+}$. Surprisingly, all DFT methods overestimate the magnitude of interaction energy by about $10-25 \%$ at $R_{\mathrm{vdW}}(2.4 \AA)$ where the dispersion energy amounts to only $5 \%$ of $E_{\text {int }}^{\mathrm{CCSD}(\mathrm{T})}$. Thus, if one accepts the hypothesis that DFT approximations recover a part of the dispersion energy near $R_{\mathrm{vdW}}$, for $\mathrm{Ar}-\mathrm{Li}^{+}$, they recover $200-500 \%$ of this quantity. This does not appear reasonable and, therefore, the only option is to attribute these errors to the dispersionless component of the DFT interaction energy. In Appendix B, similar results are shown for Ar-proton. Although there is no dispersion energy involved in this case, DFT interaction energies have significant negative errors at almost all separations included.

To further analyze the issue, let us divide the exact interaction energy into the dispersion contribution and the remainder, which we will call the dispersionless interaction energy

$$
\begin{equation*}
E_{\mathrm{dl}}=E_{\mathrm{int}}^{\mathrm{CCSD}(\mathrm{~T})}-E_{\mathrm{dispx}} . \tag{2.2}
\end{equation*}
$$



Figure 2.3: Ratio of DFT interaction energies and $E_{\text {dispx }}$ to $\operatorname{CCSD}(\mathrm{T})$ interaction energy for the $\mathrm{Ar}-\mathrm{Li}^{+}$complex.
$E_{\mathrm{dl}}$ does not contain any of the intermonomer electron correlation effects as these are, by definition, included in $E_{\text {dispx }}$. However, it still contains some intramonomer correlation effects on interaction energies. Another quantity, $E_{\text {extra }}$, is defined as

$$
\begin{equation*}
E_{\mathrm{extra}}=E_{\mathrm{int}}^{\mathrm{DFT}}-E_{\mathrm{dl}} . \tag{2.3}
\end{equation*}
$$

Thus, $E_{\text {extra }}$ represents the dispersion energy recovered by a given DFT functional, if any, as well as errors of DFT approximations unrelated to dispersion energies. The ratio $E_{\text {extra }} / E_{\text {dispx }}$ for $\mathrm{Ar}_{2}$ is plotted in Fig. 2.4. The following observations can be made: (a) The ratio is tiny in the asymptotic region for all methods; (b) While there


Figure 2.4: Comparison of $E_{\text {extra }} / E_{\text {dispx }}$ for $\mathrm{Ar}_{2}$.


Figure 2.5: The ratios $E_{\text {extra }} / E_{\text {dispx }}, \Delta E_{\mathrm{x}} / E_{\text {dispx }}, \Delta E_{\mathrm{c}} / E_{\mathrm{dispx}}$, and $\Delta E_{\mathrm{xc}} / E_{\mathrm{dispx}}$ for the argon dimer.
is a considerable spread in the values of this ratio near $R_{\mathrm{vdW}}$, the values are again very close to each other for the shortest separations shown (except for HF, LDA and dlDF [20]); (c) The ratio $E_{\text {extra }} / E_{\text {dispx }}$ reaches the value of 1 near $R=2 \AA$ for most methods, but does not remain constant and continues to increase further for shorter separations (for the special case of SCAN, see Appendix B. Thus, all functionals give $E_{\text {extra }}$ larger in magnitude than $E_{\text {dispx }}$ at these $R$ 's, which means these methods need a positive "dispersion" correction in this region. This behavior is a strong indicator that DFT approximations do not reproduce dispersion energies at the separations included in Fig. 2.4. If the dispersion energies were reproduced for the right reasons, i.e., because the exchange-correlation holes start to overlap, the behavior should be as shown in the
inset of Fig. 2.4; (d) For B3LYP and revPBE-PW92, the ratio is negative in some regions, which means that the corresponding correction should be larger than the true dispersion energy; (e) Almost all DFT methods "recover" a significant portion of the dispersion energy at separations somewhat larger than $R_{\mathrm{vdW}}$ which is well beyond the region where any overlap of exchange-correlation holes is possible; (f) An interesting example is provided by the HF curve since, by definition, the HF method cannot give any dispersion energy. Yet, $E_{\mathrm{int}}^{\mathrm{HF}}$ is not equal to $E_{\mathrm{dl}}$ since the HF method also neglects intramonomer correlation effects in interaction energies. One may wrongly think that the HF method reproduces about $23 \%$ of the dispersion energy at $1.5 \AA$. Clearly, all these findings indicate that $E_{\text {extra }}$ given by the DFT methods included in Fig. 2.4 cannot be considered to represent the dispersion energy. In contrast, Fig. 3 of Appendix B shows that $E_{\text {extra }}$ computed using wave-function methods is approximately constant with $R$.

To get insights into the origin of $E_{\text {extra }}$, we plot in Fig. 2.5 the ratios $E_{\text {extra }} / E_{\text {dispx }}$, $\Delta E_{\mathrm{c}} / E_{\text {dispx }}, \Delta E_{\mathrm{x}} / E_{\text {dispx }}$, and $\Delta E_{\mathrm{xc}} / E_{\text {dispx }}=\left(\Delta E_{\mathrm{x}}+\Delta E_{\mathrm{c}}\right) / E_{\text {dispx }}$, where $\Delta E_{\mathrm{x}}\left(\Delta E_{\mathrm{c}}\right)$ is the contribution of the exchange (correlation) energy to the interaction energy and is obtained by subtracting the sum of exchange (correlation) energies of monomers from the dimer exchange (correlation) energy (exact exchange is not included in $\Delta E_{\mathrm{x}}$ ). One may assume that if any component of DFT reproduces the dispersion energy, it should be mainly $\Delta E_{\mathrm{c}}$, but $\Delta E_{\mathrm{x}}$ can also contribute [69, 70]. Let us discuss these ratios for the SCAN functional. The behavior of $\Delta E_{\mathrm{c}}$ is reasonably physical as the ratio $\Delta E_{\mathrm{c}} / E_{\text {dispx }}$ increases gradually with the decrease of $R$ from zero to about 1 near $R=2.5 \AA$ (but then starts to decrease). However, $\Delta E_{\mathrm{c}} / E_{\text {dispx }}$ is in general different from $E_{\text {extra }} / E_{\text {dispx }}$ by up to a factor of 2 . Thus, effects other than correlation are equally important. In contrast to $\Delta E_{\mathrm{c}} / E_{\text {dispx }}, \Delta E_{\mathrm{x}} / E_{\text {dispx }}$ changes rapidly with $R$, ranging from -1 to 3.5 , the behavior clearly rooted in LDA. The negative sign for separations somewhat larger than $R_{\mathrm{vdw}}$, i.e., positive $\Delta E_{\mathrm{x}}$, means that the notion that $\Delta E_{\mathrm{x}}$ could contribute to dispersion energy for such $R$ is not true for SCAN as the dispersion energy is, by definition, a negative quantity. Furthermore, in the region


Figure 2.6: The ratios $E_{\text {extra }} / E_{\text {dispx }}$ for $\mathrm{Ar}-\mathrm{HF}$ and $\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}$.
where $\Delta E_{\mathrm{x}}$ is positive, $\Delta E_{\mathrm{c}}$ is almost zero, but $E_{\text {extra }} / E_{\text {dispx }}$ reaches values as high as 0.5 . This means that the non-exchange-correlation (non-xc) components of $E_{\text {extra }}$ "reproduce" dispersion. For other functionals in Fig. 2.5, the relations are generally more chaotic and in particular $\Delta E_{\mathrm{c}} / E_{\text {dispx }}$ and $E_{\text {extra }} / E_{\text {dispx }}$ are much farther from each other than for SCAN. We believe the important finding of this analysis is that it always requires significant non-xc contributions to explain the difference between $\Delta E_{\text {xc }} / E_{\text {dispx }}$ and $E_{\text {extra }} / E_{\text {dispx }}$. In Appendix B we present similar results for LRC$\omega$ PBEh [71] and $\omega \mathrm{B} 97$ [72], range-separated hybrid functionals, as well as analyze the non-xc contributions and the dependence on density.

Figure 2.6 shows $E_{\text {extra }} / E_{\text {dispx }}$ for $\mathrm{Ar}-\mathrm{HF}$ and $\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}$. The results for $\mathrm{Ar}-\mathrm{HF}$ are
very similar to $\mathrm{Ar}_{2}$, but significant differences are seen for the water dimer, especially at large $R$. This is because at these $R$ 's the interaction energy is dominated by the electrostatic component and errors in this component (unavoidable since the dipole moments given by the methods studied are a few percent different from the $\operatorname{CCSD}(\mathrm{T})$ ones) could be several times larger than $E_{\text {dispx }}$, as the latter quantity amounts to only $1 \%$ of $E_{\text {int }}$ at $R=10 \AA$.

If semilocal DFT approximations do not recover $E_{\text {dispx }}$ in the range of $R$ 's relevant for intermolecular interactions, the excessive damping in the dispersion corrections in DFT + D methods is unwarranted, in particular since one type of physical interaction (long-range electron correlation) is used to fix errors in another type of interaction (electrostatic, polarization and first-order exchange that do not involve long-range correlations). One way to go around this problem is to add the physical dispersion energy at all $R$ 's to those DFT methods which give interaction energies close to $E_{\mathrm{dl}}$, such as revPBE-LDA or rPW86-PBE. These functionals were paired with nonlocal density functionals in Refs. [25] and [28], respectively. One may mention here that the exchange functional rPW86 was parametrized in Ref. [43] to give interaction energies similar to the HF ones, in order to be applied with nonlocal density functionals. The fact that nonlocal functionals typically do not include excessive damping supports our thesis that such damping should be avoided. Another nearly dispersionless functional is the APF functional of Ref. [73]. Possibly the best choice is to use DFT methods optimized on $E_{\mathrm{dl}}$, such as dlDF [20], since this part of the interaction energy contains physical components not involving long-range electron correlations, so that a semilocal DFT should be able to accurately recover $E_{\mathrm{dl}}$ for good physical reasons. The observations made in the present work may guide development of future DFT +D methods as well as of nonlocal functionals.

In conclusion, we have shown that the claim that semilocal DFT methods recover a significant portion of dispersion energies at separations of vdW minima cannot be defended. For dispersion-dominated dimers, numerical results might suggest otherwise since $E_{\text {extra }}$ changes from zero at $R \rightarrow \infty$ to a value close to $E_{\text {dispx }}$ at some $R$ somewhat
smaller than $R_{\mathrm{vdw}}$. We show, however, that $E_{\text {extra }}$ does not have physical characteristics expected of dispersion energy. A major failure is that after becoming equal to $E_{\text {dispx }}$, $E_{\text {extra }}$ continues to increase in magnitude as $R$ decreases. Furthermore, $E_{\text {extra }}$ originates only in a small part from $\Delta E_{\mathrm{c}}$, whereas the major contributions come from $\Delta E_{\mathrm{x}}$ and the non-xc components of the functionals. The non-xc terms should not reproduce dispersion energies (or any correlation effects), so this behavior is unphysical. We also demonstrate that DFT gives poor interaction energies even for systems with no or very small dispersion interactions such as $\mathrm{Ar}-$ proton and $\mathrm{Ar}-\mathrm{Li}^{+}$. These observations show that DFT approximations have severe accuracy problems other than their inability to recover dispersion energies. Thus, our final conclusion is that the success of DFT +D methods is mainly due to cancellations of various errors in the exchange and non-xc components by the dispersion functions, i.e., the results are right mostly for wrong reasons.

## Chapter 3

## DISPERSION ENERGY FROM LOCAL POLARIZABILITY DENSITY

A simple functional for calculating dispersion energies is proposed. Compared with similar formulas used earlier, we introduced a regularization to remove its singularities and used a dynamic polarizability density similar to those in the recent so-called van der Waals density functionals. The performance of the new functional is tested on a set of representative dimers. It is found that it is significantly more accurate than the most recent van der Waals density functional.

Density functional theory (DFT) is the most popular method for studying the electronic properties of matter due to its reasonable accuracy relative to computational costs. The exact form of a term in the DFT energy called the exchange-correlation energy is unknown, and a large number of approximations to this term have been constructed, in particular, the local density approximations (LDA) $[6,5,58]$ and the semilocal generalized-gradient approximations (GGA) [41, 74, 13]. All local or semilocal approximations are incapable of describing long-range correlations of electron motions and hence fail to capture dispersion interactions [53, 75, 76, 77]. The van der Waals density functional (vdW-DF) [25, 26] was designed to overcome this problem and account for the nonlocal electron correlation. It uses the plasmon-pole model of Lundqvist [78] to build an approximate response function that can describe long-range collective behavior of an electronic system and therefore describe dispersion interactions.

An alternative approach is to start from the generalized Casimir-Polder formula
for the second-order dispersion energy [52, 34, 35]

$$
\begin{align*}
E_{\text {disp }}^{(2)}= & -\int_{0}^{\infty} \frac{d u}{2 \pi} \iiint \int d^{3} \boldsymbol{r}_{1} d^{3} \boldsymbol{r}_{2} d^{3} \boldsymbol{r}_{3} d^{3} \boldsymbol{r}_{4} \\
& \times \chi_{A}\left(\boldsymbol{r}_{1}, \boldsymbol{r}_{2}, \mathrm{i} u\right) \chi_{B}\left(\boldsymbol{r}_{3}, \boldsymbol{r}_{4}, \mathrm{i} u\right) w\left(r_{14}\right) w\left(r_{23}\right), \tag{3.1}
\end{align*}
$$

where $w\left(r_{i j}\right)=1 / r_{i j}=1 /\left|\boldsymbol{r}_{i}-\boldsymbol{r}_{j}\right|$ is the inverse of the interelectronic distance and $\chi_{X}$, $X=A, B$ is the density-density response function of system $X$ at imaginary frequency $\mathrm{i} u$. This response function can be written in terms of the polarizability-density tensor $\alpha_{X}^{i j}\left(\boldsymbol{r}_{1}, \boldsymbol{r}_{2}, \mathrm{i} u\right)[79,80]$

$$
\begin{equation*}
\chi_{X}\left(\boldsymbol{r}_{1}, \boldsymbol{r}_{2}, \mathrm{i} u\right)=-\sum_{i, j=1}^{3} \frac{\partial^{2}}{\partial x_{1 i} \partial x_{2 j}} \alpha_{X}^{i j}\left(\boldsymbol{r}_{1}, \boldsymbol{r}_{2}, \mathrm{i} u\right) \tag{3.2}
\end{equation*}
$$

where $x_{k i}$ are the components of $\boldsymbol{r}_{k}$. If one assumes that $\alpha_{X}^{i j}$ can be approximated by a diagonal and local quantity,

$$
\begin{equation*}
\alpha_{X}^{i j}\left(\boldsymbol{r}_{1}, \boldsymbol{r}_{2}, \mathrm{i} u\right)=\delta_{i j} \alpha_{X}\left(\boldsymbol{r}_{1}, \mathrm{i} u\right) \delta\left(\boldsymbol{r}_{1}-\boldsymbol{r}_{2}\right), \tag{3.3}
\end{equation*}
$$

where $\alpha_{X}\left(\boldsymbol{r}_{1}, \mathrm{i} u\right)$ is called the local polarizability density, Eq. (3.1) becomes

$$
\begin{align*}
E_{\mathrm{disp}}^{(2)}=-\frac{3}{\pi} \int_{0}^{\infty} d u \iint & d^{3} \boldsymbol{r}_{1} d^{3} \boldsymbol{r}_{2} \\
& \times \frac{\alpha_{A}\left(\boldsymbol{r}_{1}, \mathrm{i} u\right) \alpha_{B}\left(\boldsymbol{r}_{2}, \mathrm{i} u\right)}{r_{12}^{6}} \tag{3.4}
\end{align*}
$$

This expression is singular if $\alpha_{A}$ and $\alpha_{B}$ overlap, which shows how drastic the approximation of Eq. (3.3) is. Nevertheless, this expression was proposed by Anderson, Langreth, and Lundqvist (ALL) [31] and, independently, by Dobson and Dinte [32]. In applications of Eq. (3.4), one had to assume that $\alpha_{A}$ and $\alpha_{B}$ do not overlap, which is a reasonable assumption only for very large intermonomer separations.

To eliminate the singularity, we introduce a damping function in the integral (3.4)

$$
\begin{align*}
& E_{\mathrm{disp}}^{\mathrm{DADE}}=-\frac{3}{\pi} \int_{0}^{\infty} d u \iint d^{3} \boldsymbol{r}_{1} d^{3} \boldsymbol{r}_{2} f_{8}\left(\beta\left(r_{12}\right), r_{12}\right) \\
& \times \frac{\alpha_{A}\left(\boldsymbol{r}_{1}, \mathrm{i} u\right) \alpha_{B}\left(\boldsymbol{r}_{2}, \mathrm{i} u\right)}{r_{12}^{6}} \tag{3.5}
\end{align*}
$$

where $f\left(\beta, r_{12}\right)$ is a generalized Tang-Toennies damping function [66], $f_{8}(\beta, x)=1-$ $e^{-\beta x} \sum_{i=0}^{8} \frac{(\beta x)^{i}}{i!}$, with the short-range behavior $\lim _{x \rightarrow 0} f_{8}(\beta, x) /(\beta x)^{6}=(\beta x)^{3} / 9$ ! This function removes the singularities and damps the energy at short separations. We call the resulting quantity the damped asymptotic dispersion energy (DADE).

The polarizability density is related to the so-called polarization $S$-function used in van der Waals density functionals: $\alpha\left(\boldsymbol{r}_{1}, \mathrm{i} u\right)=1 / 4 \pi \int d^{3} \boldsymbol{r}_{2} S\left(\boldsymbol{r}_{1}, \boldsymbol{r}_{2}, \mathrm{i} u\right)$ [81]. The formula for the $S$-function assumed in Ref. [25] leads to the following expression for the local polarizability density [82, 83]:

$$
\begin{equation*}
\alpha(\boldsymbol{r}, \mathrm{i} u)=\frac{n(\boldsymbol{r})}{\omega_{0}^{2}(\boldsymbol{r})+u^{2}}, \tag{3.6}
\end{equation*}
$$

where $n(\boldsymbol{r})$ is the electron density and $\omega_{0}(\boldsymbol{r})$ is a local excitation frequency. This frequency was assumed in Ref. [25] to be of the form

$$
\begin{gather*}
\omega_{0}(\boldsymbol{r})=\frac{9}{8 \pi}\left[k_{\mathrm{F}}(\boldsymbol{r})\left(1-\frac{Z_{a b}}{9}\left(\frac{|\nabla n(\boldsymbol{r})|}{2 k_{\mathrm{F}}(\boldsymbol{r}) n(\boldsymbol{r})}\right)^{2}\right)\right. \\
\left.-\frac{4 \pi}{3} \varepsilon_{c}^{\mathrm{LDA}}(\boldsymbol{r})\right]^{2}, \tag{3.7}
\end{gather*}
$$

where $k_{\mathrm{F}}(\boldsymbol{r})=\left[3 \pi^{2} n(\boldsymbol{r})\right]^{1 / 3}$ is the length of the Fermi wave vector, $\varepsilon_{c}^{\mathrm{LDA}}(\boldsymbol{r})$ is the LDA correlation energy density, and $Z_{a b}$ is a parameter which was interpreted in Ref. [25] as originating from screened exchange. The excitation frequency $\omega_{0}$ is a special value of a more general function $\omega_{q}(\boldsymbol{r})$ defined in Ref. [25]: $\omega_{0}(\boldsymbol{r})=\left.\omega_{q}(\boldsymbol{r})\right|_{q=0}$. The choice of $\omega_{0}(\boldsymbol{r})$ given by Eq. (3.7) ensures that the polarizability density decays like $n(\boldsymbol{r})^{7 / 3}$, which leads to finite static polarizabilities and avoids nonphysical contribution from low density regions present in ALL. Using $\alpha(\boldsymbol{r}, \mathrm{i} u)$ given by Eq. (3.6) in Eq. (3.5) and integrating over the frequency, we get

$$
\begin{align*}
E_{\mathrm{disp}}^{\mathrm{DADE}} & =-\frac{3}{2} \iint d^{3} \boldsymbol{r}_{1} d^{3} \boldsymbol{r}_{2} \\
& \times \frac{f_{8}\left(\beta\left(r_{12}\right), r_{12}\right) n_{A}\left(\boldsymbol{r}_{1}\right) n_{B}\left(\boldsymbol{r}_{2}\right)}{\omega_{0}^{A}\left(\boldsymbol{r}_{1}\right) \omega_{0}^{B}\left(\boldsymbol{r}_{2}\right)\left[\omega_{0}^{A}\left(\boldsymbol{r}_{1}\right)+\omega_{0}^{B}\left(\boldsymbol{r}_{2}\right)\right] r_{12}^{6}} . \tag{3.8}
\end{align*}
$$

Thus, we end up with an expression for the dispersion energy which requires only a sixdimensional integration as compared to the thirteen-dimensional integration involved
in Eq. (3.1). The parameter $Z_{a b}$ has been chosen to have a value between those used in vdW-DF1 [25] and vdW-DF2 [26], i.e., $Z_{a b}=-1.1972$. The function $\beta\left(r_{12}\right)$ has been chosen of the form $\beta\left(r_{12}\right)=\beta_{0}+\beta_{1} e^{-\beta_{2} r_{12}^{2}}$, where $\beta_{0}=1.70, \beta_{1}=1.90$, and $\beta_{2}=\beta_{0} / 10$. The values of $Z_{a b}$ and $\beta_{i}$ were roughly adjusted to achieve the best agreement with dispersion energies from symmetry-adapted perturbation theory (SAPT) based on DFT description of monomers $[\operatorname{SAPT}(\mathrm{DFT})][34,35,36,37]$ for the argon dimer. These choices are universal, i.e., do not depend on the interacting systems. Notice that the non-empirical SCAN functional [30] also uses $\mathrm{Ar}_{2}$ data [84] to fit its parameters. Thus, our approach is non-empirical in this sense.

To perform the integration over $\boldsymbol{r}_{1}$ and $\boldsymbol{r}_{2}$ in Eq. (3.8), we rewrite this equation as

$$
\begin{equation*}
E_{\mathrm{disp}}^{\mathrm{DADE}}=-\frac{3}{2} \iint d^{3} \boldsymbol{r}_{1} d^{3} \boldsymbol{r}_{2} F\left(\boldsymbol{r}_{1}, \boldsymbol{r}_{2}\right) \tag{3.9}
\end{equation*}
$$

and use Becke's atomic partitioning scheme [85] to numerically evaluate the integral using grids centered on atoms

$$
\begin{align*}
E_{\text {disp }}^{\mathrm{DADE}}=-\frac{3}{2} \sum_{a \in A} & \sum_{b \in B} \sum_{i, j} \Delta^{3} \boldsymbol{r}_{i}^{a} \Delta^{3} \boldsymbol{r}_{j}^{b} \\
& \times W^{a}\left(\boldsymbol{r}_{i}^{a}\right) W^{b}\left(\boldsymbol{r}_{j}^{b}\right) F\left(\boldsymbol{r}_{i}^{a}, \boldsymbol{r}_{j}^{b}\right), \tag{3.10}
\end{align*}
$$

where $W^{c}$ is Becke's atomic weight for atom $c$ and $\Delta^{3} \boldsymbol{r}_{i}^{c}$ is the volume of the grid cell at the grid point $\boldsymbol{r}_{i}^{c}$. This point is defined as $\boldsymbol{r}_{i}^{c}=\boldsymbol{R}^{c}+\boldsymbol{r}_{i}$, where $\boldsymbol{R}^{c}$ is the position of atom $c$ and $\boldsymbol{r}_{i}$ belongs to the grid centered at $R^{c}$. The integration grid for electron $1(2)$ can be restricted to the atoms of molecule $\mathrm{A}(\mathrm{B})$ since the the density $n_{A}\left(n_{B}\right)$ in Eq. (3.8) is well represented on such a grid. The spatial integration is performed using the Euler-Maclaurin [86] radial grid and the Lebedev [87] angular grid with 75 and 302 points, respectively.

To test the performance of our method, we chose the dimers from a recent blind test of DFT-based methods for calculation of interaction energies [33] and, in addition, the argon dimer and the Ar-HF dimer. The benchmark dispersion energy $E_{\text {dispx }}$ is the sum of the second order dispersion and exchange-dispersion energies from


Figure 3.1: Ratios of the approximate dispersion energies from DADE and vdWDF2 to SAPT(DFT) benchmarks for ethylenedinitramine dimer (topleft), methylformate dimer (top-right), nitrobenzene dimer (bottom-left), and benzene-methane (bottom-right). The vertical lines indicate the separations of the van der Waals minima. The inserted molecular graphs have white, gray, blue, and red spheres representing hydrogen, carbon, nitrogen, and oxygen atoms, respectively.

Table 3.1: MAPEs of dispersion energies for the investigated dimers with respect to the benchmark dispersion energies $E_{\text {dispx }}$.

|  | DADE | disp(vdW-DF2) |
| :--- | :---: | :---: |
| Argon dimer | 9.55 | 26.98 |
| Ar-HF | 6.86 | 23.56 |
| Water dimer | 15.03 | 29.40 |
| Ethanol dimer | 6.77 | 25.96 |
| Nitromethane dimer | 10.52 | 26.31 |
| Methylformate dimer | 6.85 | 29.20 |
| Benzene-methane | 6.58 | 28.75 |
| Benzene-water | 9.06 | 17.14 |
| Imidazole dimer | 24.89 | 42.10 |
| Nitrobenzene dimer | 7.82 | 23.05 |
| FOX-7 dimer | 27.68 | 42.08 |
| EDNA dimer | 11.55 | 30.14 |
| average of MAPEs | 11.93 | 28.72 |

SAPT(DFT). The benchmark interaction energies are CCSD $(\mathrm{T})$ values in the complete basis set (CBS) limit. The $\operatorname{SAPT}(\mathrm{DFT})$ and $\operatorname{CCSD}(\mathrm{T})$ calculations for the argon dimer and Ar-HF were performed in the present work using the same methodology as in Ref. [33] and the ORCA codes [88], while for all the remaining systems the values were taken from Ref. [33]. Note that while $\operatorname{CCSD}(\mathrm{T})$ benchmarks are at CBS limits, $\mathrm{SAPT}(\mathrm{DFT})$ quantities are computed in an augmented triple-zeta quality basis set with midbond functions [33]. The comparisons are done at various separations of monomers, from the repulsive wall to the asymptotic region, rather than only at the equilibrium separations. The systems taken from Ref. [33] have 80 data points while for the $\mathrm{Ar}_{2}$ and $\mathrm{Ar}-\mathrm{HF}$ we used 20 more points making the total number of points 100 . The comparison of the interaction energies is done, as in Ref. [33], by calculating the median values for the absolute percentage errors (MedAPE) so that the large relative differences with the benchmarks close to the points where the interaction energy curves go through zero do not affect the whole picture. The dispersion energy does not have this problem, so we compare the mean absolute percentage errors (MAPE) in this case. The calculations for DADE and vdW-DF2 are done using a code written by us which is
available at http://www.physics.udel.edu/~szalewic/DADE-1.0. The coefficients of the molecular orbitals were calculated using ORCA [88] with PBE [13] functional and the aug-cc-pVTZ [89, 90, 91] basis sets. The dispersion energy given by the vdWDF2 method, disp(vdW-DF2), is calculated by subtracting the nonlocal correlation energies of the monomers from the nonlocal correlation energy of the dimer. These energies are counterpoise corrected as all calculations are done in the same basis as for the dimer [92].

Table 3.1 shows that the MAPE values given by DADE relative to $E_{\text {dispx }}$ are significantly better than those of disp(vdW-DF2) for all systems, and the average MAPE is $12 \%$ for DADE while it is $29 \%$ for disp(vdW-DF2). Figure 3.1 compares the performance of DADE and disp(vdW-DF2) by plotting their ratio to $E_{\text {dispx }}$ as function of the separations $R$ for the EDNA dimer, methylformate dimer, nitrobenzene dimer, and benzene-methan. DADE outperforms disp(vdW-DF2) at almost all Rs, in particular at small $R$ s and in the asymptotic region. The better performance in the asymptotic region means improved $C_{6}$ dispersion coefficients. Also for the remaining dimers, DADE agrees better with $E_{\text {dispx }}$ than disp(vdW-DF2) at a majority of $R$ values, see Appendix C and Appendix D. It is remarkable that DADE performs so well since it is an extension of an asymptotic method while disp(vdW-DF2) is formulated for an arbitrary separation.

We next calculated the interaction energies by adding the dispersion energies from DADE and disp(vdW-DF2) to the interaction energies given by the dispersionless density functional (dlDF) [20]. We denote the resulting energies as dlDF + DADE and dlDF+disp(vdW-DF2). Since DADE recovers the true dispersion energy, it can be added only to interaction energies computed by density functionals such as dIDF which were optimized to exclude dispersion interactions [20]. The dlDF functional should also be a reasonable choice for disp(vdW-DF2) as the authors of Refs. [25] and [26] paired vdW-DF nonlocal terms with functionals which give interaction energies close to the HF ones which are dispersionless. The pairing of DFT functionals with dispersion energies

Table 3.2: MedAPEs of interaction energies for the investigated dimers with respect to the benchmark interaction energies.

|  | dlDF+DADE | dlDF+disp(vdW-DF2) |
| :--- | :---: | :---: |
| Argon dimer | 11.99 | 29.52 |
| Ar-HF | 8.16 | 21.58 |
| Water dimer | 1.47 | 1.51 |
| Ethanol dimer | 5.74 | 14.52 |
| Nitromethane dimer | 11.25 | 8.68 |
| Methylformate dimer | 1.08 | 10.54 |
| Benzene-methane | 8.15 | 35.61 |
| Benzene-water | 3.86 | 10.31 |
| Imidazole dimer | 4.79 | 5.67 |
| Nitrobenzene dimer | 13.25 | 3.82 |
| FOX-7 dimer | 7.98 | 7.03 |
| EDNA dimer | 6.79 | 1.38 |
| average of MedAPEs | 7.04 | 12.51 |

has been recently discussed by the present authors in Ref. [77]. The dlDF energies for the argon dimer and Ar-HF were calculated using the Gaussian [93] package, while for all the remaining systems the dlDF values were taken from Ref. [33]. These energies are counterpoise corrected [92].

Table 3.2 shows that for the majority of systems MedAPEs given by dlDF + DADE are better than those of dlDF+disp(vdW-DF2). The average of MedAPEs for dlDF + DADE, $7.0 \%$, is smaller than for dlDF+disp(vdW-DF2), $12.5 \%$, by a factor of 1.78 , while the dispersion energies from DADE have the average of MAPEs 2.4 times smaller than that of disp(vdW-DF2). The dlDF + DADE also has relatively narrow spread of MedAPEs: $1.1 \%$ to $13.3 \%$, whereas for dlDF+disp(vdW-DF2) the spread is $1.4 \%$ to $35.6 \%$. One should note that the set of systems in the blind test of Ref. [33] was intentionally chosen to be a blend of systems encountered in typical investigations of intermolecular forces. Therefore, for all dimers the dispersion effects are relatively small at large $R$, except for the benzene-methane. For this system, the MedAPE of dIDF + DADE is 4.4 times smaller than that of dlDF+disp(vdW-DF2). Similarly large ratios are found for $\mathrm{Ar}_{2}$ and $\mathrm{Ar}-\mathrm{HF}$ which are dispersion dominated at large $R$. Thus, for systems of
this kind improvements of accuracy resulting from using DADE should be particularly large. In Ref. [33], dIDF was paired with an accurate atom-atom dispersion functions from Ref. [94] and disp(vdW-DF2) was paired with the rPW86 exchange functional [43] and the P86 correlation functional [95]. The averages of MedAPEs from Ref. [33] (denoted as MUPEs there), on the set not including $\mathrm{Ar}_{2}$ and $\mathrm{Ar}-\mathrm{HF}$, were $6.56 \%$ and $11.96 \%$, respectively, very close to what we get in Table II for the methods used by us (for the 10 dimers from Ref. [33] we get $6.44 \%$ and $9.91 \%$,respectively). Note that Ref. [33] also used MedAPEs defined as the median absolute percentage errors for the whole set of data and such errors tend to be smaller than averages of MedAPEs. We have not used the former since they tend to place too much weight on the performence in the asymptotic region.

In summary, we present a new nonlocal correlation energy functional that provides the best intermolecular interaction energies for the set of benchmarks used among the nonempirical nonlocal functionals. The DADE method for calculations of dispersion energies has the important advantage of resulting from a straightforward derivation. This is in contrast with the vdW-DF2 method which uses many approximations that are difficult to justify. In fact, as Dobson and Gould [96] wrote "a complete and self-contained derivation of this functional seems to be lacking in the literature". Since the straightforward DADE approach performs so much better than vdW-DF, this may indicate that some of these approximations are not working well. DADE is also computationally at least as effective as vdW-DF2. Both functionals can be considered nonempirical in the sense that no fitting to a large number of benchmarks was involved. In both functionals, the parameter $Z_{a b}$ was adjusted, in DADE the parameters of the function $\beta_{i}$ were adjusted as well. DADE gives significantly better dispersion energies and, paired with dlDF, interaction energies than vdW-DF2, the most widely used nonlocal density functional. Thus, the use of DADE should significantly improve the accuracy of nonlocal functional approaches.

## Chapter 4

## EVALUATION OF METHODS FOR OBTAINING DISPERSION ENERGIES USED IN DENSITY-FUNCTIONAL CALCULATIONS OF INTERMOLECULAR INTERACTIONS


#### Abstract

Since semilocal density-functional theory (DFT) approximations cannot recover the dispersion components of interaction energies at intermonomer separations near van der Waals minima and larger, dispersion energies computed by methods other than semilocal DFT's are often added to DFT interaction energies. Such dispersion energies are assessed here by comparing them to accurate dispersion energies obtained from symmetry-adapted perturbation theory on a set of molecular dimers, including variations of intermonomer separations. The evaluated methods include nonlocal DFT correlation functionals, parametrized atom-atom dispersion functions originating from the asymptotic expansion, and methods based on models of atoms in molecules. In contrast to many published comparisons of such methods focused on total interaction energies, our comparisons evaluate the performance on the actual physical quantity for which these methods have been designed. This performance is discussed in the context of the physical soundness of the methods. Our results show that atom-atom functions reproduce dispersion energies best, with a mean absolute percentage error of the order of $10 \%$. The nonlocal correlation functionals perform much worse, with errors in the range $24 \%$ to $49 \%$, far from what could be called quantitative reproduction of this quantity. The only exception is the recently proposed damped asymptotic dispersion energy functional which gave an error of $12 \%$. The atoms-in-molecule methods also gave large errors, above $29 \%$.


### 4.1 Introduction

Density functional theory (DFT) is the most widely used computational tool in studies of matter. The exact DFT should be able to describe all components of intermolecular interaction energies including dispersion interactions. However, only approximate DFT approaches are available in practice, such as the local density approximations (LDA) $[6,5,10,58]$, the generalized-gradient approximations (GGA) [50, 41, 85, 57, 42], and meta-GGA's [55, 30]. A deficiency of all these methods is their inability to capture long-range correlation effects [53], which originates from the limited spatial extent, of the order of $1 \AA$, of the exchange-correlation hole [18] (one may say that these methods are myopic). Since the dispersion energies result from long-range correlations of motions of electrons in one monomer with those in the interacting partner and since physically relevant separations between regions of interacting molecules that are closest to each other are of the order of a couple of angstroms or larger, such semilocal DFT methods cannot describe this component of intermolecular interaction energies. Only for atom-atom interactions at very short separations, not relevant for most physical applications, the electrons will eventually be close enough for DFT to capture a part of dispersion energy (for molecules, there will always be regions too far apart). These issues have been recently discussed by the present authors in Ref. [77].

The dispersion energy was identified for the first time in a 1930 paper of Eisenschitz and London [97] and is sometimes called the London dispersion energy. This quantity is a component of symmetry-adapted perturbation theory (SAPT) [3, 98]. The first calculations of dispersion energies for many-electron monomers at arbitrary separations appeared in the 1970s $[99,100,101,1]$. While initial work computed dispersion energies for monomers described by the Hartree-Fock (HF) approximation [99, 100, 101], later developments $[1,2,102,103,104]$ included gradually higher and higher levels of electron correlation. Another method of computing dispersion energies is to use a DFT description of monomers, a part of SAPT(DFT) approach [105, 34, 35, 106, 36, 37, 107], a method that gives dispersion energies nearly as accurate as those of SAPT at the highest levels of intramonomer electron correlation and at the same time is much less
expensive. Antisymmetrization of the dispersion wave functions produces an additional, short-range dispersion component called the exchange-dispersion energy. This contribution is also not recovered by semilocal DFT approximations, so it has to be included in the correction to the semilocal DFT interaction energies.

A large number of methods going beyond semilocal DFT have been developed to amend semilocal DFT interaction energies for the missing dispersion effects. The dispersion energies computed using such methods are then simply added to semilocal DFT interaction energies. Thus, all these methods can be labeled as DFT plus dispersion (DFT +D ) methods, although this term is usually applied only to the methods that use parametrized atom-atom dispersion functions originating from the asymptotic expansion. The most accurate DFT + D approach would be to use SAPT dispersion plus exchange-dispersion energies. While this method was applied occasionally [108], it has not become a mainstream DFT + D method due to the costs of calculations of SAPT dispersion energies compared to simple atom-atom functions. In fact, these costs are not unreasonable: in the density-fitting version [107, 109, 108], the method scales with system size as $N^{4}$ for pure functionals and as $N^{5}$ for hybrid functionals, i.e., one power of $N$ worse than the corresponding calculations of DFT interaction energies. Furthermore, since the dispersion energies computed with pure functionals are very close to those computed with hybrid ones, one can use a hybrid functional to compute DFT interaction energies (which usually gives more accurate results) and a pure functional to compute dispersion energies. The exchange-dispersion energy which should also be included scales as $N^{5}$, but its magnitude is relatively small compared to the magnitude of the dispersion energy, so it could possibly be neglected. However, most of the methods computing the " +D " correction that will be discussed below are much less expensive than DFT, often of negligible costs, which is one of the reasons for their popularity.

Physically the most appealing DFT + D approaches are those that compute dispersion energies using nonlocal correlation density functionals [25, 26, 27, 28, 29]. In fact, most of such methods can be used self-consistently [110], i.e., the derivative of
the nonlocal functional can be included in the Kohn-Sham (KS) equations. However, the self-consistency effects were found to be small [111] so that this method is often applied in the $\mathrm{DFT}+\mathrm{D}$ fashion.

The most popular $\mathrm{DFT}+\mathrm{D}$ approach uses dispersion functions of the form originating from the $\sum C_{n} / R^{n}$ asymptotic expansion of dispersion energies [3, 112], where $R$ is the separation between monomers and $C_{n}$ are van der Waals (vdW) constants. This approach uses a distributed form of such an expansion [113, 114, 112, 115, 116], i.e., a sum of atom-atom interactions. The atom-atom $C_{n}^{a b}$ parameters are either fitted to empirical van der Waals constants [15, 62, 63] or computed using time-dependent DFT (TD-DFT) [16, 117]. The coefficients can also be fitted to SAPT dispersion plus exchange-dispersion energies computed on a training set of dimers [20, 21]. In methods of this type, the dispersion function for any dimer is defined by a set of parameters (the actual atom-atom $C_{n}^{a b}$ constants are usually obtained using combination rules from atom-specific constants). The parameters can be partly dependent on environment by fitting a reference set of parameters for an atom in several chemical environments and interpolating between these values for a specific environment of this atom. The $\mathrm{DFT}+\mathrm{D}$ methods of this type are also popular in condensed phase calculations [118].

The exchange-hole dipole moment (XDM) method [23, 24] was derived using heuristic arguments to express dispersion energies via interactions of exchange holes represented by their dipole moments. An alternative and more rigorous derivation was given by Ángyán [119]. Another method, called many-body dispersion (MBD) approach [22, 17], approximates atom-atom dispersion interactions by interactions between quantum harmonic oscillators centered on each atom. The atomic oscillators are parametrized to reproduce empirical van der Waals constants. An important feature of both methods is that dispersion energies depend on the density assigned to each atom, thus, are seamlessly depending on the environment. Robust condensed matter implementations of MBD were developed in Refs. [120, 121, 122, 123].

Several of the methods discussed above include multiplicative factors that switch off dispersion energies at shorter $R$. These factors are parametrized to make DFT +D
total interaction energies agree as close as possible with benchmarks obtained using wave function methods. This switching off is much stronger than the physical damping of asymptotic dispersion energies accounting for the overlap effects (in this way removing the singularity of the asymptotic expansion for $R \rightarrow 0$ ). The excess damping is often justified by the need to avoid double counting as semilocal DFTs presumably start to partially recover dispersion energies at the region of van der Waals minimum and for shorter separations. In Ref. [77], the validity of this assumption has been questioned by showing that although some semilocal DFT methods may appear as if they behave this way, this behaviour originates to a large extent from DFT components which are not supposed to describe correlation effects, i.e., from the non-exchange-correlation components. All but one of these components originate from the one-electron parts of the Hamiltonian, which by definition are unrelated to correlation energies while the two-electron Hartree term is a part of the Hartree-Fock theory, also by definition not including correlation energies. The methods that apply the excessive damping are not expected to reproduce dispersion energies at the van der Waals minima and for shorter $R$. Therefore, in the present work, we tried to remove this damping from all methods that use it, but in some cases we were not able to achieve this for technical reasons.

An important question is what is the most appropriate benchmark to compare with for each approximate dispersion energy method. The goal for all such methods is to reproduce the complete dispersion energy (with charge-overlap effects, i.e., obtained without use of the multipole expansion of the intermolecular interaction operator $V$ ) plus the exchange-dispersion energy. However, atom-atom functions with no damping should agree most closely with the asymptotic dispersion energies. Then, some of the methods, based on their derivation, include charge-overlap effects but do not include exchange effects and these methods should be compared with dispersion energies only. We attempted to finesse these subtleties in our comparisons.

One may note here that the excessive damping can be avoided if the DFT functional chosen in a DFT + D is selected to reproduce well the dispersionless part of
the interactions energy, i.e., the interaction energy with the dispersion and exchangedispersion components removed. This is an appealing approach from physics point of view since semilocal DFT includes all the necessary mechanisms to recover this part of the interaction energies. Several approaches of this type have been proposed in literature $[20,43,73]$. In particular, the dispersionless density functional (dlDF) of Ref. [20] was optimized to recover benchmark dispersionless interaction energies.

We have examined virtually all popular methods which can be classified as belonging to the DFT + D class. There are also methods which use DFT in combination with some wave function approach, for example, mixing a range-separated hybrid (RSH) DFT with the second-order many-body perturbation correction based on the Møller-Plesset partition of the Hamiltonian (MP2), leading to the RSH-MP2 method of Refs. [124, 125, 126]. Another option is to combine an RSH functional with the random-phase approximation (RPA) method for the correlation energy [127, 128, 129, 130, 131, 132, 133]. In such methods, it is not possible to isolate the dispersion energies from other physical components, therefore we could not include them in our comparisons.

The methods for computation of dispersion energies were evaluated using the set of dimers from Ref. [33] plus the $\mathrm{Ar}_{2}$ and Ar-HF dimers. For each dimer, several values of $R$ were included, sampling regions from repulsive walls to the asymptotic separations. The test set is diverse in terms of dominant interaction energy components and includes mostly dimers that have not been used in fitting DFT+D methods.

While a large number of papers evaluating the performance of $\mathrm{DFT}+\mathrm{D}$ methods have been published, among them Ref. [33] and a very recent one of Ref. [134], all such evaluations made the comparisons at the level of interaction energies. In this way, errors coming from the DFT and the ' +D ' components are not distinguishable. Our comparison appears to be the first one that applies directly to dispersion energies.

### 4.2 Benchmark dispersion energies

The main component of the dispersion energy appears in SAPT at the second order in $V$. The contributions of higher orders are substantially smaller [2, 4, 135]. One should also point out that beyond the second order, SAPT includes mixed, inductiondispersion terms [4, 135]. In Ref. [77], the dispersion energy was represented by the sum of the following terms

$$
\begin{equation*}
E_{\text {dispx }}=E_{\text {disp }}^{(20)}+E_{\text {disp }}^{(21)}+E_{\text {disp }}^{(22)}+E_{\text {exch-disp }}^{(20)}+E_{\text {disp }}^{(30)}+E_{\text {exch-disp }}^{(30)} \tag{4.1}
\end{equation*}
$$

where the first superscript denotes the order with respect to intermolecular interaction operator $V$ and the second one with respect to the intramolecular correlation operator (Møller-Plesset fluctuation potential) W. An analysis performed in Ref. [77] shows that the uncertainty of $E_{\text {dispx }}$ resulting from the truncation of perturbation expansion in powers of $V$ and $W$ is only of the order of $1 \%$.

In the present work, we could not use the expression (B.2) since some of the dimers in our benchmark set were so large that calculations would be too time consuming. Therefore, we considered only the terms of second-order in $V$ and applied SAPT(DFT) [105, 34, 35, 106, 36, 37, 107]. This approach uses the so-called generalized Casimir-Polder expression for the second-order dispersion energy in terms of density-density response functions [called also frequency-dependent density susceptibilites (FDDSs)] [34, 35]

$$
\begin{equation*}
E_{\mathrm{disp}}^{(2)}=-\frac{1}{2 \pi} \int_{0}^{\infty} d u \iiint \int d^{3} \boldsymbol{r} d^{3} \boldsymbol{r}^{\prime} d^{3} \boldsymbol{r}^{\prime \prime} d^{3} \boldsymbol{r}^{\prime \prime \prime} \frac{\chi_{a}\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}, \mathrm{i} u\right) \chi_{b}\left(\boldsymbol{r}^{\prime \prime}, \boldsymbol{r}^{\prime \prime \prime}, \mathrm{i} u\right)}{\left|\boldsymbol{r}-\boldsymbol{r}^{\prime \prime}\right|\left|\boldsymbol{r}^{\prime}-\boldsymbol{r}^{\prime \prime \prime}\right|}, \tag{4.2}
\end{equation*}
$$

where $\chi_{a}$ and $\chi_{b}$ are the FDDSs of monomers and $u$ is the frequency. Note that this expression is exact if exact FDDSs are used. In SAPT(DFT), FDDSs are obtained from the TD-DFT level of theory and are sometimes called coupled KS (CKS) FDDSs. To the dispersion energy computed in this way, we add exchange-dispersion energies computed from CKS amplitudes (i.e., we do not use scaled uncoupled KS amplitudes). Thus, our benchmark energy is

$$
\begin{equation*}
E_{\text {dispx }}=E_{\text {disp }}^{(2)}(\mathrm{CKS})+E_{\text {exch-disp }}^{(2)}(\mathrm{CKS}) \tag{4.3}
\end{equation*}
$$

The values of $E_{\text {dispx }}$ defined by this equation have been taken from the calculations in Taylor et al. [33], except for the $\mathrm{Ar}_{2}$ and Ar-HF dimers for which the values were taken from Ref. [29].

### 4.3 Nonlocal Correlation Functionals

The physically most appealing way to cure problems of semilocal DFT approximations is to develop nonlocal correlation functionals and several such methods have been proposed. These methods are usually derived from the adiabatic-connection fluctuation-dissipation (ACFD) theorem [44, 45, 9]. This theorem expresses the correlation energy $E_{\mathrm{c}}$ of a system (note that this correlation energy is different from the one defined as the difference of exact and Hartree-Fock energies) in terms of the density-density response functions of the interacting and noniteracting systems. This relation is exact and, in contrast to the usual way of approximating $E_{\mathrm{c}}$ in terms of ground-state density and its gradient, uses the complete orbital space, i.e., includes all virtual orbitals. Thus, one may expect that approximations derived from ACFD will not suffer the shortsightedness of semilocal DFTs. However, since methods including virtual orbitals are significantly more time consuming than DFT, the FDDSs have to be severely approximated to produce nonlocal functionals applicable to large systems. The exact FDDS at real frequencies can be expressed by a spectral expansion with poles at the values of excitation energies of a system. In the theory of homogeneous electron gas (HEG), it is possible to approximate the response function with a singlepole model [136, 137, 138], often called the plasmon model since it is used to describe collective excitations of HEG called plasmons. In the 1990s, this model was applied for the first time to systems with dispersion interactions [139, 31, 140, 141, 32, 142, 143]. These functionals require a physical cutoff in the resulting integrals to give reasonable results and were applicable only for large intermolecular separations. In 2004, Dion et al. [25] proposed a nonlocal functional, called the van der Waals density functional (vdW-DF), which did not suffer from this problem. The essential quantity in this method is the $\boldsymbol{r}$-dependent pole frequency which was assumed to be a simple function
depending also on the magnitude of the wave vector $q$

$$
\begin{equation*}
\omega_{q}(\boldsymbol{r})=\frac{q^{2}}{2}\left[1-e^{-\frac{4 \pi}{9}\left(\frac{q}{q_{0}(r)}\right)^{2}}\right]^{-1} . \tag{4.4}
\end{equation*}
$$

where

$$
\begin{equation*}
q_{0}(\boldsymbol{r})=k_{\mathrm{F}}(\boldsymbol{r})\left[1-\frac{Z_{a b}}{9}\left(\frac{|\nabla \rho(\boldsymbol{r})|}{2 k_{F}(\boldsymbol{r}) \rho(\boldsymbol{r})}\right)^{2}\right]-\frac{4 \pi}{3} \varepsilon_{\mathrm{c}}^{\mathrm{LDA}}(\boldsymbol{r}) . \tag{4.5}
\end{equation*}
$$

The quantities appearing in Eq. (4.5) are the same as used in semilocal DFTs: $\rho(\boldsymbol{r})$ is the ground-state electron density, $k_{\mathrm{F}}(\boldsymbol{r})=\left[3 \pi^{2} \rho(\boldsymbol{r})\right]^{1 / 3}$ is the magnitude of the Fermi vector, and $\varepsilon_{\mathrm{c}}^{\mathrm{LDA}}(\boldsymbol{r})$ is the correlation energy density in LDA. The value of the parameter $Z_{a b}$ was taken to be -0.8491 in the original version denoted as vdW-DF1 [25] and -1.887 in the 2010 version denoted as vdW-DF2 [26]. Note that also the factor $4 \pi / 9$ is a parameter of the method and has been chosen differently in Ref. [81] discussed later on. The nonlocal correlation energy can be written in terms of $\omega_{q}(\boldsymbol{r})$ as

$$
\begin{equation*}
E_{\mathrm{c}}^{\mathrm{nl}} \approx \frac{1}{2} \iint d^{3} \boldsymbol{r} d^{3} \boldsymbol{r}^{\prime} \rho(\boldsymbol{r}) \Phi\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}\right) \rho\left(\boldsymbol{r}^{\prime}\right) \tag{4.6}
\end{equation*}
$$

with the so-called nonlocal correlation kernel $\Phi\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}\right)$ given by

$$
\begin{equation*}
\Phi\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}\right)=\frac{2}{\pi^{2}} \int_{0}^{\infty} d a \int_{0}^{\infty} d b a^{2} b^{2} W(a, b) T\left(\nu(a), \nu(b), \nu^{\prime}(a), \nu^{\prime}(b)\right), \tag{4.7}
\end{equation*}
$$

where

$$
\begin{align*}
& T(w, x, y, z)=\frac{1}{2}\left[\frac{1}{w+x}+\frac{1}{y+z}\right]\left[\frac{1}{(w+y)(x+z)}+\frac{1}{(w+x)(y+z)}\right]  \tag{4.8}\\
& \begin{aligned}
W(a, b)= & {\left[\left(a^{2}+b^{2}-3\right) \sin a \sin b-3 a b \cos a \cos b\right.} \\
& \left.+a\left(3-b^{2}\right) \cos a \sin b+b\left(3-a^{2}\right) \sin a \cos b\right] \frac{2}{a^{3} b^{3}}
\end{aligned}
\end{align*}
$$

and the auxiliary variables are $\nu(a)=\omega_{q}(\boldsymbol{r})\left|\boldsymbol{r}-\boldsymbol{r}^{\prime}\right|^{2}$ and $\nu^{\prime}(a)=\omega_{q}\left(\boldsymbol{r}^{\prime}\right)\left|\boldsymbol{r}-\boldsymbol{r}^{\prime}\right|^{2}$ with $q=a /\left|\boldsymbol{r}-\boldsymbol{r}^{\prime}\right|$ and similarly for $b$. Thus, $E_{\mathrm{c}}^{\mathrm{nl}}$ is given entirely in terms of ground-state densities and density gradients.

Since the vdW-DF methods give contributions to the total energies, the contributions to the interaction energies are computed by the supermolecular method, i.e., by subtracting the nonlocal energies of monomers from that of the dimer. We used here and in all other cases the counterpoise correction, i.e., all these energies were computed in the exactly the same basis set.

The vdW-DF nonlocal functionals were not fitted to any benchmark interaction energies, although the change of the parameter $Z_{a b}$ was partly made to improve agreement with such benchmarks. Therefore, these functionals do not include excessive damping discussed earlier and have to be paired with DFT functionals which are dispersionless to a large extent. The functional vdW-DF1 was paired with revPBEPW92 [42, 60, 58], but in vdW-DF2 the revPBE [42, 60] exchange functional was replaced by rPW86 [43, 41]. Later, several other choices have been made [144, 145, $146,147]$. Based on the derivation, vdW-DF functionals should recover the dispersion energies with overlap, as well as exchange-dispersion energies. Thus, these methods should be compared to $E_{\text {dispx }}$.

Another method tested here is the damped asymptotic dispersion energy (DADE) [29] approach. It modifies the dispersion energy expression of Anderson, Langreth, and Lundqvist (ALL) [31] by including a damping function analogous to the Tang-Toennies function [66]. In this way, the singularities present in the ALL method are avoided and the expression can be applied at any separations. DADE uses the polarizability density from vdW-DF, however, with a different value of $Z_{a b}$.

One more set of nonlocal correlation functionals was developed by Vydrov and van Voorhis. In 2009, they proposed a simplified version of vdW-DF1 with changed parameters and a simplified pole frequency, called vdW-DF-09 [81]. The parameters were chosen to make the method perform better when paired with DFT functionals that are far from dispersionless. In the same year, they introduced another functional, called VV09 [27]. Its main feature was the removal of the wave vector dependence in the pole frequency and a simplification of the expression for this quantity to the form $\omega_{0}^{2}(\boldsymbol{r})=C\left|\frac{\nabla \rho(\boldsymbol{r})}{\rho(\boldsymbol{r})}\right|^{4}+4 \pi \rho(\boldsymbol{r}) / 3$. The constant $C$ was fitted to reproduce empirical
$C_{6}$ constants for a number of molecular dimers. A flaw in VV09 is the violation of charge conservation (f-sum rule) [148]. In 2010, Vydrov and van Voorhis [28] proposed a functional, referred to as VV10, with the kernel not derived from the ACFD theorem but rather postulated directly in the form

$$
\begin{equation*}
\Phi_{\mathrm{VV} 10}\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}\right)=-\frac{3}{2} \frac{1}{g(\boldsymbol{r}) g\left(\boldsymbol{r}^{\prime}\right)\left[g(\boldsymbol{r})+g\left(\boldsymbol{r}^{\prime}\right)\right]} \tag{4.10}
\end{equation*}
$$

where $g(\boldsymbol{r})=\sqrt{\omega_{0}^{2}(\boldsymbol{r})}\left|\boldsymbol{r}-\boldsymbol{r}^{\prime}\right|^{2}+\kappa(\boldsymbol{r})$. The term $\kappa(\boldsymbol{r})=b k_{\mathrm{F}}^{2}(\boldsymbol{r}) /(2 \pi \rho(\boldsymbol{r}))$ controls here the short-range damping where $b$ is a constant determined by fitting to benchmark data of $a b$ initio computed interaction energies for a number of dimers. The VV10 functional is more flexible and became more successful than its predecessor, but is also significantly empirical. Since the fitting in the VV09 method did not involve any $R$-dependent dimer data, this method should be compared to $E_{\text {dispx }}$. VV10, in contrast, used such data. However, there is no simple way to establish a value of the parameter $b$ which would correspond to only physical damping. However, since $b$ was fitted using VV10 paired with rPW86-PBE which is close to a dispersionless functional the comparison of unmodified VV10 to $E_{\text {dispx }}$ should be adequate.

### 4.4 Asymptotics-based atom-atom dispersion functions

The simplest way to correct semilocal DFT results is the addition of asymptotic dispersion energies, possibly damped to account for charge-overlap effects, to DFT interaction energies, analogously to the so-called HFD method [149], known since 1975 (note that such an addition is completely rigorous in this case since HF interaction energies by definition do not include any electron correlation effects). The DFT + D idea of this type was first applied by Gianturco et al. [61] and later by Wu et al. [14] to some specific systems. Wu and Yang [15] proposed a universal approach by constructing atom-atom dispersion functions similar to those used in biomolecular force fields. In 2004, Grimme [62] used the same $C_{6}^{a b}$ constants, but introduced damping functions (switching off factors) with parameters fitted in such a way that DFT + D reproduces as closely as possible benchmark interaction energies obtained using wave-function
methods. As discussed earlier, such functions damp dispersion energies much stronger than physical damping functions [77], but this excessive damping led to dramatically improved predictions for interaction energies. Consecutive versions of this method were published in Refs. [63, 16]. The latter dispersion function, denoted by D3, replaced empirical van der Waals constants by the $C_{6}^{a b}$ constants computed from the CasimirPolder expression using TD-DFT FDDSs. The $C_{8}^{a b}$ and higher constants were then computed from $C_{6}^{a b}$ using approximate formulas [16]. The calculations were performed for molecules involving a given atom in several chemical environments. Then for an atom in a molecule of interest its coefficients are interpolated between these values depending on the coordination number of this atom. A popular damping function used with D3 is Becke-Johnson's damping function (BJ) [19, 24] forming an approach denoted as D3BJ. In 2016, Smith et al. [150] refitted BJ parameters to a larger training set, resulting in a method denoted as D3MBJ.

The D3 energies are calculated for the whole dimer including interactions between atoms inside each monomer (as programmed in the D3 codes available at https: //www. chemie.uni-bonn.de/pctc/mulliken-center/software/dft-d3/get-the -current-version-of-dft-d3). Thus, the dispersion energies have to be calculated using the supermolecular method, i.e., subtracting monomer values from the dimer value. While one would expect that the interactions within monomers cancel exactly during this subtraction, this is not the case since the coordination numbers are slightly different in monomers and dimer calculations. We found that in some cases this led to artifacts such as positive dispersion energies at large separations. Therefore, we computed the D3BJ dispersion function from a "perturbational" expression

$$
\begin{equation*}
E_{\mathrm{disp}}=-\sum_{a \in \mathrm{~A}, b \in \mathrm{~B}} \sum_{n=6,8,10} s_{n} \frac{C_{n}^{a b}}{r_{a b}^{n}+\left[f_{\text {damp }}\left(a_{1}, a_{2}, R_{0}^{a b}\right)\right]^{n}} \tag{4.11}
\end{equation*}
$$

where $r_{a b}$ is the separation between atoms $a$ and $b$ and $s_{n}$ are overall scaling parameters. Only $n=6$ and 8 terms were used in our calculations. The function $f_{\text {damp }}=a_{1} R_{0}^{a b}+a_{2}$, where $a_{1}$ and $a_{2}$ are adjustable parameters and $R_{0}^{a b}=\sqrt{C_{8}^{a b} / C_{6}^{a b}}$.

As discussed earlier, the damping/scaling parameters have been fitted to a set of $a b$ initio interaction energies separately for each DFT method that the correction will be paired with, which leads to excessive, unphysical damping (cf. Ref. [77]). In fact, this unphysical damping is the reason for success of such DFT + D approaches since the ' + D' functions cancel DFT interaction energy errors due to reasons other than dispersion interactions.

As discussed in the Introduction, a solution of this somewhat unsatisfactory situation is to use DFT methods which give interaction energies close to HF interaction energies [43, 73]. Even better, one can develop a DFT method with parameters fitted to benchmark interaction energies with dispersion energies subtracted, such as the dlDF method of Ref. [20]. One can then add to dlDF interaction energies dispersion energies developed by fitting an atom-atom expansion to $E_{\text {dispx }}$ from SAPT. Such a dispersion function, $\mathrm{D}_{\text {as }}$, was developed in Ref. [20]. An improved function was developed in Ref. [21]. In our comparisons, we used an extended version of the latter (version 2), available at http://www.physics.udel.edu/~szalewic/dldf/dispersion.

### 4.5 Exchange-hole dipole moment model

The XDM model was proposed by Becke and Johnson [23, 24] in 2005. The original derivation was heuristic and used arguments based on induction (polarization) interactions which are physically distinct from dispersion interactions. A rigorous derivation from the generalized Casimir-Polder formula was later presented by Ángyán [119]. This derivations clearly delineates the set of approximations that have to be made. Ángyán has also shown that the XDM formula for $C_{6}$ is equivalent to the expression derived earlier by Salem, Tang, and Karplus [151, 152].

The XDM method defines position-dependent exchange-hole dipole moments of the form

$$
\begin{equation*}
\boldsymbol{d}_{\mathrm{X} \sigma}(\boldsymbol{r})=\frac{1}{\rho_{\sigma}(\boldsymbol{r})} \sum_{i j} \phi_{i \sigma}(\boldsymbol{r}) \phi_{j \sigma}(\boldsymbol{r}) \int \boldsymbol{r}^{\prime} \phi_{i \sigma}\left(\boldsymbol{r}^{\prime}\right) \phi_{j \sigma}\left(\boldsymbol{r}^{\prime}\right) d^{3} \boldsymbol{r}^{\prime}-\boldsymbol{r} \tag{4.12}
\end{equation*}
$$

where $\rho_{\sigma}(\boldsymbol{r})$ is the density of electrons with spin $\sigma$ and $\phi_{i \sigma}$ 's are occupied HF or KS orbitals with spin $\sigma$ (the orbitals are assumed to be real). The average of the square of this moment assigned to atom $a$ is defined as

$$
\begin{equation*}
\left\langle d_{X}^{2}\right\rangle_{a}=\sum_{\sigma} \int \omega_{a}(\boldsymbol{r}) \rho_{\sigma}(\boldsymbol{r})\left|\boldsymbol{d}_{\mathrm{X} \sigma}(\boldsymbol{r})\right|^{2} d^{3} \boldsymbol{r} \tag{4.13}
\end{equation*}
$$

where $\omega_{a}(\boldsymbol{r})$ is the Hirshfeld atomic partition weight [153]. The dispersion coefficients are then calculated as

$$
\begin{equation*}
C_{6}^{a b}=\frac{\alpha_{a} \alpha_{b}\left\langle d_{X}^{2}\right\rangle_{a}\left\langle d_{X}^{2}\right\rangle_{b}}{\left\langle d_{X}^{2}\right\rangle_{a} \alpha_{b}+\left\langle d_{X}^{2}\right\rangle_{b} \alpha_{a}}, \tag{4.14}
\end{equation*}
$$

where $\alpha_{c}$ is the effective atom-in-molecule polarizability of atom $c, c=a, b$. This polarizability is calculated from the free atomic polarizability, $\alpha_{a}^{\text {free }}$, using the following expression

$$
\begin{equation*}
\alpha_{a}=\frac{\int r^{3} w_{a}(\boldsymbol{r}) \rho(\boldsymbol{r}) d^{3} \boldsymbol{r}}{\int r^{3} \rho_{a}^{\text {free }}(\boldsymbol{r}) d^{3} \boldsymbol{r}} \alpha_{a}^{\text {free }}=\frac{V_{a}^{\text {eff }}}{V_{a}^{\text {free }}} \alpha_{a}^{\text {free }} \tag{4.15}
\end{equation*}
$$

where $\rho_{a}^{\text {free }}(\boldsymbol{r})$ is the density of the free atom $a$. The ratio is often interpreted as the ratio of effective volumes of the atom-in-molecule, $V_{a}^{\text {eff }}$, and of the free atom, $V_{a}^{\text {free }}$. The coefficients $C_{8}^{a b}$ and $C_{10}^{a b}$ are defined in an analogous way. The dispersion energy is then computed from a formula similar to Eq. (4.11), except that the scaling parameters $s_{n}$ are omitted and the constant $R_{0}^{a b}$ is replaced by $\frac{1}{3}\left[\left(\frac{C_{8}^{i j}}{C_{6}^{i j}}\right)^{1 / 2}+\left(\frac{C_{10}^{i j}}{C_{6}^{i j}}\right)^{1 / 4}+\left(\frac{C_{10}^{i j}}{C_{8}^{i j}}\right)^{1 / 2}\right]$ (Ref. [154]). Note that the original XDM formulation uses the supermolecular variant of the expression (4.11).

### 4.6 Many-Body Dispersion

The MBD method [17] maps the atoms of a given system onto a model system of quantum harmonic oscillators. Using an expression for $C_{6}$ coefficients in terms of polarizabilities of these oscillators, the parameters defining the oscillators are fitted to accurate empirical $C_{6}$ 's for more than one thousand of atoms and small molecules. The effects of immediate environment of an atom are included using Eq. (4.15). The polarizabilites assigned to the oscillators are then adjusted for each particular system by solving a self-consistent set of equations involving a dipole-dipole interaction tensor.

The oscillators consist of charged particles which interact with particles of other oscillators via the Coulomb potential in the multipole expansion truncated at the dipole-dipole term. The Hamiltonian of this system is diagonalized in the basis set of the noninteracting oscillators [155]. The dipole-dipole interaction tensor is assumed in the form $[17,156,157]$

$$
\begin{equation*}
\tau_{a b}=\sum_{i, j=1}^{3} \frac{\partial^{2}}{\partial x_{a}^{i} \partial x_{b}^{j}} \frac{1-\exp \left[\left(r_{a b} / \bar{r}_{a b}^{\mathrm{vdW}}\right)^{\beta}\right]}{r_{a b}}, \tag{4.16}
\end{equation*}
$$

where $\bar{r}_{a b}^{\mathrm{vdW}}=\bar{r}_{a}^{\mathrm{vdW}}+\bar{r}_{b}^{\mathrm{vdW}}$ is sum of van der Waals radii. The term in the numerator introduces damping in the MBD method and the parameter $\beta$ is fitted to match $\mathrm{DFT}+\mathrm{D}$ interaction energies to accurate dimer interaction energy benchmarks.

Note that the phrase "many-body" in MBD is confusing in the context of intermolecular interactions where "many-body (nonadditive) effects" is the term used to describe interactions in a cluster of several atoms or molecules that are beyond the sum of pair (two-body) interactions [158]. In contrast, MBD gives "many-body" effects already in molecular dimers. Clearly, MBD views each atom in a molecules as a separate body. The name may also suggest that MBD will reproduce well the many-body effects defined in the standard way. However, it has been recently shown [159] that MBD is not capable of predicting reliable nonadditive three-body interaction energies.

### 4.7 Computational Details

The benchmark values of $E_{\text {dispx }}$ defined by Eq. (4.3) were taken from Ref. [33] except for those for $\mathrm{Ar}_{2}$ and Ar-HF which were taken from Ref. [29]. The aug-cc-pVTZ basis [160, 161, 91] set plus a set of (3s3p2d2f) midbond functions in the monomercentered 'plus' basis set (MC+BS) [162] format were used in all cases. All the supermolecular calculations of dispersion energies used the aug-cc-pVTZ basis set and were counterpoise corrected by performing monomer calculations using same basis as for the dimer. There is no need to use midbond functions here since these functions are important only if dispersion energies are computed from expressions depending on virtual orbitals.

Five nonlocal functionals have been considered. The results for DADE were taken from Ref. [29] where they were computed using a program written by the present authors. This program is available at http://www.physics.udel.edu /~szalewic/DADE. As a check, we have also programmed the vdW-DF method and our codes were used to obtain the vdW-DF1 and vdW-DF2 dispersion energies. For the VV09 and VV10 methods, we used Q-Chem [163] and ORCA [88], respectively. All calculations, except those for VV09, were done in the non-self-consistent way, i.e., not using the derivatives of the nonlocal correlation energies in KS equations. The differences with self-consistent calculations are expected to be very small [110, 111]. The Q-Chem program used for VV09 apparently does not offer the non-self-consistent option. The authors of nonlocal methods recommended to pair them with some specific DFT functionals. However, the choice of the base functional makes little difference in our work since it affects only the density used to compute the nonlocal correlation energies and the sensititvity of these energies to density differences given by modern DFT methods is weak. In particular, the authors of Ref. [27] recommended that VV09 should be used with a range-separated hybrid (RSH) functional designed by them, but we decided to use a more popular LRC- $\omega$ PBE [71] RSH functional. The VV10 calculations were done withe PBE base functional but parameters "b" and "C" were taken to be 5.9 and 0.0093 respectively. These are the values of these parameters fitted for rPW86-PBE. For DADE, vdW-DF1, and vdW-DF2, we used the densities and density-gradients obtained from PBE calculations performed using ORCA [88].

The MBD calculations were done non-self-consistently in terms of affecting KS equations, but self-consistently in terms of iterating the polarizabilities and fully coupling the quantum harmonic oscillators. The PBE method was used to compute densities needed for calculations of Hirshfeld weighting functions. MBD calculations were performed using the stand-alone DFT/MBD program from Ref. [164].

The D3BJ[PBE] and D3MBJ[PBE] calculations used damping and scaling parameters corresponding to the PBE functional, while D3BJ[HF] used those corresponding to the HF method. D3[No-switching] does not use any scaling or damping and is
the sum of $C_{6}^{a b} / r_{a b}^{6}$ and $C_{8}^{a b} / r_{a b}^{8}$ terms only. All D3 dispersion energies were calculated in the perturbative way as defined in Sec. 4.4 using the dispersion coefficients computed for the dimers and then using only those involving pairs of atoms from different monomers. We used the D3 codes referenced in Sec. 4.4.

XDM calculations were done using NWChem [165] with PW86 [166] exchange and PBE correlation functionals. Since supermolecular calculations gave positive values of dispersion energies in some range of $R$, the XDM dispersion energies here were calculated perturbatively, as in the case of D3, cf. Eq. (4.11). Also as in the cases of D3, the coefficients were calculated using dimer densities. We will denote by XDM8[PW86PBE] the approach that uses terms involving $C_{6}^{a b}$ and $C_{8}^{a b}$, while XDM10[PW86-PBE] uses $C_{10}^{a b}$ as well with the damping corresponding to PW86-PBE. XDM8[No-switching] and XDM10[No-switching] are XDM8[PW86-PBE] and XDM10[PW86-PBE], respectively, without any damping.

The dispersion energies used to compute the errors and ratios of dispersion energies presented in the following sections are included in Appendix D.

### 4.8 Results

The mean absolute percentage errors (MAPEs) of various dispersion energies relative to $E_{\text {dispx }}$ are listed in Table 4.1 and shown as scatter plots in Fig. 4.1. The ratios of the dispersion energies to $E_{\text {dispx }}$ as functions of intermonomer separation $R$ are plotted in Figs. 4.2, 4.3, and 4.4. The MAPEs obtained by us are rather large, tens of percent, compared to the several percent errors of total interaction energies computed in Ref. [33] for some of the same dispersion methods as we use [note that Ref. [33] used the median absolute percentage errors (MedAPEs), see a discussion of this issue below]. The reason for this disparity is that dispersion energies are only a relatively small fraction of the total energies for most systems considered in Ref. [33]. For example, for the water dimer at $R=10 \AA$, the dispersion energy is only $1 \%$ of the total interaction energy. Thus, the very large errors of dispersion energies given by some methods at large $R$, as seen in Figs. 4.2, 4.3, and 4.4, have almost no effect
Table 4.2: MAPEs of dispersion energy from investigated methods relative to $E_{\text {disp }}$. DADE results are from Ref. [29].

| Dimer | $\mathrm{D}_{\text {as }}$ | D3[Noswitching | DADE | D3BJJ[HF] | XDM8 [Noswitching] | disp(VV10) | disp(VV09) | disp (MBD) | XDM10 [PW86-PBE] | D3BJ [PBE] | disp (vdW- <br> DF2 | D3MBJ <br> [PBE] | XDM8[PW86 <br> PBE] | disp(vdW- <br> DF1) | XDM10[Noswitching |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Argon dimer | 10.34 | 6.48 | 12.07 | 11.22 | 14.63 | 22.52 | 26.27 | 39.87 | 31.13 | 28.77 | 29.05 | 29.64 | 36.72 | 47.91 | 5.10 |
| Ar-HF | 5.16 | 11.20 | 8.71 | 14.81 | 7.43 | 20.49 | 28.25 | 33.06 | 23.72 | 27.97 | 25.19 | 30.49 | 27.92 | 78.84 | 7.51 |
| Water dimer | 11.41 | 33.56 | 19.75 | 18.78 | 72.06 | 33.52 | 49.74 | 37.62 | 35.93 | 36.38 | 32.50 | 39.22 | 37.34 | 78.06 | 336.71 |
| Ethanol dimer | 6.30 | 2.87 | 7.29 | 9.50 | 23.71 | 23.96 | 33.04 | 24.76 | 30.94 | 25.56 | 29.20 | 28.42 | 31.41 | 50.50 | 56.89 |
| Nitromethane dimer | 2.24 | 6.38 | 15.06 | 14.04 | 3.65 | 24.90 | 36.35 | 29.18 | 28.26 | 31.78 | 30.44 | 34.30 | 31.82 | 44.06 | 28.00 |
| Methylformate dimer | 12.89 | 4.77 | 12.48 | 14.82 | 10.46 | 26.08 | 27.00 | 31.57 | 28.57 | 32.96 | 33.34 | 35.97 | 32.76 | 43.74 | 43.81 |
| Benzene-methane | 9.83 | 4.86 | 6.39 | 9.80 | 20.78 | 22.72 | 27.12 | 29.02 | 29.74 | 23.80 | 32.84 | 25.32 | 30.93 | 43.16 | 47.88 |
| Benzene-water | 11.63 | 15.18 | 9.13 | 11.55 | 43.83 | 30.50 | 26.36 | 29.11 | 39.21 | 30.13 | 20.30 | 30.17 | 40.06 | 68.94 | 97.79 |
| Imidazole dimer | 11.60 | 33.04 | 30.40 | 26.49 | 50.78 | 33.41 | 26.90 | 33.82 | 32.88 | 40.02 | 45.55 | 42.37 | 37.38 | 36.84 | 235.25 |
| Nitrobenzene dimer | 8.31 | 8.92 | 7.20 | 12.03 | 8.60 | 27.21 | 45.46 | 25.01 | 29.23 | 24.86 | 27.04 | 24.35 | 30.91 | 37.40 | 28.91 |
| FOX-7 dimer | 9.65 | 20.70 | 32.14 | 23.19 | 32.46 | 36.70 | 22.78 | 36.66 | 41.60 | 43.75 | 45.58 | 43.75 | 46.46 | 24.84 | 103.23 |
| EDNA dimer | 4.42 | 11.24 | 16.46 | 17.93 | 13.84 | 20.57 | 27.31 | 29.35 | 30.78 | 36.32 | 34.45 | 38.87 | 36.68 | 31.21 | 42.69 |
| Average of MAPEs | 8.65 | 13.27 | 14.76 | 15.35 | 25.19 | 26.88 | 31.38 | 31.59 | 31.83 | 31.86 | 32.12 | 33.57 | 35.03 | 48.79 | 86.15 |

on MedAPEs of Ref. [33]. Consequently, the criterion used by us gives a far more stringent evaluation of the quality of dispersion energies. Some of the differences also come from comparing MAPEs with MedAPEs. The MedAPE measure has to be used for evaluations of interaction energy curves since otherwise the percentage errors near the points where the curves cross zero, which can sometimes be huge, would bias the picture. This problem does not appear in assessments of dispersion energies. Note that if errors are changing linearly over the set, MAPEs and MedAPEs have the same value. Also note that our MAPEs include two additional systems compared to Ref. [33], but these systems have errors comparable to other systems.

In some cases, it is not clear if the benchmarks should include the exchangedispersion energies. To enable comparisons without the latter terms, we have prepared Table 4.2 which is analogous to Table 4.1 but the errors are computed relative to the values of $E_{\text {disp }}$ (i.e., it is $E_{\text {dispx }}$ with the exchange-dispersion energy removed). In majority of cases, the changes are negligible and we will not discuss much the data from Table 4.2 later on.

Table 4.1 and Fig. 4.1 show that the ability of the investigated methods to recover dispersion interactions varies enormously, with averages of MAPEs ranging from $7 \%$ to $113 \%$. For individual dimers, the range is from $1.5 \%$ to $455 \%$. Even if the large outliers are removed, the upper limits are $49 \%$ and $102 \%$, respectively. The asymptotics-based atom-atom functions give most accurate dispersion energies, followed by the best nonlocal corelation functionals (but most functionals of this type perform poorly). The atoms-in-molecules-type methods have the worst overall performance. There is also a significant spread of MAPEs among individual dimers for each method, which is well visible in Fig. 4.1. Generally, methods with best overall performance have also narrowest spread.

### 4.8.1 Asymptotics-based methods

Table 4.1 and Fig. 4.1 show that the lowest MAPEs for individual dimers are generally those given by $\mathrm{D}_{\text {as }}$, this method also gives the lowest average of MAPE of
$7.3 \%$. Also the spread of MAPEs for individual dimers is very narrow: between $1.5 \%$ and $12.7 \%$. This good performance is also well visible in Figs. 4.2, 4.3, and 4.4 where the $\mathrm{D}_{\text {as }}$ curves are everywhere very close to the 1.0 value, with deviations observed only at the smallest $R$ 's (with a few exceptions like the error of about $20 \%$ at the largest $R$ for the FOX-7 dimer). This very good performance could partly be expected since this function was fitted to a benchmark set of $E_{\text {dispx }}$ values and therefore includes the physical damping of asymptotic expansion. However, the training set used to fit $\mathrm{D}_{\text {as }}$ was [20, 21], with a couple exceptions, completely different from our test set, so our results do confirm robustness of $\mathrm{D}_{\text {as }}$.

The next best performance, with $11.3 \%$ error, is given by the D3BJ method with damping fitted to the Hartree-Fock method, D3BJ[HF]. Since HF interaction energies are reasonably close to dispersionless energies, the D3BJ[HF] dispersion energies can be treated as containing very little of unphysical damping. This good performance is consistent with the fact that the reference D3 van der Waals coefficients are computed using TD-DFT which is known to give accurate values for these coefficients [SAPT(DFT) gives asymptotically the same coefficients]. Also, the account for chemical environment effects apparently works well in D3, i.e., the precomputed atom-specific constants are combined properly to get distributed van der Waals constants. Figures 4.2, 4.3, and 4.4 show that $\mathrm{D} 3 \mathrm{BJ}[\mathrm{HF}]$ is quite accurate at large $R$ for smaller dimers, but for benzenewater and the four dimers in Fig. 4.4 the errors are up to about 20\%. For most systems, D3BJ[HF] tends to understimate the magnitude of dispersion energy at small $R$. This is clearly connected with the truncation of this expansion at $1 / r_{a b}^{8}$.

D3[No-switching] does not use any scaling or damping and its MAPE of $17.5 \%$ is about $6 \%$ larger than that of D3BJ[HF]. This increase of the error is expected since the benchmark values do contain damping. At large $R$, D3[No-switching] nearly concides with $\mathrm{D} 3 \mathrm{BJ}[\mathrm{HF}]$. At small $R$, it overstimates the magnitude of dispersion energy (except for $\mathrm{Ar}_{2}$ and $\mathrm{Ar}-\mathrm{HF}$ ), as expected for a completely undamped asymptotic expansion. Note that it would be very difficult to create precise benchmarks for undamped methods since the undamped expansions diverge quite strongly in the region of the van der Waals
minimum and for smaller $R$ for all dimers containing monomers with more than a few atoms. Different truncations of the expansions and different distribution schemes lead to dramatically different values of dispersion energies at small $R$. One may add that the MAPE of D3[No-switching] decreases by $4 \%$ if comparisons are made with respect to $E_{\text {disp }}$ rather than to $E_{\text {dispx }}$, see Table 4.2. This is an expected improvement since D3[No-switching] does not include exchange-dispersion effects.

The $\mathrm{D} 3 \mathrm{BJ}[\mathrm{PBE}]$ and $\mathrm{D} 3 \mathrm{MBJ}[\mathrm{PBE}]$ methods, i.e., methods with the switchingoff functions fitted for the PBE method, have much larger errors, $30 \%$ and $31 \%$, respectively, than the D3 variants discussed above. They also strongly underestimate the magnitude of dispersion energy at short $R$. This shows how highly unphysical is the excessive damping included in these methods. The two methods are very close to each other for all dimers and for all $R$.

It can be noticed in the figures that $\mathrm{D} 3 \mathrm{BJ}[\mathrm{PBE}]$ is quite different from $\mathrm{D} 3[$ Noswitching] not only at short, but also at large $R$ 's. The reason is the scaling parameter for $C_{8}^{a b}$ terms, see a discussion of this issue in Ref. [77].

### 4.8.2 Nonlocal functionals

Out of the nonlocal functional methods, DADE performs best and its error, $11.9 \%$, is close to the errors of $\mathrm{D}_{\mathrm{as}}$ and $\mathrm{D} 3 \mathrm{BJ}(\mathrm{HF})$ and better than those of all other methods. DADE's average error is strongly affected by two systems, the FOX-7 dimer and the imidazole dimer, systems for which $D_{\text {as }}$ performs quite well but most other methods considered here give large errors, similarly to DADE. Still, the spread of DADE predictions is among the smallest. For the largest $R$, DADE underestimates the magnitude of the dispersion energy typically by about $15 \%$, but for the FOX-7 dimer the underestimation is about $40 \%$. This is clearly related to the approximate representation of dynamic polarizability in the vdW-DF methods from which this quantity has been taken. As $R$ decreases, the ratio curve of DADE to $E_{\text {dispx }}$ increases until it reaches a maximum at some $R$, and then starts to decrease. This behaviour is common with the vdW-DF methods.

The next in performance among nonlocal-functional methods is VV10 which gives the average MAPE of $24 \%$, twice as large as that for DADE. As mentioned earlier, this functional is more empirical than the other investigated nonlocal ones. It was fitted paired with rPW86-PBE, a DFT method which gives interaction energies fairly close to HF ones. Thus, it should include physical damping and one could expect that it should not be much affected by excessive damping. However, Figs. 4.2-4.4 show that this is not the case since at shorter $R$ the VV10 functional gives results somewhat better but still very close to methods that include significant amounts of excessive damping. The overall $24 \%$ error is also in line with the errors of such methods. Clearly, errors of this size are too large to consider these methods as providing a faithful description of dispersion interactions. However, VV10 performs reasonably well at the largest $R$. Another functional from the same group, VV09, has a larger overall error, $29 \%$, and quite different dependence on $R$. For most systems, it has very large errors at large $R$ (interestingly, VV09 results are very accurate at large $R$ for the FOX-7 dimer, where most other methods perform poorly). VV09 usually overestimates the magnitude of dispersion energy at large $R$ (except for the water dimer where it strongly underestimates), and then in most cases the ratios shown in Figs. 4.2-4.4 decrease, leading to an underestimation at small $R$.

The vdW-DF2 method with its $29 \%$ overall error is close in performance to the VV methods. However, at large $R$ vdW-DF2 performs much worse than any other method, recovering typically only about $50 \%$ of the magnitude of the dispersion energy. In all cases, this performance is significantly worse than that of DADE, which indicates that the value of the parameter $Z_{a b}$ used in DADE represents monomer polarizabilities better. As $R$ decreases, the vdW-DF2 ratio goes through a maximum and then decreases. This behavior is similar to DADE, but the recovery of the dispersion energy at small $R$ is significantly worse than in the case of DADE. The related vdW-DF1 functional performs much worse than vdW-DF2, with the overall MAPE of $49 \%$. Figures 4.2-4.4 show that the behavior of vdW-DF1 is very irregular and errors at various $R$ can be as large as $250 \%$. This method overestimates the magnitude of
dispersion energy at most $R$ for all systems. Clearly, the value of the parameter $Z_{a b}$, the only difference between vdW-DF1 and vdW-DF2, was not well chosen in the case of vdW-DF1.

### 4.8.3 Atoms-in-molecules methods

The best performance in the family of XDM methods, average MAPE of $30 \%$, was achieved by XDM10[PW86-PBE], with XDM8[PW86-PBE] following with $33 \%$. Thus, the performance of these methods is close to that of D3BJ/MBJ $[\mathrm{PBE}]$ and this closeness results from fitting to similar interaction energy benchmarks. Indeed, the XDM8[PW86-PBE] and D3BJ[PBE] curves are very close to each other for all systems and all distances, with minor exceptions, cf. Figs. 4.2-4.4, and XDM10[PW86-PBE] is quite close too. On the other hand, the average MAPE of XDM8[No-switching] is $35 \%$, twice larger than that of D3[No-switching] which was $17.5 \%$. Clearly, the van der Waals constants in the latter case are much better than in the former. If comparisons are made to $E_{\text {disp }}$, cf. Table 4.2, both errors decrease, to $25 \%$ and $13 \%$, respectively, but the ratio remains close to two. Figures 4.2-4.4 show that for most systems and most Rs, the XDM8[No-switching] curve is above the D3[No-switching] curve and further from the 1.0 line, consistent with MAPEs.

The XDM10[No-switching] method performs still much worse, giving the average MAPE of $113 \%$ ( $86 \%$ if compared to $E_{\text {disp }}$ ). This is due to various inaccuracies of XDM10, but also partly reflects the strong divergence of the asymptotic expansion for small separations of large monomers. XDM10[No-switching] acquires particularly large errors for two dimers: $455 \%$ for the water dimer and $310 \%$ for the imidazole dimer. Concluding from this observation, as well as from the earlier observation concerning XDM8[No-switching] vs. D3[No-switching], one may say that that the XDM method gives significantly less accurate van der Waals coefficients than D3.

A comparison of dispersion energies from all completely undamped methods: D3[No-switching], XDM8[No-switching], and XDM10[No-switching] shows that for shorter
$R$ s the ordering of their magnitudes depends on the dimer, but in most cases the magnitude of energy from XDM10[No-switching] is the largest and from D3[No-switching] the smallest. The reasons for the former were discussed above and the reason for the latter is the lack of the most divergent terms with tenth inverse powers of separations.

As mentioned earlier, for the MBD method we were not able to remove switching and we used the switching resulting from pairing with the PBE functional. Expectedly, the performance of $\operatorname{disp}(\mathrm{MBD})$ is similar to all other methods with significant switching. Consequently, we cannot evaluate how well MBD reproduces dispersion effects as a function of $R$. At the largest $R$, where sixth inverse power dominates, MBD performs similarly to $\mathrm{D}_{\text {as }}$ and $\mathrm{D} 3 \mathrm{BJ}[\mathrm{HF}]$, as expected from the fact that it was fitted to asymptotic constants.

### 4.9 Summary and Conclusions

Various methods of supplementing the DFT interaction energies for the dispersion effects that DFT cannot describe have been evaluated by comparing the dispersion energies predicted by such methods to dispersion energies from SAPT(DFT). The comparisons have been made on a diverse set of dimers using for each dimer the whole range of intermolecular distances, from the repulsive region of the total potential, through the van der Waals minimum region, to asymptotic distances. The overall conclusion is that most of the methods in use reproduce dispersion energies poorly, with tens of percent errors. The best performance, about $10 \%$ average errors, is found for the asymptotics-based atom-atom functions which do not include excessive damping (unphysical switching off of dispersion energy for very small $R$ ). If switching-off is included, the errors increase to about $30 \%$. At small $R$, the ratio of dispersion energies from such methods to $E_{\text {dispx }}$ is often about 0.2 , which means that these energies are five times too small in magnitude (one can hardly consider them to be dispersion energies in this region). Most nonlocal correlation functionals perform much worse, with errors in the range $24 \%$ to $49 \%$, far from what could be called quantitative reproduction of this quantity. The only exception is the recently proposed DADE functional which
gave error of $12 \%$. The atoms-in-molecule methods (XDM and MBD) also gave large errors, above $29 \%$. For the XDM case, the quality of van der Waals constants is shown to be poor compared to the D3 constants. For the MBD method we were not able to compute undamped values, so we cannot comment on the constants except for the leading one which is of good quality.

At the largest $R$, where the dispersion energy is dominated by terms that decay as the sixth inverse power of interatomic distances, both the asymptotics-based and atoms-in-molecules methods perform generally well, with typical errors of a few percent for most systems. This is expected as these methods have been trained to reproduce the dipole-dipole polarizabilities and/or the leading van der Waals constants. One exception is the XDM method which for most systems gives errors larger than $10 \%$ at such separations. Another exception are the four largest dimers, depicted in Fig. 4.4, where the errors of theses methods at such separations are around $20 \%$ for all methods in this category. This is partly due to the fact that for these systems the largest $R$ included by us may be still not far enough in the asymptotic region or perhaps the performance of these types of methods deteriorates for large molecules.

The generally adequate performance of the asymptotics-based and atoms-inmolecular methods at large $R$ is not shared by the nonlocal functionals. Both vdW-DF functionals can have $50 \%$ errors in this region (with overestimation in the case of vdWDF1 and underestimation in the case of vdW-DF2). DADE does somewhat better, with errors closer to $15 \%$ and underestimation in all cases. Also VV09 significantly overestimates for most dimers. VV10 performs at large $R$ best of all nonlocal methods, with errors similar to those of the asymptotics-based functions.

As $R$ decreases, the desired behavior is that the ratios of the approximate dispersion energies to the $E_{\text {dispx }}$ values remain approximately constant. This is not the case in general and the ratios change dramatically for most methods except for $\mathrm{D}_{\text {as }}$ in which case the change is modest. The other method with modest changes is D3BJ[HF]. For the methods with excessive damping, the ratio decreases more or less continuously
to reach a value generally in the range of $0.1-0.3$ at the shortest $R$. One should realize that the excessive damping depends strongly on the density functional that the dispersion energy is paired with (see Fig. 2 in Ref. [77]). If we included several such functionals, the results for the same method and different functionals would be all over the place.

The methods without damping behave in just the opposite way: the ratio increases and the approximate dispersion energies become a few times larger than the reference values at the shorter $R$. This is an expected effect due to the divergence of the asymptotic expansion. This divergence is particularly dramatic for the XDM10[Noswitching] method due to the use of terms with tenth inverse powers and generally too large values of van der Waals coefficients. The latter can be seen from the fact that the XDM8[No-switching] dispersion energies are are always much larger in magnitude than the D3[No-switching] energies at short separations (except for the argon dimer).

The dependence on $R$ is completely different for nonlocal functionals, especially for vdW-DFs. As $R$ decreases, the ratio of the approximate dispersion energy to the $E_{\text {dispx }}$ first increases, then goes through a maximum which in the case of vdW-DF2 is close to 1.0 , and then decreases. This decrease is actually beneficial for applications of the vdW-DF2 method since, as shown in Ref. [77], all semilocal functionals behave at those $R$ as if they were gradually starting to reproduce dispersion energy (note, however, that we argued in Ref. [77] that this behavior is due to components of DFT that should not be able to describe electron correlation phenomena such as dispersion energies). This decline of the ratio for nonlocal functionals is due to the design of such methods. In particular, note that Eq. (4.5) includes the LDA correlation energy density and the interplay between this quantity and other terms may possibly contribute to the observed behavior of nonlocal functionals at small $R$. Although DADE largely overcomes the behavior of vdW-DF functionals described above, i.e., its curves are much more flat, it still exhibits the decline at small $R$. There is one more reason for the decline of the ratio for nonlocal functionals at short $R$ : the restriction to dipole-dipole-type terms in the polarization function whereas higher-rank multipolar effects
become important at short separation.
The VV and vdW-DF methods have become enormously popular in recent years. It appears that the replacement of these functionals by DADE should lead to significantly improved predictions in applications of nonlocal-functional methods. Although DADE performs somewhat worse than $\mathrm{D}_{\text {as }}$ and $\mathrm{D} 3 \mathrm{BJ}[\mathrm{HF}]$, the latter two methods are just parametrized atom-atom functions with tabulated parameters, whereas DADE is essentially a first-principles approach as it was only minimally fitted to benchmark data.


Figure 4.1: The mean absolute percentage errors of dispersion energies from the considered methods relative to $E_{\text {dispx }}$.


Figure 4.2: The ratios of dispersion energies from investigated methods to $E_{\text {dispx }}$ for $\mathrm{Ar}_{2}$, Ar-HF, water dimer, and ethanol dimer. The method disp(MBD) uses switching factors fitted by pairing it to the PBE functional. The vertical lines indicate positions of van der Waals minima. The inserted molecular graphs have cyan, lime, white, gray, and red spheres representing argon, fluorine, hydrogen, carbon, and oxygen atoms, respectively.


Figure 4.3: The ratios of dispersion energies from investigated methods to $E_{\text {dispx }}$ for nitromethane dimer, methyl formate dimer, benzene-methane, and benzene-water. The blue spheres represent nitrogen atoms. For other details, see Fig. 4.2.


Figure 4.4: The ratios of dispersion energies from investigated methods to $E_{\text {dispx }}$ for homogeneous dimers of imidazole, nitrobenzene, FOX-7, and EDNA. For other details, see Figs. 4.2 and 4.3.

## Chapter 5 <br> POLARIZABILITY DENSITY FROM TIME DEPENDENT DENSITY-FUNCTIONAL THEORY AND FURTHER DEVELOPMENT OF DADE

In previous two chapters, we discussed the development of a new method for dispersion energy calculations and comparison of most methods used in DFT for this purpose. Our new method of dispersion energy calculation, DADE, takes the polarizability density expression from nonlocal correlation functionals. Thus, one may ask question if this expression can be improved or replaced by a more adequate one. The polarizability is an important physical quantity in itself, so such improvements are relavant not only for dispersion energy. If we could develop a polarizability function which is physically more sound than the one used in DADE, the predictions of DADE should improve.

In Chapter 3, we wrote the density-density response function $\chi\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}, \mathrm{i} u\right)$ in terms of the polarizability-density tensor $\alpha_{i j}\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}, \mathrm{i} u\right)[79,80]$ as

$$
\begin{equation*}
\chi\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}, \mathrm{i} u\right)=-\sum_{i, j=1}^{3} \frac{\partial^{2}}{\partial x_{i} \partial x_{j}^{\prime}} \alpha_{i j}\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}, \mathrm{i} u\right), \tag{5.1}
\end{equation*}
$$

where $x_{i}$ are the components of $\boldsymbol{r}$. Furthermore, we introduced an approximate $\alpha_{i j}$, a local and isotropic quantity by

$$
\begin{equation*}
\alpha_{i j}\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}, \mathrm{i} u\right)=\delta_{i j} \alpha(\boldsymbol{r}, \mathrm{i} u) \delta\left(\boldsymbol{r}-\boldsymbol{r}^{\prime}\right) \tag{5.2}
\end{equation*}
$$

where $\alpha(\boldsymbol{r}, \mathrm{i} u)$ is called the local polarizability density.
The Cartesian dipole-dipole polarizability can be obtained from the densitydensity response function $\chi\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}, \mathrm{i} u\right)$ of time-dependent DFT (TD-DFT) as [167]

$$
\begin{equation*}
\alpha_{i j}(\mathrm{i} u)=-\iint d^{3} \boldsymbol{r} d^{3} \boldsymbol{r}^{\prime} x_{i} x_{j}^{\prime} \chi\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}, \mathrm{i} u\right) \tag{5.3}
\end{equation*}
$$

where $x_{i}$ are components of $\boldsymbol{r}$. Plugging Eq. (5.1) into Eq. (5.3) we get

$$
\begin{equation*}
\alpha_{i j}(\mathrm{i} u)=\sum_{i^{\prime}, j^{\prime}=1}^{3} \iint d^{3} \boldsymbol{r} d^{3} \boldsymbol{r}^{\prime} x_{i} x_{j}^{\prime} \frac{\partial^{2}}{\partial x_{i^{\prime}} \partial x_{j^{\prime}}^{\prime}} \alpha_{i^{\prime} j^{\prime}}\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}, \mathrm{i} u\right), \tag{5.4}
\end{equation*}
$$

Now integrating by parts and assuming $\alpha_{i j}$ and its gradient vanish when coordinates go to infinity we get

$$
\begin{equation*}
\alpha_{i j}(\mathrm{i} u)=\iint d^{3} \boldsymbol{r} d^{3} \boldsymbol{r}^{\prime} \alpha_{i j}\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}, \mathrm{i} u\right) . \tag{5.5}
\end{equation*}
$$

Thus, $\alpha_{i j}\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}, \mathrm{i} u\right)$ can be called two-electron dipole-dipole polarizability density at points $\boldsymbol{r}$ and $\boldsymbol{r}^{\prime}$ since integration of this quantity over all coordinates gives us dipoledipole polarizability of the system. Comparing Eq. (5.5) and Eq. (5.3) we get

$$
\begin{equation*}
\alpha_{i j}\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}, \mathrm{i} u\right)=-x_{i} x_{j}^{\prime} \chi\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}, \mathrm{i} u\right) \tag{5.6}
\end{equation*}
$$

Although the knowledge of $\chi$ gives $\alpha_{i j}$ in a trivial way, it does not allow us to find $\alpha(\boldsymbol{r}, \mathrm{i} u)$ in Eq. (5.2). The polarizability density $\alpha_{i j}(\boldsymbol{r}, \mathrm{i} u)$ can be defined from Eq. (5.6) as

$$
\begin{equation*}
\alpha_{i j}(\boldsymbol{r}, \mathrm{i} u)=\int d^{3} \boldsymbol{r}^{\prime} \alpha_{i j}\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}, \mathrm{i} u\right)=-x_{i} \int d^{3} \boldsymbol{r}^{\prime} x_{j}^{\prime} \chi\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}, \mathrm{i} u\right) \tag{5.7}
\end{equation*}
$$

Now integrating Eq. (5.2) and using Eq. (5.7) we can write

$$
\begin{align*}
\int d^{3} \boldsymbol{r} \alpha_{i j}\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}, \mathrm{i} u\right) & =\delta_{i j} \int d^{3} \boldsymbol{r} \alpha(\boldsymbol{r}, \mathrm{i} u) \delta\left(\boldsymbol{r}-\boldsymbol{r}^{\prime}\right) \\
\alpha_{i j}\left(\boldsymbol{r}^{\prime}, \mathrm{i} u\right) & =\delta_{i j} \alpha\left(\boldsymbol{r}^{\prime}, \mathrm{i} u\right) \tag{5.8}
\end{align*}
$$

Therefore, the polarizability density given in Eq. (5.2) is $\alpha(\boldsymbol{r}, \mathrm{i} u)=\sum_{i} \alpha_{i i}(\boldsymbol{r}, \mathrm{i} u) / 3$ which is the polarizability density defined for nonlocal functionals in Ref. [83]. To calculate the same quantity in TD-DFT we use density-density response function from TD-DFT in Eq. (5.7). The density-density response function can be computed as [34]

$$
\begin{equation*}
\chi\left(\boldsymbol{r}, \boldsymbol{r}^{\prime}, \mathrm{i} u\right)=-\sum_{i v, i^{\prime} v^{\prime}} C_{i v, i^{\prime} v^{\prime}}(\mathrm{i} u) \phi_{i}(\boldsymbol{r}) \phi_{v}(\boldsymbol{r}) \phi_{i^{\prime}}\left(\boldsymbol{r}^{\prime}\right) \phi_{v^{\prime}}\left(\boldsymbol{r}^{\prime}\right), \tag{5.9}
\end{equation*}
$$



Figure 5.1: Comparison of the polarizability density $\alpha(\boldsymbol{r}, \mathrm{i} u)$ for the argon atom in the case $x=z, y=0.0$, and $u=0.79$ in atomic units.
where $\phi_{i}$ and $\phi_{v}$ are occupied and virtual orbitals of the considered system and $C_{i v, i^{\prime} v^{\prime}}(\mathrm{i} u)$ linear coefficients determined by equations of TD-DFT. Using Eq. (5.9) in Eq. (5.7), the polarizability density can be written as

$$
\begin{equation*}
\alpha_{j k}(\boldsymbol{r}, \mathrm{i} u)=\sum_{i v, i^{\prime} v^{\prime}} C_{i v, i^{\prime} v^{\prime}}(\mathrm{i} u) x_{j} \phi_{i}(\boldsymbol{r}) \phi_{v}(\boldsymbol{r}) \int d^{3} \boldsymbol{r}^{\prime} x_{k}^{\prime} \phi_{i^{\prime}}\left(\boldsymbol{r}^{\prime}\right) \phi_{v^{\prime}}\left(\boldsymbol{r}^{\prime}\right) . \tag{5.10}
\end{equation*}
$$

We computed polarizability density $\alpha(\boldsymbol{r}, \mathrm{i} u)$ using this quantity and compared it to the polarizability densities from different nonlocal functionals in Figs. 5.1 and 5.2. The polarizability densities corresponding to vdW-DF2 and DADE, denoted as $\alpha_{\text {vdWDF2 }}$ and $\alpha_{\text {DADE }}$, are obtained from Eqs. (3.6) and (3.7) with values of $Z_{a b}$ taken to be -1.887 and -1.1972 , respectively. For VV09 and VV10 cases, the polarizability density is same,
denoted as $\alpha_{V V}$ and given by Eq. (3.6) with $\omega_{0}(\boldsymbol{r})=\sqrt{4 \pi n(\boldsymbol{r}) / 3+0.0089\left|\frac{\nabla n(\boldsymbol{r})}{n(\boldsymbol{r})}\right|^{4}}$ from Ref. [83]. The density-density response function for the argon atom was obtained using the TD-DFT codes from the SAPT2016 package [168]. The basis set aug-ccpVDZ [91] were used and the orbital coefficients for nonlocal functionals were obtained using ORCA [88]. Both response function and ORCA calculations were done using the PBE0 $[42,56]$ method. The polarizability densities were obtained using density-density response function and orbital coefficients through a code written by us.


Figure 5.2: Comparison of polarizability density $\alpha(\boldsymbol{r}, \mathrm{i} u)$ for the argon atom from vdW-DF2 (bottom-right), VV09/10 (top-right), and DADE (bottomleft) with the one obtained from TD-DFT (top-left) for $y=0.0$ and $u=0.79$ in atomic units.

The polarizability densities $\alpha_{\mathrm{vdW}-\mathrm{DF} 2}(\boldsymbol{r}, \mathrm{i} u)$ and $\alpha_{\mathrm{DADE}}(\boldsymbol{r}, \mathrm{i} u)$ agree reasonably
closely with $\alpha_{\mathrm{TD}-\mathrm{DFT}}(\boldsymbol{r}, \mathrm{i} u)$, in particular when compared to $\alpha_{\mathrm{VV}}(\boldsymbol{r}, \mathrm{i} u)$ which gives too much large values at about 1 bohr from the nucleus. The agreement of DADE with TD-DFT is the best of the methods studied, which is in line with DADE giving better dispersion energies. Note that the difference between the polarizability densities from vdW-DF2 and DADE are due only to the different values of $Z_{a b}$. When we approach close to the nucleus, TD-DFT and VV have pronounced wiggles. Around this region, close to the nucleus, all nonlocal functionals give much larger values than TD-DFT. Furthermore, in the density tail the decay rate of polarizability densities from nonlocal functionals is faster than in the case of TD-DFT. Figure 5.2 gives 3D surface plots of the polarizability densities in order to provide an overall view of these quantities.

In future work we plan to improve the nonlocal correlation functionals by improving the accuracy of polarizability density so that it agrees better with TD-DFT. Yet, another step is to go beyond the dipole-dipole polarizability and include higher order multipole effects which are included in TD-DFT response functions. A more significant improvement can be made if we go beyond the severe approximations of Eq. (5.2) and use the two-electron polarizability density instead of the present one, i.e., replace the Dirac delta function $\delta\left(\boldsymbol{r}-\boldsymbol{r}^{\prime}\right)$ in this equation by less severe approximation.

## Chapter 6

## POTENTIAL ENERGY SURFACE DEVELOPMENT FOR CRYSTAL STRUCTURE PREDICTION

The advancement of technology is possible if new materials with the novel properties can be designed. If the properties of such systems could be predicted computationally, the development processes might be shortened by screening the candidate materials, and new classes of materials could be suggested based on theoretical insights. An important element of the theoretical study of molecular crystals is the development of intermolecular potential energy surfaces (PES) for the considered dimers. PES is used to run molecular dynamics for the system and predict the crystal structure and properties. We developed PESs for the molecular dimers given in Table 6.1 using data from quantum calculations. The autoPES code [169], which automates the PES generation, was used. It divides the PES generation into five different parts. In the first part, the asymptotic interaction energies are calculated from monomer properties using multipole expansion. The asymptotic interaction energies have sufficient accuracy up to 1.5 times the van der Waals minimum separation. Thus, asymptotic expansion causes an enormous reduction in the computational cost of PES development. Moreover, as asymptotic calculations use the same level of theory as $\mathrm{SAPT}(\mathrm{DFT})$, the two regions connect seamlessly. For the region of shorter separations, a suitable grid is generated using a guided Monte Carlo procedure such that the energetically favorable region has relatively more grid points, especially, around the local minima. Then SAPT(DFT) calculations are performed on these grid points and then following analytic function $V$
of the form

$$
\begin{align*}
V & =\sum_{a \in A, b \in B} u_{a b}\left(r_{a b}\right)=V_{\mathrm{elst}}+V_{\exp }+V_{\mathrm{asymp}}^{(2)} \\
& =\sum_{a \in A, b \in B}\left[u_{\mathrm{elst}, a b}\left(r_{a b}\right)+u_{\mathrm{exp}, a b}\left(r_{a b}\right)+u_{\mathrm{asymp}, a b}^{(2)}\left(r_{a b}\right)\right] \tag{6.1}
\end{align*}
$$

where $a(b)$ goes over the sets of atoms in monomer A (B), respectively. The atom-atom function are of the form

$$
\left.\begin{array}{rl}
u_{\text {elst }, a b}\left(r_{a b}\right) & =\frac{q_{a} q_{b}}{r_{a b}} \\
u_{\exp , a b}\left(r_{a b}\right) & =\left[1+\sum_{i=1}^{k} a_{i}^{a b}\left(r_{a b}\right)^{i}\right] e^{\alpha^{a b}-\beta^{a b}} r_{a b}
\end{array}+\frac{A_{12}^{a b}}{\left(r_{a b}\right)^{12}}\right) ~=-\sum_{n=6,8} f_{n}\left(\delta_{n}^{a b}, r_{a b}\right) \frac{C_{n}^{a b}}{\left(r_{a b}\right)^{n}}, ~ l
$$

where $f_{n}$ are Tang-Toennies damping functions [66]

$$
\begin{equation*}
f_{n}\left(\delta_{n}^{a b}, r_{a b}\right)=1-e^{-\delta r} \sum_{m=0}^{n} \frac{(\delta r)^{m}}{m!} . \tag{6.3}
\end{equation*}
$$

The partial charges $q_{x}$ and induction plus dispersion coefficients $C_{n}^{a b}$ are fitted on asymptotic data and then keeping them fixed, parameters $\alpha^{a b}, \beta^{a b}, \delta_{n}^{a b}, a_{i}^{a b}$, and $A_{12}^{a b}$ are fit to the grid of short-range interaction energy. The PES obtained in this way is first checked for the presence of holes on the repulsive wall. Holes are regions where PES on the repulsive wall suddenly deviates from the physically expected behavior. If holes are present then more grid points are selected in this region to perform the SAPT(DFT) calculations and refit the surface. The PES is fitted on $85 \%$ of the grid points while remaining $15 \%$ points are used as a test set. If the root mean square error (RMSE) on the test set is $20 \%$ or larger than that for PES then it is assumed that PES has not converged, more grid points are added and the whole cycle is repeated to get a new PES.

The quality of each component of $V$ is tested by comparing them to corresponding components of SAPT(DFT) as shown in Figs. 1 for 4-amino-2,3,6-trinitrophenol and 4-amino-2,3,6-trinitrophenol dimer. The reasonable agreement of PES to SAPT(DFT)


Figure 6.1: 4,4-bipyridine (left) and 4-amino-2,3,6-trinitrophenol (right) with the atomic partial charges. The integer label on each ball is to specify the atoms treated equivalently for PES calculations. The white, grey, blue, and red balls denote hydrogen, carbon, nitrogen, and oxygen atom respectively.
for individual components and the total interaction energy shows the physical soundness of the methods. A similar agreement exists in other cases. There are two manuscripts in preparation $[170,171]$ which include these molecular dimers for prediction of crystal structures. Our PES generation part is complete and contributions from our collaborators who will run molecular dynamics and experimental prepare these crystals are needed to publish them.

Table 6.1: The combinations of monomers, number of atoms, number of electrons, number of grid points, and corresponding RMSEs of the PESs.

| Monomer A | Monomer B | $N_{\text {atoms }}$ | $N_{\text {electrons }}$ | $N_{\text {grid }}$ | $\begin{gathered} \text { RMSE } \\ E<0 \\ (\mathrm{kcal} / \mathrm{mol}) \end{gathered}$ | RMSE $E<10$ $(\mathrm{kcal} / \mathrm{mol})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 4-amino-2,3,6-trinitrophenol | 4-amino-2,3,6trinitrophenol | $21+21$ | $124+124$ | 1132 | 0.3 | 0.52 |
| 4-amino-2,3,6-trinitrophenol | 4,4-bipyridine | $21+20$ | $124+82$ | 1298 | 0.22 | 0.51 |
| 4,4-bipyridine | 4,4-bipyridine | $20+20$ | $82+82$ | 884 | 0.19 | 0.44 |
| 5,5-dinitro-2H,2H-3,3-bi-1,2,4- <br> triazole | 2,4,6-Trinitrophenol | 18+19 | $114+116$ | 2100 | 0.32 | 0.58 |



Figure 6.2: 5,5-dinitro-2H,2H-3,3-bi-1,2,4-triazole (left) and 2,4,6-Trinitrophenol (right) with the atomic partial charges. The integer label on each ball is to specify the atoms treated equivalently for PES calculations. The white, grey, blue, and red balls denote hydrogen, carbon, nitrogen, and oxygen atom respectively.


Figure 6.3: PES for 4-amino-2,3,6-trinitrophenol with 4,4-bipyridine compared with $\mathrm{SAPT}(\mathrm{DFT})$ for the the orientation corresponding to first minimum.

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## Appendix A

## LIST OF PUBLICATIONS

- M. Shahbaz and K. Szalewicz, "Do semilocal density-functional approximations recover dispersion energies at small intermonomer separations?," Phys. Rev. Lett., vol. 121, no. 11, p. 113402, 2018.
- M. Shahbaz and K. Szalewicz, "Evaluation of methods for obtaining dispersion energies used in density-functional calculations of intermolecular interactions," Theor Chem Acc (2019) 138: 25.
- M. Shahbaz and K. Szalewicz, "Dispersion energy from local polarizability density." submitted, 2018.
- M. Shahbaz, M. P. Metz, K. Szalewicz, L. Vogt, S. Song, M. Tuckerman, and C. B. Aakeröy, "Theoretical and experimental investigations of cocrystals of dinitrobenzotriazole and aminotrinitrophenol with pyrazine, bipyridine, and bipyridine dioxide." Manuscript in preparation.
- R. Nikhar, M. Shahbaz, M. P. Metz, K. Szalewicz, L. Vogt, S. Song, M. Tuckerman, and A. Matzger, "Theoretical and experimental investigations of cocrystals of dinitrobitriazole with trinitro derivatives of benzene, toluene, and phenol." Manuscript in preparation.


## Appendix B

## APPENDIX FOR CHAPTER 2

## B. 1 Basis sets and CBS Extrapolation

The interaction energies presented here were obtained (except for data plotted in Fig. 2.2, see below) by an extrapolation to the complete basis set (CBS) limit. The Hartree-Fock parts of SAPT and $\operatorname{CCSD}(\mathrm{T})$ interaction energies, as well as the DFT interaction energies, were extrapolated using $E_{\mathrm{Y}}=E_{\mathrm{CBS}}+B \mathrm{e}^{-\alpha Y}$, where $Y$ is the cardinal number and $B$ and $\alpha$ are constants. The constant $\alpha$ was chosen to be 1.63, as recommended in Refs. [172, 173]. The correlation parts of SAPT and $\operatorname{CCSD}(\mathrm{T})$ interaction energies were extrapolated using the formula $E_{\mathrm{Y}}=E_{\mathrm{CBS}}+A / Y^{3}$, where $A$ is a constant. The calculations were performed using the aug-cc-pVTZ and aug-ccpVQZ basis sets [160, 161, 91]. The (3s3p2d2f1g) set of midbond functions was used for $\mathrm{Ar}-\mathrm{Ar}, \mathrm{Ar}-\mathrm{HF}$, and $\mathrm{Ar}-\mathrm{Li}^{+}$dimers whereas the set (3s3p2d2f) was used for the water dimer $[174,4]$. Such functions were not used for Ar-proton. The calculations were done using Orca [88], Erkale [175], Q-Chem [176], and SAPT2016 [177]. The supermolecular energies were counterpoise corrected by performing monomer calculations with the same basis as used for the dimer [92]. Also SAPT calculations were done in exactly the same basis set, i.e., using the dimer-centered plus midbond basis set ( $\mathrm{DC}^{+} \mathrm{BS}$ ) [162]. All listed energies are in $\mathrm{kcal} / \mathrm{mol}$ and the distances between centers of mass, $R$, of the interacting monomers are given in angstroms. All electrons were correlated in $\operatorname{CCSD}(\mathrm{T})$ and SAPT calculations.

## B. 2 Level of SAPT Theory

The SAPT [1, 2, 3, 4] interaction energy was calculated as the sum of the following corrections

$$
\begin{align*}
E_{\text {int }}^{\text {SAPT }}= & E_{\text {elst }}^{(10)}+E_{\text {exch }}^{(10)}+E_{\text {ind,resp }}^{(20)}+E_{\text {exch-ind,resp }}^{(20)}+E_{\text {elst,resp }}^{(12)}+E_{\text {elst,resp }}^{(13)}+\epsilon_{\text {exch }}^{(1)}(\text { CCSD }) \\
& +{ }^{t} E_{\text {ind }}^{(22)}+{ }^{t} E_{\text {exch-ind }}^{(22)}+E_{\text {disp }}^{(20)}+E_{\text {disp }}^{(21)}+E_{\text {disp }}^{(22)}+E_{\text {exch-disp }}^{(20)}+E_{\text {ind-disp }}^{(30)} \\
& +E_{\text {exch-ind-disp }}^{(30)}+E_{\text {ind }}^{(30)}+E_{\text {exch-ind }}^{(30)}+E_{\text {disp }}^{(30)}+E_{\text {exch-disp }}^{(30)}, \tag{B.1}
\end{align*}
$$

where $E^{(i j)}$ are corrections of the $i$ th-order in intermolecular interaction operator $V$ and of the $j$ th-order in the Møller-Plesset fluctuation operator $W$, and $\epsilon_{\text {exch }}^{(1)}(\operatorname{CCSD})=$ $E_{\text {exch }}^{(1)}(\mathrm{CCSD})-E_{\text {exch }}^{(10)}$ is the intramonomer correlation contribution to the first-order exchange energy calculated with CCSD wave functions. The subscripts denote electrostatic (elst), exchange (exch), induction (ind), and dispersion (disp) contributions, whereas "resp" indicates the coupled HF level of theory. An additional term was included for $\mathrm{Ar}_{2}$ and $\mathrm{Ar}-\mathrm{HF}$ at very small separations, see below.

The dispersion energy $E_{\text {dispx }}$ defined in Eq.(2.1) approximates the leading term by the following expansion in $W$

$$
\begin{equation*}
E_{\mathrm{disp}}^{(2)}=E_{\mathrm{disp}}^{(20)}+E_{\mathrm{disp}}^{(21)}+E_{\mathrm{disp}}^{(22)} \tag{B.2}
\end{equation*}
$$

whereas the remaining terms are of zeroth-order in $W$.

## B. 3 Uncertainties of SAPT Results

An important question is how well the dispersion energy given by Eq. (2.1) reproduces the "exact" dispersion energy. Since the dispersion energy can be defined only within SAPT, this question actually concerns the convergence of SAPT and uncertainties resulting from the truncations assumed in $E_{\text {dispx }}$. One has to point out first that the dispersion energy cannot be uniquely defined beyond the second order in $V$. Already in the third order, there are mixed, induction-dispersion terms [4, 135], cf. Eq. (B.1), which we have not included in $E_{\text {dispx }}$. For the purpose of the present work, we have to determine if the truncation of the dispersion energy in the third order in $V$
is adequate, i.e., the higher-order terms can be neglected. Since the higher-order terms are unknown, we can only infer from the rate of convergence. At the vdW minimum, the ratio of the magnitude of the third-order dispersion terms to the second-order ones is $0.021,0.018,0.022$, and 0.032 for $\mathrm{Ar}_{2}, \mathrm{Ar}-\mathrm{HF}, \mathrm{Ar}-\mathrm{Li}^{+}$, and $\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}$, respectively. This indicates that the terms of higher order in $V$ are completely negligible.

One may add that if terms of higher order in $V$ were available, the uncertainty of the dispersion energy would be reduced, since the SAPT series is semi-convergent. Convergence of this series has been extensively investigated (see Ref. [178] for a review of this work). This convergence depends on the type of symmetry adaptation. The method used by us, called symmetrized Rayleigh-Schrödinger (SRS) expansion, is not convergent, but is semi-convergent in the sense that a sum of several lowest-order corrections provides an excellent approximation to the exact interaction energy and the divergence is visible only in a very high order. Furthermore, low-order SRS corrections are identical to the corresponding corrections of the Jeziorski-Kolos theory (JK) which is convergent. One may also note that since SAPT does not use the asymptotic (longrange) multipole expansion of $V$ and properly antisymmetrizes the wave function, it includes all overlap and exchange effects. Although SAPT does not utilize the asymptotic expansion in powers of $1 / R$, it is seamlessly connected to such expansion, i.e., for sufficiently large $R$ the SAPT and the properly truncated asymptotic expansion interaction energies agree to an arbitrary number of digits.

The next question are the uncertainties resulting from the truncations in powers of $W$ assumed in $E_{\text {dispx }}$. For some terms, higher level of theory than we used is available and can be applied to provide estimates of uncertainties. Equation (B.2) truncates the series in $W$ at the second order. A higher-level treatment can use the dispersion energy based on the CCD description of intramonomer correlation [102] and compute

$$
\begin{equation*}
\tilde{E}_{\text {disp }}^{(2)}=E_{\text {disp }}^{(2)}[\mathrm{CCD}]+E_{\text {disp }}^{(2)}[\mathrm{S}(\mathrm{CCD})]+E_{\text {disp }}^{(2)}[\mathrm{T}(\mathrm{CCD})] . \tag{B.3}
\end{equation*}
$$

A still higher level, based on CCSD description of monomers, was developed in Ref. [104]. The argon dimer was not investigated in this work, but Ar-Ne was. For this system,
the use of the CCD level increases the value of $E_{\text {disp }}^{(2)}$ defined by Eq. (B.2) by $0.15 \%$, while the use of the CCSD level by $1.4 \%$. The analogous changes for the water dimer are $-1.7 \%$ and $0.7 \%$, respectively.

Now consider the neglected terms $\epsilon_{\text {exch-disp }}^{(n)}=E_{\text {exch-disp }}^{(n)}-E_{\text {exch-disp }}^{(n 0)}, n=2,3$. For $n=2$, one can use the values of $E_{\text {exch-disp }}^{(2)}$ computed at the CCSD level in Ref. [179]. For $\mathrm{Ar}_{2}$ near the vdW minimum, $\epsilon_{\text {exch-disp }}^{(2)}$ constitutes $11 \%$ of $E_{\text {exch-disp. }}^{(20)}$. Since the latter correction accounts for $7.6 \%$ of $E_{\text {dispx }}$, the addition of $\epsilon_{\text {exch-disp }}^{(2)}$ would have changed $E_{\text {dispx }}$ by less than $1 \%$. Such a change is negligible from the point of view of comparisons made in our work. The neglected effects of intramonomer correlation in the third order in $V, \epsilon_{\text {exch-disp }}^{(3)}$, are unknown, but since the third-order corrections are about 50 times smaller in magnitude than the second-order ones, this effect is certainly negligible. Thus, one can conclude that our analysis based on the convergence patterns in $V$ and $W$ shows that $E_{\text {dispx }}$ has uncertainties of the order of $1 \%$.

Another way to estimate uncertainies of $E_{\text {dispx }}$ is provided by comparisons of SAPT results with $\operatorname{CCSD}(\mathrm{T})$ ones. For $\mathrm{Ar}_{2}$, Fig. (2.1) and Table B. 1 here show that the two methods agree reasonably well. The relative discrepancies between SAPT and $\operatorname{CCSD}(\mathrm{T})$ interaction energies at the vdW minima are $4.9 \%, 5.4 \%, 1.7 \%$, and $5.1 \%$ for $\mathrm{Ar}_{2}$, $\mathrm{Ar}-\mathrm{HF}, \mathrm{Ar}-\mathrm{Li}^{+}$, and $\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}$, respectively (see Tables B.1, B.2, B.3, and B.4). [Many papers comparing SAPT and $\operatorname{CCSD}(\mathrm{T})$ can be found in literature, see, e.g., Refs. [98, 180, 64, 181]]. Since a part of the discrepancy between SAPT and CCSD(T) is due to the dispersion terms, we conclude that the dispersion energies have to be at least similarly accurate as the total interaction energies. In fact, they should be more accurate since the largest part of the discrepancy between SAPT and CCSD (T) interaction energy results from truncations of theory level in SAPT, so the physical components already accounted for should be more accurate than it is suggested by the percentages given above, closer to $1 \%$. Therefore, both estimates (from the convergence in $V$ and $W$ and from comparisons with $\operatorname{CCSD}(\mathrm{T}))$ of the accuracy of $E_{\text {dispx }}$ suggest that its uncertainty is of the order of $1 \%$. Thus, when subtracted from $E_{\text {int }}^{\mathrm{CCSD}(\mathrm{T})}$, it will give equally accurate values of $E_{\mathrm{dl}}$. One more source of uncertainty of the latter quantity
is, of course, the fact that $\operatorname{CCSD}(\mathrm{T})$ interaction energies are at least $1 \%$ different from the exact interaction energies. Nevertheless, even if all these uncertainties sum up to a couple percent of $E_{\mathrm{dl}}$, they are unimportant relative to the differences between $E_{\mathrm{dl}}$ and interaction energies given by DFT methods.

In our work, we have performed SAPT calculations also for distances much smaller than in any previous investigations of the convergence of SAPT. The estimates made above may not extend to such short distances. We discuss these issues in the next section.

## B. 4 SAPT at small $R$ 's

Our calculations for the argon dimer extend to a very small distance of $1.5 \AA$, where the interaction energy is more than three orders of magnitude larger than the absolute value of this quantity at the vdW minimum, while in studies of intermolecular interactions one typically includes only separations where this ratio is less than 10 . Thus, one may ask if the use of dispersion energies from SAPT is justified at such separations since SAPT, being a perturbation theory starting from isolated monomers, may diverge at very small $R$. Table B. 1 indicates that apparently there may be a problem since the SAPT energy of Eq. (B.1) is very different from CCSD(T) interaction energy for $R \leq 2.4 \AA$. However, the reason is not a divergence of SAPT but the so-called $S^{2}$ approximation, i.e., the restriction to terms which are quadratic in orbital-overlap integrals, used for all exchange corrections but $E_{\text {exch }}^{(10)}$. The performance of the $S^{2}$ approximation was recently investigated by Schäffer and Jansen [182] who computed the exchange-induction energies without this approximation and have shown that the addition of the $\delta_{\mathrm{int}}^{\mathrm{HF}}$ correction effectively cures the $S^{2}$ problem for small $R$. The quantity $\delta_{\text {int }}^{\mathrm{HF}}$ is defined as

$$
\begin{equation*}
\delta_{\mathrm{int}}^{\mathrm{HF}}=E_{\mathrm{int}}^{\mathrm{HF}}-E_{\text {elst }}^{(10)}-E_{\text {exch }}^{(10)}-E_{\text {ind,resp }}^{(20)}-E_{\text {exch-ind,resp }}^{(20)}-E_{\text {ind }}^{(30)}-E_{\text {exch-ind }}^{(30)}, \tag{B.4}
\end{equation*}
$$

where $E_{\mathrm{int}}^{\mathrm{HF}}$ is the supermolecular Hartree-Fock interaction energy. One should note, however, that the addition of $\delta_{\mathrm{int}}^{\mathrm{HF}}$ is not recommended for nonpolar systems, as emphasized in Ref. [135] where it was shown that such addition increases the SAPT error
relative to $\operatorname{CCSD}(\mathrm{T})$ interaction energies (this behaviour is also seen in Table B. 1 for $R$ 's down to $3.2 \AA$ ). This is because while the inclusion of $\delta_{\mathrm{int}}^{\mathrm{HF}}$ adds induction and exchange-induction terms beyond the third order and removes the $S^{2}$ approximation, it involves some double counting at the first three orders. Therefore, the addition of $\delta_{\text {int }}^{\mathrm{HF}}$ is not recommended for systems with small induction effects like $\mathrm{Ar}_{2}$ at separations relevant in studies of intermolecular interactions. We have therefore decided to include $\delta_{\text {int }}^{\mathrm{HF}}$ in Fig. 2.1 only at $R \leq 2.8 \AA$. This results in a reasonably good agreement between the SAPT and $\operatorname{CCSD}(\mathrm{T})$ interaction energies for all separations, in particular, at $R=1.5 \AA$ the two quantities differ by only $6 \%$. This agreement indicates that the $E_{\text {dispx }}$ contribution, a part of the SAPT interaction energy, also has to be similarly accurate. One may note that although the addition of $\delta_{\mathrm{int}}^{\mathrm{HF}}$ cannot improve over the $S^{2}$ approximation in the $E_{\text {exch-disp }}^{(i 0)}$ terms, this approximation works much better in this case than in the case of $E_{\text {exch-ind }}^{(i 0)}$ contributions [182].

The SAPT interaction energies for Ar-HF differ significantly from the CCSD(T) ones for $R \leq 3 \AA$ (see Table B.2) due to the failure of $S^{2}$ approximation, however, the addition of $\delta_{\mathrm{int}}^{\mathrm{HF}}$ at these distances makes the agreement reasonably good. This justifies the usage of $E_{\text {dispx }}$ for all separations displayed in Fig. (2.6).

For $\mathrm{Ar}-\mathrm{Li}^{+}$and for the water dimer, the agreement between $\operatorname{SAPT}$ and $\operatorname{CCSD}(\mathrm{T})$ is reasonable even at the smallest $R$ (see Tables B. 3 and B.4), therefore we have not included $\delta_{\text {int }}^{\mathrm{HF}}$ in the SAPT interaction energies (the use of $\delta_{\text {int }}^{\mathrm{HF}}$ is actually recommended for such systems, but if the third order of SAPT is used, the improvements are small).

As an aside, let us note that an alternative definition of the dispersionless energy could be

$$
\begin{equation*}
\tilde{E}_{\mathrm{dl}}=E_{\mathrm{int}}^{\mathrm{SAPT}}-E_{\mathrm{dispx}} \tag{B.5}
\end{equation*}
$$

For $\mathrm{Ar}_{2}$ at $R>3.5 \AA$, it would lead to identical conclusions as the definition used, based on $\operatorname{CCSD}(\mathrm{T})$, since the differences between SAPT and $\operatorname{CCSD}(\mathrm{T})$ interaction energies are less than $4 \%$ of $E_{\text {dispx }}$ (see Table B.1). However, for smaller $R$, as it has been discussed above, while the differences between SAPT and $\operatorname{CCSD}(\mathrm{T})$ interaction
energies remain reasonably small as a fraction of either energy ( $6 \%$ at $R=1.5 \AA$ ), they are large as a fraction of $E_{\text {dispx }}(52 \%$ at $R=1.5 \AA)$. Since this is the region where a perturbation expansion starting from isolated monomers has to decline in accuracy, the use of the definition based on $\operatorname{CCSD}(\mathrm{T})$ is the only choice.


Figure B.1: The ratio of the interaction energies from DFT to the corresponding $\operatorname{CCSD}(\mathrm{T})$ values for the Ar-proton complex.

## B. 5 Physical Damping

To estimate the physical damping, we calculated the dispersion energy $E_{\text {disp }}^{(2)}$ using the SAPT formulation based on DFT description of monomers, SAPT(DFT) [34,


Figure B.2: The ratio of the DFT interaction energies and the dispersion energies to the $\operatorname{CCSD}(\mathrm{T})$ interaction energies for the $\mathrm{Ar}-\mathrm{Li}^{+}$complex.
$35,106,37,107]$. The asymptotic expansion of this quantity, $E_{\text {disp,as }}^{(2)}$, in powers of $1 / R$ up to the term $1 / R^{12}$ was computed using the asymptotic part of the autoPES package [169] (see the appendix of that paper), based on earlier work of Refs. [183, 184, 185, 186]. The calculations were performed for the argon dimer using the aug-cc-pVTZ basis (this is the only exception of not using CBS extrapolations). Both quantities were computed from density-density response functions of the time-dependent densityfunctional theory (TD-DFT) and are seamlessly connected: for sufficiently large $R$, they agree to an arbitrary number of digits. For any finite $R$, the physical damping is


Figure B.3: The ratio $E_{\text {extra }} / E_{\text {dispx }}$ for the argon dimer calculated using MP2, MP3, and CCSD methods. The scale is same as in Fig. 2.4.
the difference between $E_{\text {disp }}^{(2)}$ and $E_{\text {disp,as }}^{(2)}$. In chapter 2, we compare this damping with the switching included in the D3BJ dispersion correction. The asymptotic expansion used in D3 is also based on TD-DFT calculations in a basis set of a similar size to aug-cc-pVTZ, which is why we used SAPT(DFT) and no CBS extrapolations.

## B. 6 "Antidamping" in D3BJ

The D3BJ dispersion energy $[16,19,24]$ is given by

$$
\begin{equation*}
\operatorname{D3BJ}(\mathrm{DFT})=-\sum_{a \in \mathrm{~A}, b \in \mathrm{~B}} \sum_{n=6,8} s_{n} \frac{C_{n}^{a b}}{R_{a b}^{n}+\left[f_{\mathrm{damp}}\left(a_{1}, a_{2}, R_{0}^{a b}\right)\right]^{n}} \tag{B.6}
\end{equation*}
$$

where $C_{n}^{a b}$ is the effective isotropic vdW dispersion constant for atom pair $a b$ and $R_{a b}$ is the separation between these atoms. The parameters $s_{n}$ are the overall scaling parameters. [D3BJ is usually computed in the supermolecular way rather than the perturbative way as in Eq. (B.6), but differences between the two approaches are usually negligible]. The Becke-Johnson (BJ) damping function [24, 19] is

$$
\begin{equation*}
f_{\text {damp }}\left(a_{1}, a_{2}, R_{0}^{a b}\right)=a_{1} R_{0}^{a b}+a_{2}, \tag{B.7}
\end{equation*}
$$

where $a_{i}, i=1,2$ are adjustable parameters and $R_{0}^{a b}=\sqrt{C_{8}^{a b} / C_{6}^{a b}}$. The parameters $s_{n}$ and $a_{i}$ are different for each DFT method and are fitted to minimize the error of $\mathrm{DFT}+\mathrm{D}$ on a set of wave function benchmarks. Table B. 5 gives values of D3BJ $\times R^{6}$ corresponding to various DFT methods for $\mathrm{Ar}_{2}$. D3(no-switching) uses neither damping nor scaling, i.e., $a_{i}=0$ and $s_{n}=1$. It can be seen in this table and in Fig. 2.2 that for most methods there is an "antidamping" effect for $R \geq 4 \AA$. To understand it, we show in Table B. 6 the components of D3BJ(revPBE) at $R=6 \AA$. Clearly, the damping coming from $f_{\text {damp }}$ is almost negligible at this $R$ (about $3 \%$ relative to the undamped dispersion energy). However, the contribution from $C_{8}$ is still large and this contribution multiplied by the factor $s_{8}=2.355$ leads to an overestimation of the magnitude of the dispersion energy by about $26 \%$ relative to the undamped value (the multiplication by such a large $s_{8}$ leads to a decrease of the $1 / R^{8}$ term from -244 $\AA^{6}$ $\mathrm{kcal} / \mathrm{mol}$ to $\left.-574 \AA^{6} \mathrm{kcal} / \mathrm{mol}\right)$.

## B. 7 Argon-proton

The argon-proton interaction energies obtained using various DFT methods and $\operatorname{CCSD}(\mathrm{T})$ are listed in Table B.7. The energies were computed using the aug-cc-pVTZ and aug-cc-pVQZ basis sets without any midbond functions (as these functions are important only for dispersion energies) and extrapolated to the CBS limit. The ratios of the DFT interaction energies to their $\operatorname{CCSD}(\mathrm{T})$ counterparts are plotted in Fig. B.1. In addition to the functionals considered in chapter 2, we included in this figure two range-separated hybrid (RSH) functionals, LRC- $\omega$ PBEh [71] and $\omega$ B97 [72]. Almost


Figure B.4: The ratios $E_{\text {extra }} / E_{\text {dispx }}, \Delta E_{\mathrm{x}} / E_{\text {dispx }}, \Delta E_{\mathrm{c}} / E_{\text {dispx }}$, and $\Delta E_{\mathrm{xc}} / E_{\text {dispx }}$ for the argon dimer using LRC- $\omega$ PBEh (Ref. [71]).
everywhere, $E_{\mathrm{int}}^{\mathrm{DFT}}$ is below $E_{\text {int }}^{\mathrm{CCSD}(\mathrm{T})}$. The errors at the vdW minimum, $R=1.4$ $\AA$, are between $0.04 \%$ and $3.6 \%$, whereas at $R=2.5 \AA$ between $2.5 \%$ and $9.2 \%$. Since there is no dispersion energy in this system, these results show that the DFT methods considered here give substantial errors in recovering the dispersionless parts of interaction energies. The two RSH methods perform better for large $R$ than other methods except PBE0 which performs equally well. This shows that the inclusion of the HF ("exact") exchange, in the RSH or regular hybrid form, does help in this region. LRC- $\omega$ PBEh and PBE0 give a ratio that is fairly constant with $R$, which is a desired


Figure B.5: The ratios $E_{\text {extra }} / E_{\text {dispx }}, \Delta E_{\mathrm{x}} / E_{\text {dispx }}, \Delta E_{\mathrm{c}} / E_{\mathrm{dispx}}$, and $\Delta E_{\mathrm{xc}} / E_{\mathrm{dispx}}$ for the argon dimer using $\omega$ B97 (Ref. [72]). behavior.

## B. 8 Argon-Lithium Cation ( $\mathrm{Ar}-\mathrm{Li}^{+}$)

Figure B. 2 is an extended version of Fig. 2.3 with the curves for the two RSH functionals added. As in Fig. B. 1 here, the LRC- $\omega$ PBEh functional behaves very similarly to PBE0 and these two functionals give smaller errors at large $R$ than the other functionals except for $\omega$ B97. All functionals considered switch the sign of the error at very short separations.

## B. $9 \quad E_{\text {extra }}$ for Wave Function Methods

In contrast to DFT approximations, the values of $E_{\text {extra }} / E_{\text {dispx }}$ are approximately constant for wave-function methods, as shown in Fig. B. 3 [MPn denotes the $n$th order of many-body perturbation theory based on the Møller-Plesset partition of the Hamiltonian]. The constant ratio provides one more argument that our values of $E_{\text {dispx }}$ are sufficiently accurate at all $R$.

## B. 10 RSH Functionals

The RSH functionals use the HF ("exact") exchange for large inter-electron separations. Since the HF exchange assures correct asymptotics of the exchange-correlation potentials, one may expect that this approximation leads to electron densities behaving better at large separations. This was recently shown not to be true for the standard values of the range-separation parameter, but densities were improved if system-specific ionization-potential adjusted values of this parameter were used [187]. Still, it is of interest to check how $E_{\text {extra }}$ from RSH functionals behaves. We have computed this quantity for two RSH functionals: LRC- $\omega$ PBEh [71] and $\omega$ B97 [72] (with the standard values of the range-separation parameter). The results are presented in Figs. B. 4 and B. 5 (as in chapter 2, the exact exchange is not included in $\Delta E_{\mathrm{x}}$ ). The two RSH functional give $E_{\text {extra }} / E_{\text {dispx }}$ which behaves smoothly, similar to the most smoothly performing functionals included in chapter 2 . In the case of $\mathrm{LRC}-\omega \mathrm{PBEh}$, the ratio is a function very similar to that for rPW86-PBE, except around vdW minimum where it is smaller than that of rPW86-PBE. The ratio for $\omega \mathrm{B} 97$ is different from all other functionals in that it flattens after reaching 1 at $R$ of about $3.5 \AA$, i.e., it has the behavior of a functional which recovers the dispersion energy for right reasons. However, the wild behavior of all components of $E_{\text {extra }} / E_{\text {dispx }}$, even $\Delta E_{\mathrm{c}} / E_{\text {dispx }}$, and the very large contribution of the non-xc terms in this region do not allow one to conclude that $\omega \mathrm{B} 97$ genuinely reproduces dispersion interactions for $1.5 \leq R \leq 3.5 \AA$. The components behave more smoothly in the case of LRC- $\omega$ PBEh, but this behavior is similar to those of DFT methods included in Fig. 2.5. Thus, apparently the RSH functionals
with the standard values of the range-separation parameter do not offer improvements over standard pure or hybrid functionals.

## B. 11 Dependence of non-xc interaction energy on density

In chapter 2, we used an ad absurdum argument to demonstrate that $E_{\text {extra }}$ cannot be considered to represent dispersion energy in the vdW well region. Let us repeat this argument in greater detail. For the SCAN functional at $R=5 \AA, E_{\text {extra }}$ is about $0.4 E_{\text {dispx }}$ and $\Delta E_{\mathrm{c}}$ is close to zero. Since we assume that $E_{\text {extra }}$ is the dispersion energy, the only remaining component of SCAN which may give this type contribution is $\Delta E_{\mathrm{x}}$. However, $\Delta E_{\mathrm{x}}$ is positive and equal to about $-E_{\text {dispx }}$. Thus, it cannot represent dispersion [of course, one may also say that $\Delta E_{\mathrm{x}}$ consists of two components: $E_{\text {dispx }}$ and $-2 E_{\text {dispx }}$, but this is hardly a convincing explanation]. Thus, the only source of $E_{\text {extra }}$ is the non-xc part of $E_{\mathrm{int}}^{\mathrm{DFT}}$, but since non-xc components cannot describe correlation effects, we conclude that $E_{\text {extra }}$ cannot be considered to be dispersion energy. The reason that the non-xc contributions cannot describe correlation effects is a follows. Such contributions include integrals of one-electron operators: the kinetic energy operator and the external potential operator, i.e., electron-nuclei interaction, by definition unrelated to electron-electron interactions. They also include a two-electron component, the Hartree term which describes electron-electron interactions, but only in a mean-field approximation which by definition does not include correlation effects.

Although the equation

$$
E_{\mathrm{int}}^{\mathrm{DFT}}=\Delta E_{\mathrm{non}-\mathrm{xc}}+\Delta E_{\mathrm{x}}+\Delta E_{\mathrm{c}}=E_{\mathrm{dl}}+E_{\mathrm{extra}}
$$

does not allow any partition of DFT components into dispersionless part and the remainder, some approximate classification can be done on physical grounds. As discussed in chapter $2, \Delta E_{\mathrm{c}}$ appears to be related to $E_{\text {extra }}$. As discussed above, $\Delta E_{\text {non-xc }}$ should contribute only to $E_{\mathrm{dl}}$. Furthermore, all the terms included in $\Delta E_{\text {non-xc }}$ are also a part of $E_{\mathrm{int}}^{\mathrm{HF}}$. The latter quantity includes in addition the exchange energy. As seen in Fig. 2.4, $E_{\mathrm{int}}^{\mathrm{HF}}$ is a reasonably good approximation of $E_{\mathrm{dl}}$. Thus, we can evaluate DFT methods by checking how close is $\Delta E_{\mathrm{non}-\mathrm{xc}}$ to its HF counterpart. Such
results are shown in Fig. B. 6 for SCAN, PBE, and B3LYP functionals. Perhaps surprisingly, the curves for each regular DFT method (DFT@KS) are very similar to those in Fig. 2.1, except that they are shifted to the right by about $0.5 \AA$. The SCAN and PBE curves show significant attractive interactions, which is, of course, physically not allowed: the attractive interactions in $\mathrm{Ar}_{2}$ come almost exclusively from the dispersion component and $\Delta E_{\text {non-xc }}$ has no physical mechanisms to describe dispersion interactions. If $\Delta E_{\text {non-xc }}$ is computed with HF densities, it becomes repulsive, as expected on physical grounds since such a contribution is by definition purely dispersionless. In contrast to SCAN and PBE, the B3LYP@KS curve, however, is repulsive and close to the corresponding B3LYP@HF curve. Thus, from this point of view, B3LYP is a more sound functional than SCAN or PBE. The $\Delta E_{\text {non-xc }}$ components of SCAN and PBE functionals exhibit what is sometimes called "density-driven error". Thus, more sound version of these functionals should be constructed by requiring that the electron density is closer to the HF density than it is the case for the current version. The SCAN@HF and PBE@HF curves are, of course, identical since all non-xc terms are the same in both methods. These terms are also the same for B3LYP@HF, but this method includes one additional term in the non-xc part, the exact exchange, leading to the differences seen in Fig. B.6. This figure also shows $E_{\mathrm{int}}^{\mathrm{HF}}$ which is below both DFT@HF curves. The reason is that the negative exact exchange contribution is either not included in the latter curves or only a fraction of it is included. The $E_{\mathrm{int}}^{\mathrm{HF}}$ curve is very close to the $E_{\mathrm{dl}}$ curve, also shown in Fig. B.6. Thus, either curve shows what one would expect a semilocal DFT to recover for right reasons.

To get more insight into the issue of density-driven error, we show in Figs. B.7, B.8, and B. 9 the values of the remaining DFT contributions computed with HF versus KS orbitals and densities. For SCAN, $\Delta E_{\mathrm{c}}$ is virtually the same in the KS and HF cases. The same is true for $E_{\text {extra }}$. On the other hand, the KS vs. HF differences are very large for $\Delta E_{\mathrm{x}}$, even the sign is different in some ranges of $R$. The @HF curve is physically more sound than the @KS one, as it does not have a region of positive values of $\Delta E_{\mathrm{x}}$. The differences in $\Delta E_{\mathrm{x}}$ partly cancel with the differences in
the non-xc contribution and the total interaction energies $E_{\mathrm{int}}^{\mathrm{DFT}} @ \mathrm{KS}$ and @HF shown in Fig. B. 10 are closer to each other than are the non-xc energies in Fig. B. 6 (several times closer near the minimum of each curve). The results for the PBE functional are essentially identical to those for SCAN. The SCAN and PBE @HF interaction energies are attractive for $R$ larger than about 3.5-3.7 $\AA$ and the attractive interaction comes from the xc term. In the case of SCAN@HF, the value at $R=3.76 \AA$ is about 0.4 $\mathrm{kcal} / \mathrm{mol}$ below $E_{\mathrm{dl}}$, the energy that it should recover. Thus, this $0.4 \mathrm{kcal} / \mathrm{mol}$ lower value should be considered a failing of SCAN@HF rather than a good performance. The reason for this failing is probably a functional-driven error. Thus, our previous suggestion for improvement of densities is insufficient to make SCAN and PBE give physically sound (i.e., positive) interaction energies at these distances and changes of the exchange-correlation functional are needed to make the $\Delta E_{\mathrm{xc}}$ contribution less negative with HF densities.

The B3LYP results are also similar to the SCAN results for $\Delta E_{\mathrm{c}}$ and $E_{\text {extra }}$ in terms of @KS vs. @HF closeness. However, the $\Delta E_{\mathrm{x}} @ K S$ vs. @HF values are in this case also quite close to each other for all $R$ smaller than $4.1 \AA$. Overall, the behavior of B3LYP is more acceptable on physical grounds than that of SCAN and PBE. On the other hand, the undulatory dependence of the B3LYP components on $R$ does not appear to be physical.

## B. 12 Detailed results for Figs. 2.3, 2.4, 2.5, and 2.6.

The interaction energies for $\mathrm{Ar}-\mathrm{Li}^{+}$are listed in Table B.3. The ratios of DFT interaction energies $E_{\mathrm{int}}^{\mathrm{DFT}}$ and $E_{\text {dispx }}$ to $E_{\mathrm{int}}^{\mathrm{CCSD}(\mathrm{T})}$ are listed in Table B.8. These ratios are plotted in Fig. 2.3.

Table B. 9 gives the ratios of the apparent dispersion energy from DFT methods, $E_{\text {extra }}$, to $E_{\text {dispx }}$ for the argon dimer. These are plotted in Fig. 2.4. Tables B. 10 and B. 11 give the exchange, $\Delta E_{\mathrm{x}}$, and correlation, $\Delta E_{\mathrm{c}}$, contributions to the interaction energy. Figure 2.5 shows the ratio of these contributions to $E_{\text {dispx }}$.

Table B. 2 gives CBS extrapolated interaction energies for Ar-HF. The contributions of the exchange and correlation energy to these interaction energies are listed in Tables B. 12 and B.13. The ratios of $E_{\text {extra }}$ to $E_{\text {dispx }}$ listed in Table B. 14 are plotted in Fig. 2.6.

The interaction energies, exchange contributions, and correlation contributions for the water dimer are listed in Tables B.4, B.15, and B.16, respectively. The ratios $E_{\text {extra }} / E_{\text {dispx }}$ plotted in Fig. 2.6 are given in Table B.17.

## B. 13 SCAN at small $R$ 's

As seen in Figs. 2.4 and 2.5, the SCAN functional [30] exhibits one of the best behaviors among the investigated functionals in that after reaching the value of 1 at $R=\sim 2.2 \AA, E_{\text {extra }} / E_{\text {dispx }}$ is reasonably flat for smaller $R$, getting up to 1.017 at 1.5 $\AA$, the smallest $R$ included. However, this curve would flatten even better had we used a more accurate benchmark. The reason is that SCAN was fitted to accurate $\operatorname{Ar}_{2} \operatorname{CCSD}(\mathrm{~T})$ interaction energies from Ref. [84]. The separation $R=1.5 \AA$ is not included in that work, but at $1.8 \AA$ the values relative to our benchmarks and to Ref. [84] benchmarks are 1.09 and 1.02 , respectively. At $2.0 \AA$, one can additionally compare with even more accurate benchmarks of Ref. [188] and the corresponding ratios are $1.03,0.98$, and 0.97 . This shows that in this region our ratios may have uncertainties up to 0.07 . However, this does not change any conclusions of our work since, as seen in Table B.9, those functionals that cross 1 for $R>2.0 \AA$ have the value of $E_{\text {extra }} / E_{\text {dispx }}$ at $1.5 \AA$ between 0.99 and 1.77 , with the average value of 1.30 . Thus, the typical ratios are much larger than the differences resulting from uncertainties of the benchmarks.

For Ar-HF, the ratio $E_{\text {extra }} / E_{\text {dispx }}$ from SCAN also flattens quite well: it crosses 1 at about $3.7 \AA$, goes up to 1.11 at $3.0 \AA$, and then down to 1.06 at the shortest $R$ of $1.8 \AA$, cf. Table B.14. For the water dimer, the crossing is at about $3.3 \AA$, whereas the value at the shortest distance of $2.5 \AA$ is 1.15 , cf. Table B.17. Note that only SCAN, PBE, PBE0, and LDA functionals reach 1 in the range of $R$ 's shown in Table B.17.


Figure B.6: The non-xc part of the $\mathrm{Ar}_{2}$ interaction energy (in kcal/mol), i.e., the sum of the electron-nuclei interaction energy (external potential energy), the Hartree term, and of the nuclear repulsion $Z^{2} / R$. The curves computed with KS orbitals and densities are components from a standard sumpermolecular DFT calculation. The HF ones are computed using the same density functional expressions but the orbitals and densities are taken from an HF calculations for $\mathrm{Ar}_{2}$.


Figure B.7: Ratios of SCAN $\mathrm{Ar}_{2}$ interaction energy components to $E_{\text {dispx }}$ computed with KS and HF densities.


Figure B.8: Ratios of $\mathrm{PBE} \mathrm{Ar}_{2}$ interaction energy components to $E_{\text {dispx }}$ computed with KS and HF densities.


Figure B.9: Ratios of B3LYP $\mathrm{Ar}_{2}$ interaction energy components to $E_{\text {dispx }}$ computed with KS and HF densities.


Figure B.10: Total interaction energy from SCAN, PBE, and B3LYP functionals computed with KS versus HF orbitals and densities.

Table B.2: The interaction energies (kcal/mol) of $\mathrm{Ar}-\mathrm{HF}$ in the CBS limit. The midbond functions ( 3 s 3 p 2 d 2 f 1 g ) were

| $R$ | B3LYP | SCAN | TPSS | PBE0 | PBE | rPW86-PBE | PW91 | LDA | $E_{\text {dispx }}$ | SAPT | $\delta_{\text {int }}^{\mathrm{HF}}$ | SAPT $+\delta_{\text {int }}^{\text {HF }}$ | CCSD(T) | $E_{\text {dl }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1.80 | 93.6139 | 90.7037 | 91.8335 | 90.7823 | 90.4809 | 93.1504 | 89.7418 | 78.8848 | -16.6176 | -1.0731 | 83.1233 | 82.0502 | 91.6568 | 108.2745 |
| 2.00 | 45.6150 | 43.1437 | 44.7715 | 43.8005 | 43.9975 | 45.2845 | 43.3852 | 35.4210 | -10.5500 | 23.0121 | 17.1363 | 40.1484 | 43.6466 | 54.1966 |
| 2.50 | 6.8568 | 5.3933 | 6.9870 | 6.2555 | 6.3835 | 6.4918 | 6.0592 | 2.7518 | -3.5418 | 5.5563 | -0.1958 | 5.3605 | 5.6797 | 9.2215 |
| 3.00 | 0.9094 | 0.1338 | 0.9501 | 0.5869 | 0.5451 | 0.6355 | 0.3339 | -0.7566 | -1.2350 | 0.2867 | -0.0795 | 0.2071 | 0.2695 | 1.5046 |
| 3.40 | 0.1978 | -0.2573 | 0.0766 | -0.0521 | -0.1209 | 0.0077 | -0.3137 | -0.6194 | -0.5553 | -0.2235 | -0.0162 | -0.2397 | -0.2128 | 0.3425 |
| 3.50 | 0.1454 | -0.2518 | 0.0036 | -0.0879 | -0.1556 | -0.0267 | -0.3451 | -0.5391 | -0.4583 | -0.2349 | -0.0108 | -0.2456 | -0.2228 | 0.2355 |
| 3.60 | 0.1120 | -0.2336 | -0.0425 | -0.1045 | -0.1694 | -0.0434 | -0.3547 | -0.4614 | -0.3795 | -0.2303 | -0.0072 | -0.2375 | -0.2181 | 0.1614 |
| 4.00 | 0.0586 | -0.1340 | -0.0885 | -0.0894 | -0.1361 | -0.0411 | -0.2928 | -0.2231 | -0.1854 | -0.1595 | -0.0014 | -0.1609 | -0.1521 | 0.0334 |
| 4.50 | 0.0341 | -0.0534 | -0.0545 | -0.0430 | -0.0673 | -0.0173 | -0.1690 | -0.0799 | -0.0829 | -0.0832 | -0.0002 | -0.0834 | -0.0802 | 0.0027 |
| 5.00 | 0.0176 | -0.0199 | -0.0240 | -0.0170 | -0.0275 | -0.0059 | -0.0773 | -0.0273 | -0.0407 | -0.0431 | 0.0000 | -0.0432 | -0.0417 | -0.0010 |
| 6.00 | 0.0033 | -0.0026 | -0.0034 | -0.0024 | -0.0038 | -0.0007 | -0.0080 | -0.0033 | -0.0124 | -0.0135 | 0.0000 | -0.0135 | -0.0129 | -0.0005 |
| 7.00 | 0.0004 | -0.0005 | -0.0006 | -0.0005 | -0.0007 | -0.0003 | -0.0007 | -0.0006 | -0.0047 | -0.0051 | 0.0000 | -0.0051 | -0.0049 | -0.0002 |
| 8.00 | 0.0000 | -0.0002 | -0.0002 | -0.0002 | -0.0002 | -0.0002 | -0.0002 | -0.0002 | -0.0020 | -0.0022 | 0.0000 | -0.0022 | -0.0021 | -0.0001 |
| 9.00 | -0.0001 | -0.0001 | -0.0001 | -0.0001 | -0.0001 | -0.0001 | -0.0001 | -0.0001 | -0.0010 | -0.0011 | 0.0000 | -0.0011 | -0.0010 | -0.0001 |
| 10.00 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | -0.0005 | -0.0006 | 0.0000 | -0.0006 | -0.0005 | 0.0000 |


| $R$ | basis sets aug-cc-pVTZ and aug-cc-pVQZ. These data are used to construct Table B.8. |  | B3LY | TPSS | PBE0 | PBE | PW91 | rPW86-PBE | LDA | $E_{\text {dispx }}$ | SAPT | CCSD(T) | $E_{\text {dl }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1.80 | 8.9836 | 10.6281 | 8.9611 | 9.1914 | 8.8324 | 8.8541 | 8.3273 | 9.3353 | 5.7989 | -1.84012 | 11.3546 | 10.0842 | 1.9243 |
| 2.00 | -2.8812 | -1.8143 | -3.0343 | -2.8654 | -3.0310 | -3.1622 | -3.6086 | -2.8225 | -5.0960 | -0.99220 | -2.0830 | -2.0849 | -1.0927 |
| 2.40 | -7.1959 | -6.8464 | -7.4737 | -7.4563 | -7.3477 | -7.6924 | -8.0585 | -7.5096 | -8.3855 | -0.30907 | -6.8368 | -6.7249 | -6.4158 |
| 2.80 | -5.3079 | -5.1937 | -5.5502 | -5.6015 | -5.4291 | -5.7845 | -6.0701 | -5.6765 | -5.9908 | -0.10770 | -4.8868 | -5.0142 | -4.9065 |
| 3.20 | -3.3267 | -3.2550 | -3.4799 | -3.5409 | -3.4018 | -3.6654 | -3.8455 | -3.6030 | -3.7096 | -0.04290 | -3.0205 | -3.1535 | -3.1106 |
| 3.50 | -2.3065 | -2.2502 | -2.4041 | -2.4569 | -2.3523 | -2.5408 | -2.6464 | -2.5031 | -2.548 | -0.02304 | -2.0958 | -2.1960 | -2.1730 |
| 4.00 | -1.2955 | -1.2649 | -1.3388 | -1.3676 | -1.3111 | -1.4099 | -1.4391 | -1.3957 | -1.4077 | -0.00924 | -1.1890 | -1.2390 | -1.2297 |
| 5.00 | -0.4938 | -0.4842 | -0.5057 | -0.5105 | -0.4946 | -0.5239 | -0.5226 | -0.5225 | -0.5245 | -0.00229 | -0.4594 | -0.4742 | -0.4719 |
| 6.00 | -0.2300 | -0.2255 | -0.2352 | -0.2366 | -0.2301 | -0.2418 | -0.2409 | -0.2417 | -0.2428 | -0.00073 | -0.2138 | -0.2216 | -0.2209 |
| 7.00 | -0.1213 | -0.1192 | -0.1240 | -0.1245 | -0.1214 | -0.1271 | -0.1263 | -0.1273 | -0.1277 | -0.00028 | -0.1125 | -0.1172 | -0.1169 |
| 8.00 | -0.0698 | -0.0695 | -0.0715 | -0.0715 | -0.0699 | -0.0731 | -0.0725 | -0.0736 | -0.0734 | -0.00012 | -0.0646 | -0.0676 | -0.0674 |
| 9.00 | -0.0432 | -0.0434 | -0.0444 | -0.0442 | -0.0433 | -0.0452 | -0.0447 | -0.0458 | -0.0455 | -0.00006 | -0.0396 | -0.0420 | -0.0420 |
| 10.00 | -0.0284 | -0.0285 | -0.0292 | -0.0290 | -0.0285 | -0.0297 | $-0.0293$ | -0.0301 | -0.0300 | -0.00003 | -0.0255 | -0.0276 | -0.0276 |

Table B.4: Water dimer interaction energies ( $\mathrm{kcal} / \mathrm{mol}$ ) from various methods in the CBS limit. The basis sets utilized are aug-cc-pVTZ and aug-cc-pVQZ with midbond functions (3s3p2d2f). These data are used to construct
Table B. 17.

| $R$ | B3LYP | SCAN | TPSS | PBE0 | PBE | rPW86-PBE | LDA | $E_{\text {dispx }}$ | SAPT | CCSD $(T)$ | $E_{\text {dl }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2.50 | -0.1259 | -1.7595 | -0.3211 | -1.1854 | -0.9864 | -0.4188 | -6.5035 | -5.9498 | -0.0436 | -0.8442 | 5.1056 |
| 3.00 | -4.4296 | -5.1651 | -4.3483 | -4.8376 | -4.8571 | -4.7938 | -7.3009 | -2.0927 | -4.6938 | -4.9435 | -2.8508 |
| 3.50 | -3.0224 | -3.3734 | -3.0158 | -3.2796 | -3.3243 | -3.2186 | -4.2508 | -0.7734 | -3.4245 | -3.4042 | -2.6308 |
| 4.00 | -1.8047 | -1.9787 | -1.8941 | -1.9914 | -2.0117 | -1.8905 | -2.3266 | -0.3072 | -2.1120 | -2.0681 | -1.7609 |
| 4.50 | -1.1263 | -1.2080 | -1.2035 | -1.2415 | -1.2388 | -1.1563 | -1.3486 | -0.1340 | -1.3249 | -1.2903 | -1.1563 |
| 5.00 | -0.7554 | -0.7897 | -0.7913 | -0.8161 | -0.8011 | -0.7574 | -0.8508 | -0.0639 | -0.8757 | -0.8508 | -0.7868 |
| 5.50 | -0.5374 | -0.5480 | -0.5448 | -0.5663 | -0.5476 | -0.5270 | -0.5788 | -0.0332 | -0.6093 | -0.5909 | -0.5578 |
| 6.00 | -0.3982 | -0.3982 | -0.3928 | -0.4114 | -0.3936 | -0.3841 | -0.4166 | -0.0185 | -0.4422 | -0.4283 | -0.4098 |
| 6.50 | -0.3037 | -0.2997 | -0.2943 | -0.3098 | -0.2944 | -0.2898 | -0.3123 | -0.0109 | -0.3320 | -0.3212 | -0.3103 |
| 7.00 | -0.2368 | -0.2319 | -0.2271 | -0.2399 | -0.2270 | -0.2245 | -0.2412 | -0.0067 | -0.2560 | -0.2475 | -0.2408 |
| 7.50 | -0.1882 | -0.1835 | -0.1794 | -0.1898 | -0.1792 | -0.1778 | -0.1906 | -0.0043 | -0.2020 | -0.1951 | -0.1908 |
| 8.00 | -0.1520 | -0.1478 | -0.1444 | -0.1530 | -0.1442 | -0.1433 | -0.1535 | -0.0029 | -0.1623 | -0.1567 | -0.1538 |
| 8.50 | -0.1245 | -0.1210 | -0.1181 | -0.1252 | -0.1179 | -0.1172 | -0.1255 | -0.0019 | -0.1325 | -0.1278 | -0.1259 |
| 9.00 | -0.1033 | -0.1003 | -0.0979 | -0.1039 | -0.0977 | -0.0971 | -0.1041 | -0.0014 | -0.1096 | -0.1058 | -0.1044 |
| 10.00 | -0.0734 | -0.0712 | -0.0695 | -0.0738 | -0.0693 | -0.0690 | -0.0739 | -0.0007 | -0.0776 | -0.0749 | -0.0742 |

Table B.5: The dispersion correction multiplied by $R^{6}\left(\AA^{6} \mathrm{kcal} / \mathrm{mol}\right)$ for the argon dimer corresponding to various DFT functionals. D3(no-switching) is obtained by setting $a_{1}=a_{2}=0$ and $s_{6}=s_{8}=1$. The dispersion energy from the asymptotic expansion $E_{\text {disp,as }}$, $\operatorname{SAPT}(\mathrm{DFT})$ term $E_{\text {disp }}^{(2)}$, and the sum $E_{\text {disp }}^{(2)}+E_{\text {exch-disp }}^{(2)}$ is also listed. These data are plotted in Figs. 2.2 and B.2.

| $R$ | D3BJ(B3LYP) | D3BJ(TPSS) | D3BJ(PBE) | D3BJ(rPW86-PBE) | D3BJ(revPBE) | D3(no-switching) | $E_{\text {disp,as }}^{(2)}$ | $E_{\text {disp }}^{(2)}$ | $E_{\text {disp }}^{(2)}+E_{\text {exch-disp }}^{(2)}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1.80 | -35.1336 | -23.3947 | -18.2506 | -18.1226 | -46.8925 | -3634.7170 | -8451.2051 | -959.9901 | -734.4276 |
| 2.00 | -65.5546 | -43.7550 | -34.0441 | -33.8899 | -87.4027 | -3113.3689 | -5629.2311 | -1148.5780 | -904.0558 |
| 2.40 | -188.1684 | -127.0349 | -97.8515 | -98.4007 | -249.4446 | -2434.2444 | -3150.3087 | -1381.7046 | -1157.5271 |
| 2.80 | -429.8938 | -298.6532 | -225.8133 | -231.8400 | -560.9712 | -2024.7537 | -2184.6563 | -1455.9841 | -1295.6572 |
| 3.20 | -781.5818 | -574.0162 | -423.0281 | -449.0563 | -988.5546 | -1758.9786 | -1728.4102 | -1435.9632 | -1342.3525 |
| 3.50 | -1051.7995 | -818.0945 | -591.9335 | -647.3145 | -1289.4380 | -1616.5231 | -1530.7961 | -1387.7360 | -1331.9884 |
| 3.65 | -1167.0738 | -935.8670 | -672.5505 | -746.0287 | -1407.9254 | -1558.0986 | -1458.2640 | -1359.2328 | -1317.4727 |
| 3.76 | -1239.1004 | -1015.6294 | -727.3139 | -814.5178 | -1477.8739 | -1519.6245 | -1413.0482 | -1337.4758 | -1304.0924 |
| 3.85 | -1289.5193 | -1075.3146 | -768.6803 | -866.8932 | -1524.3842 | -1490.5676 | -1380.1979 | -1319.3539 | -1291.7738 |
| 4.00 | -1356.5933 | -1161.8175 | -829.8660 | -945.1687 | -1581.8012 | -1446.4270 | -1332.3692 | -1289.0590 | -1269.3001 |
| 4.25 | -1426.1650 | -1268.0802 | -909.7547 | -1047.5751 | -1630.5843 | -1382.9793 | -1267.8402 | -1242.4250 | -1231.4309 |
| 4.50 | -1454.8252 | -1331.2276 | -964.7075 | -1116.1303 | -1637.4600 | -1329.8096 | -1217.4230 | -1201.5335 | -1195.6194 |
| 5.00 | -1442.1934 | -1368.4610 | -1020.9776 | -1177.7570 | -1586.9128 | -1246.3939 | -1144.6500 | -1135.2930 | -1133.7492 |
| 6.00 | -1334.4495 | -1304.5869 | -1034.3594 | -1165.8135 | -1430.1856 | -1137.7340 | -1060.5440 | -1053.4248 | -1053.3497 |
| 7.00 | -1233.6303 | -1218.8651 | -1013.6292 | -1116.2472 | -1302.2883 | -1072.2155 | -1015.1621 | -1008.6378 | -1008.6366 |
| 8.00 | -1159.7099 | -1149.8400 | -991.9221 | -1072.5261 | -1210.7043 | -1029.6915 | -987.6799 | -981.6035 | -981.6035 |
| 9.00 | -1103.8330 | -1100.4982 | -973.7742 | -1037.1362 | -1147.1860 | -1000.5372 | -969.6851 | -963.6885 | -963.6885 |
| 10.00 | -1066.7662 | -1060.4911 | -960.0896 | -1010.2904 | -1098.1417 | -979.6832 | -957.2193 | -951.3900 | -951.3900 |

Table B.6: The antidamping effect for D3BJ(revPBE) at $R=6 \AA$ for the argon dimer. The parameters are $C_{6}=64.646200, C_{8}=2304.037662, s_{6}=1.00$, $s_{8}=2.3550, a_{1}=0.5238$, and $a_{2}=3.5016$ in atomic units.

|  | $R^{6} \times$ Dispersion Energy $\left(\AA^{6} \mathrm{kcal} / \mathrm{mol}\right)$ |
| :---: | :---: |
| $-C_{6} / R^{6}$ | -890.7797 |
| $-C_{8} / R^{8}$ | -246.9544 |
| $-C_{6} / R^{6}-C_{8} / R^{8}$ | -1137.7341 |
| $-C_{6} /\left(R^{6}+f_{\text {damp }}^{6}\right)$ | -856.5795 |
| $-C_{8} /\left(R^{8}+f_{\text {damp }}^{8}\right)$ | -243.6297 |
| $-C_{6} /\left(R^{6}+f_{\text {damp }}^{6}\right)-C_{8} /\left(R^{8}+f_{\text {damp }}^{8}\right)$ | -1100.2092 |
| $-s_{6} C_{6} /\left(R^{6}+f_{\text {damp }}^{6}\right)$ | -856.5795 |
| $-s_{8} C_{8} /\left(R^{8}+f_{\text {damp }}^{8}\right)$ | -573.7480 |
| $-s_{6} C_{6} /\left(R^{6}+f_{\text {damp }}^{6}\right)-s_{8} C_{8} /\left(R^{8}+f_{\text {damp }}^{8}\right)$ | -1430.3275 |

Table B.8: The ratio $E_{\text {int }}^{\mathrm{DFT}} / E_{\text {int }}^{\mathrm{CCSD}(\mathrm{T})}$ and $E_{\text {dispx }} / E_{\text {int }}^{\mathrm{CCSD}(\mathrm{T})}$ for $\mathrm{Ar}-\mathrm{Li}^{+}$. All energies were computed in the CBS limit with (3s3p2d2f1g) midbond functions added to aug-cc-pVTZ and aug-cc-pVQZ basis sets. These data are plotted

Table B.9: The ratio $E_{\text {extra }} / E_{\text {dispx }}$ for the argon dimer. These data are plotted in Fig. 2.4.

| $R$ | LRC- $\omega$ PBEh | $\omega \mathrm{B} 97$ | B3LYP | SCAN | TPSS | PBE0 | PBE | rPW86-PBE | PW91 | revPBE-PW92 | LDA | dlDF | HF |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1.50 | 1.1651 | 0.9946 | 1.0747 | 1.1677 | 1.2639 | 1.2280 | 1.4084 | 1.2498 | 1.4084 | 0.9631 | 1.7655 | 0.3533 | 0.2325 |
| 1.80 | 1.1155 | 0.9676 | 0.9617 | 1.0931 | 1.1139 | 1.1526 | 1.2566 | 1.0698 | 1.2714 | 0.6964 | 1.7189 | 0.1672 | 0.2595 |
| 2.00 | 1.0494 | 0.9339 | 0.8751 | 1.0313 | 1.0204 | 1.0834 | 1.1443 | 0.9609 | 1.1729 | 0.4818 | 1.7134 | 0.0166 | 0.2328 |
| 2.40 | 0.8777 | 0.9831 | 0.7055 | 0.9506 | 0.8283 | 0.9241 | 0.9225 | 0.8071 | 0.9799 | 0.0826 | 1.7018 | -0.1673 | 0.1740 |
| 2.80 | 0.6908 | 1.0952 | 0.5517 | 0.9337 | 0.6018 | 0.7750 | 0.7584 | 0.7119 | 0.8441 | -0.1795 | 1.6848 | -0.1756 | 0.1260 |
| 3.20 | 0.5251 | 1.0900 | 0.3954 | 0.9167 | 0.4145 | 0.6646 | 0.6817 | 0.6261 | 0.8154 | -0.2346 | 1.6283 | -0.0755 | 0.0902 |
| 3.50 | 0.4319 | 0.9162 | 0.2590 | 0.8819 | 0.3747 | 0.6145 | 0.6779 | 0.5467 | 0.8910 | -0.1421 | 1.5374 | 0.0011 | 0.0717 |
| 3.65 | 0.3936 | 0.7765 | 0.1817 | 0.8537 | 0.3871 | 0.5971 | 0.6858 | 0.5006 | 0.9607 | -0.0654 | 1.4731 | 0.0261 | 0.0646 |
| 3.76 | 0.3679 | 0.6607 | 0.1215 | 0.8302 | 0.4048 | 0.5859 | 0.6928 | 0.4647 | 1.0231 | -0.0013 | 1.4181 | 0.0383 | 0.0601 |
| 3.85 | 0.3480 | 0.5631 | 0.0709 | 0.8102 | 0.4223 | 0.5770 | 0.6982 | 0.4345 | 1.0797 | 0.0541 | 1.3688 | 0.0453 | 0.0568 |
| 4.00 | 0.3163 | 0.4049 | -0.0144 | 0.7694 | 0.4533 | 0.5616 | 0.7046 | 0.3835 | 1.1812 | 0.1489 | 1.2790 | 0.0538 | 0.0524 |
| 4.50 | 0.2119 | 0.0375 | -0.2602 | 0.6107 | 0.5160 | 0.4872 | 0.6764 | 0.2262 | 1.4875 | 0.4268 | 0.9416 | 0.0931 | 0.0419 |
| 5.00 | 0.1161 | -0.0745 | -0.3686 | 0.4217 | 0.4689 | 0.3699 | 0.5559 | 0.1146 | 1.5183 | 0.5416 | 0.6155 | 0.1569 | 0.0312 |
| 6.00 | 0.0387 | -0.0204 | -0.2532 | 0.1614 | 0.2220 | 0.1527 | 0.2466 | 0.0308 | 0.6401 | 0.3372 | 0.2168 | 0.1564 | 0.0290 |
| 7.00 | 0.0447 | 0.0331 | -0.0943 | 0.0767 | 0.0951 | 0.0741 | 0.1033 | 0.0309 | 0.1273 | 0.1400 | 0.0903 | 0.0860 | 0.0439 |
| 8.00 | 0.0463 | 0.0436 | -0.0100 | 0.0508 | 0.0540 | 0.0497 | 0.0568 | 0.0385 | 0.0503 | 0.0676 | 0.0533 | 0.0559 | 0.0449 |
| 9.00 | 0.0293 | 0.0270 | 0.0094 | 0.0300 | 0.0304 | 0.0296 | 0.0308 | 0.0275 | 0.0280 | 0.0356 | 0.0313 | 0.0304 | 0.0285 |
| 10.00 | 0.0332 | 0.0331 | 0.0250 | 0.0314 | 0.0304 | 0.0309 | 0.0309 | 0.0301 | 0.0307 | 0.0262 | 0.0306 | 0.0309 | 0.0320 |


| Table B.10: Exchange energy contributions $\Delta E_{\mathrm{x}}(\mathrm{kcal} / \mathrm{mol})$ in the interaction energy of the argon dimer in the CBS limit. These data are used in Fig. 2.5. |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $R$ | LRC- $\omega$ PBEh | $\omega \mathrm{B} 97$ | B3LYP | SCAN | TPSS | PBE0 | PBE | RPW86PBE | PW91 | revPBE-PW92 | LDA |
| 1.50 | -151.0601 | -184.4228 | -145.2499 | -157.7725 | -170.8250 | -135.8978 | -176.4667 | -168.2746 | -177.8487 | -170.9996 | -216.9670 |
| 1.80 | -91.5284 | -107.8890 | -92.9395 | -106.4426 | -109.3381 | -85.1712 | -111.4299 | -107.3402 | -112.6483 | -109.3425 | -138.3774 |
| 2.00 | -59.5784 | -69.6170 | -61.6607 | -72.0564 | -73.1282 | -55.9407 | -73.7076 | -72.0307 | -74.7006 | -73.0283 | -93.1199 |
| 2.40 | -22.0224 | -24.2702 | -23.4273 | -28.2954 | -27.8849 | -21.0343 | -28.1514 | -28.3178 | -28.6328 | -28.9208 | -36.9260 |
| 2.80 | -7.0991 | -6.0499 | -7.5138 | -9.2601 | -9.0326 | -6.9537 | -9.5234 | -9.5767 | -9.7497 | -10.6443 | -12.5151 |
| 3.20 | -2.1094 | -0.3713 | -1.9377 | -2.3440 | -2.8408 | -2.1262 | -2.9802 | -2.7544 | -3.1892 | -3.9001 | -3.4213 |
| 3.50 | -0.8241 | 0.5468 | -0.5353 | -0.5728 | -1.2772 | -0.8479 | -1.1870 | -0.9411 | -1.4304 | -1.8513 | -0.9678 |
| 3.65 | -0.5074 | 0.5677 | -0.2292 | -0.1820 | -0.8560 | -0.5267 | -0.7260 | -0.5150 | -0.9731 | -1.2689 | -0.3989 |
| 3.76 | -0.3519 | 0.5022 | -0.0975 | -0.0215 | -0.6295 | -0.3665 | -0.4939 | -0.3173 | -0.7342 | -0.9557 | -0.1426 |
| 3.85 | -0.2586 | 0.4256 | -0.0293 | 0.0680 | -0.4828 | -0.2690 | -0.3519 | -0.2053 | -0.5808 | -0.7531 | -0.0038 |
| 4.00 | -0.1509 | 0.2896 | 0.0313 | 0.1497 | -0.2979 | -0.1548 | -0.1853 | -0.0871 | -0.3849 | -0.4973 | 0.1298 |
| 4.50 | -0.0161 | 0.0250 | 0.0345 | 0.1455 | -0.0185 | -0.0055 | 0.0278 | 0.0205 | -0.0366 | -0.0856 | 0.1748 |
| 5.00 | 0.0017 | -0.0147 | -0.0010 | 0.0755 | 0.0323 | 0.0153 | 0.0471 | 0.0149 | 0.0829 | 0.0214 | 0.0919 |
| 6.00 | 0.0004 | -0.0034 | -0.0076 | 0.0121 | 0.0126 | 0.0051 | 0.0139 | 0.0015 | 0.0498 | 0.0186 | 0.0149 |
| 7.00 | 0.0000 | -0.0003 | -0.0022 | 0.0015 | 0.0019 | 0.0007 | 0.0021 | -0.0002 | 0.0044 | 0.0033 | 0.0020 |
| 8.00 | 0.0000 | 0.0000 | -0.0005 | 0.0002 | 0.0002 | 0.0001 | 0.0003 | -0.0001 | 0.0002 | 0.0004 | 0.0003 |
| 9.00 | 0.0000 | 0.0000 | -0.0001 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 10.00 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |


| Table B.11: Correlation energy contributions $\Delta E_{\mathrm{c}}(\mathrm{kcal} / \mathrm{mol})$ in the interaction energy of the argon dimer in the CBS limit. These data are used in Fig. 2.5. |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $R$ | LRC- $\omega$ PBEh | $\omega \mathrm{B} 97$ | B3LYP | SCAN | TPSS | PBE0 | PBE | RPW86PBE | PW91 | revPBE-PW92 | LDA |
| 1.50 | -30.4473 | -32.3097 | -18.7508 | -36.4957 | -28.7636 | -29.9518 | -29.7612 | -29.7096 | -29.0067 | -11.0460 | -11.2185 |
| 1.80 | -21.3282 | -21.6633 | -14.4641 | -23.4462 | -20.2098 | -21.2217 | -21.2802 | -21.1848 | -20.8005 | -8.8287 | -8.7268 |
| 2.00 | -15.3282 | -16.2481 | -11.1538 | -16.1467 | -14.4567 | -15.2819 | -15.4067 | -15.3229 | -15.1253 | -6.5762 | -6.3879 |
| 2.40 | -7.1043 | -9.9606 | -6.1406 | -7.3736 | -6.7075 | -7.0908 | -7.2208 | -7.2223 | -7.1897 | -3.2894 | -3.0285 |
| 2.80 | -2.9008 | -5.6812 | -3.1481 | -3.1985 | -2.7712 | -2.8946 | -2.9991 | -3.0303 | -3.0431 | -1.5512 | -1.2911 |
| 3.20 | -1.0351 | -2.7075 | -1.5024 | -1.2950 | -1.0079 | -1.0258 | -1.0939 | -1.1025 | -1.1346 | -0.7102 | -0.4983 |
| 3.50 | -0.4388 | -1.2885 | -0.8187 | -0.6257 | -0.4416 | -0.4269 | -0.4678 | -0.4639 | -0.4965 | -0.3879 | -0.2273 |
| 3.65 | -0.2786 | -0.8155 | -0.5935 | -0.4289 | -0.2868 | -0.2663 | -0.2958 | -0.2908 | -0.3189 | -0.2841 | -0.1496 |
| 3.76 | -0.1976 | -0.5573 | -0.4651 | -0.3242 | -0.2068 | -0.1854 | -0.2077 | -0.2036 | -0.2270 | -0.2250 | -0.1088 |
| 3.85 | -0.1482 | -0.3952 | -0.3790 | -0.2567 | -0.1569 | -0.1362 | -0.1534 | -0.1508 | -0.1696 | -0.1852 | -0.0831 |
| 4.00 | -0.0904 | -0.2072 | -0.2668 | -0.1732 | -0.0967 | -0.0790 | -0.0894 | -0.0899 | -0.1005 | -0.1328 | -0.0521 |
| 4.50 | -0.0143 | -0.0060 | -0.0762 | -0.0451 | -0.0113 | -0.0061 | -0.0050 | -0.0131 | -0.0007 | -0.0388 | -0.0085 |
| 5.00 | -0.0013 | 0.0051 | -0.0205 | -0.0108 | 0.0043 | 0.0038 | 0.0068 | -0.0008 | 0.0192 | -0.0077 | -0.0001 |
| 6.00 | 0.0000 | 0.0007 | -0.0021 | -0.0004 | 0.0018 | 0.0012 | 0.0021 | 0.0001 | 0.0076 | 0.0010 | 0.0005 |
| 7.00 | 0.0000 | 0.0000 | -0.0004 | 0.0000 | 0.0003 | 0.0002 | 0.0003 | 0.0000 | 0.0006 | 0.0003 | 0.0001 |
| 8.00 | 0.0000 | 0.0000 | -0.0001 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 9.00 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 10.00 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

Table B.12: Exchange energy contributions $\Delta E_{\mathrm{x}}(\mathrm{kcal} / \mathrm{mol})$ in the interaction energy of $\mathrm{Ar}-\mathrm{HF}$ in the complete basis set limit. The midbond functions (3s3p2d2f1g) were added to aug-cc-pVTZ and aug-cc-pVQZ basis sets. These data are not discussed in chapter 2 but are included for compatibility with $\mathrm{Ar}_{2}$ molecule.

| $R$ | B3LYP | SCAN | TPSS | PBE0 | PBE | rPW86-PBE | PW91 | LDA |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1.80 | -53.7950 | -65.1496 | -64.7076 | -49.1420 | -64.6667 | -63.8483 | -65.5186 | -82.0288 |
| 2.00 | -33.1455 | -40.9974 | -40.0471 | -30.1820 | -40.2611 | -40.2542 | -40.8148 | -51.6911 |
| 2.50 | -7.8619 | -10.0812 | -9.7717 | -7.4821 | -10.3124 | -10.3121 | -10.4972 | -13.2241 |
| 2.75 | -3.3838 | -4.3566 | -4.6430 | -3.5268 | -4.9400 | -4.7437 | -5.1156 | -5.9525 |
| 3.00 | -1.2720 | -1.6080 | -2.2605 | -1.6180 | -2.2873 | -2.0086 | -2.4991 | -2.3506 |
| 3.25 | -0.3618 | -0.3999 | -1.1242 | -0.7192 | -1.0069 | -0.7541 | -1.2454 | -0.6978 |
| 3.40 | -0.1157 | -0.0630 | -0.7321 | -0.4318 | -0.5896 | -0.3817 | -0.8265 | -0.2161 |
| 3.50 | -0.0234 | 0.0641 | -0.5426 | -0.3024 | -0.4000 | -0.2269 | -0.6275 | -0.0223 |
| 3.60 | 0.0310 | 0.1451 | -0.3951 | -0.2078 | -0.2608 | -0.1229 | -0.4727 | 0.1014 |
| 4.00 | 0.0643 | 0.1997 | -0.0712 | -0.0269 | 0.0047 | 0.0279 | -0.1067 | 0.2272 |
| 4.50 | 0.0145 | 0.1155 | 0.0364 | 0.0192 | 0.0627 | 0.0297 | 0.0766 | 0.1396 |
| 5.00 | -0.0076 | 0.0527 | 0.0370 | 0.0161 | 0.0447 | 0.0128 | 0.1113 | 0.0628 |
| 5.50 | -0.0089 | 0.0214 | 0.0203 | 0.0082 | 0.0226 | 0.0040 | 0.0763 | 0.0251 |
| 6.00 | -0.0056 | 0.0080 | 0.0091 | 0.0035 | 0.0098 | 0.0009 | 0.0327 | 0.0096 |
| 7.00 | -0.0015 | 0.0010 | 0.0014 | 0.0005 | 0.0015 | -0.0001 | 0.0024 | 0.0013 |
| 8.00 | -0.0003 | 0.0001 | 0.0002 | 0.0001 | 0.0002 | 0.0000 | 0.0002 | 0.0002 |
| 9.00 | -0.0001 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 10.00 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

Table B.13: Correlation energy contributions $\Delta E_{\mathrm{c}}$ ( $\mathrm{kcal} / \mathrm{mol}$ ) in the interaction energy of $\mathrm{Ar}-\mathrm{HF}$ in the complete basis set limit. The midbond functions (3s3p2d2f1g) were added to aug-cc-pVTZ and aug-cc-pVQZ basis sets. These data are not discussed in chapter 2 but are included for compatibility with $\mathrm{Ar}_{2}$ molecule.

| $R$ | B3LYP | SCAN | TPSS | PBE0 | PBE | rPW86-PBE | PW91 | LDA |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1.80 | -10.2732 | -12.8710 | -11.8352 | -12.5320 | -12.6716 | -12.6019 | -12.5072 | -5.3175 |
| 2.00 | -7.6239 | -8.6668 | -8.0754 | -8.5046 | -8.6841 | -8.6566 | -8.6404 | -3.7203 |
| 2.50 | -3.2952 | -3.0308 | -2.6659 | -2.7471 | -2.8908 | -2.9080 | -2.9422 | -1.2904 |
| 2.75 | -2.0767 | -1.7284 | -1.4259 | -1.4433 | -1.5529 | -1.5610 | -1.5992 | -0.7146 |
| 3.00 | -1.2709 | -0.9612 | -0.7357 | -0.7205 | -0.7961 | -0.7935 | -0.8303 | -0.3800 |
| 3.25 | -0.7536 | -0.5224 | -0.3680 | -0.3401 | -0.3870 | -0.3804 | -0.4104 | -0.1932 |
| 3.40 | -0.5419 | -0.3588 | -0.2382 | -0.2098 | -0.2428 | -0.2373 | -0.2610 | -0.1256 |
| 3.50 | -0.4319 | -0.2780 | -0.1761 | -0.1494 | -0.1747 | -0.1708 | -0.1896 | -0.0932 |
| 3.60 | -0.3423 | -0.2145 | -0.1285 | -0.1045 | -0.1233 | -0.1214 | -0.1351 | -0.0685 |
| 4.00 | -0.1278 | -0.0736 | -0.0287 | -0.0180 | -0.0208 | -0.0264 | -0.0209 | -0.0172 |
| 4.50 | -0.0340 | -0.0182 | 0.0025 | 0.0033 | 0.0062 | -0.0018 | 0.0165 | -0.0011 |
| 5.00 | -0.0093 | -0.0041 | 0.0047 | 0.0034 | 0.0060 | 0.0006 | 0.0181 | 0.0010 |
| 5.50 | -0.0031 | -0.0008 | 0.0026 | 0.0017 | 0.0031 | 0.0003 | 0.0108 | 0.0008 |
| 6.00 | -0.0012 | -0.0001 | 0.0011 | 0.0007 | 0.0013 | 0.0001 | 0.0043 | 0.0004 |
| 7.00 | -0.0002 | 0.0000 | 0.0002 | 0.0001 | 0.0002 | 0.0000 | 0.0003 | 0.0001 |
| 8.00 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 9.00 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 10.00 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

Table B.14: The ratio $E_{\text {extra }} / E_{\text {dispx }}$ for $\operatorname{Ar}-\mathrm{HF}$ in the CBS limit. The midbond functions (3s3p2d2f1g) were added to aug-cc-pVTZ and aug-cc-pVQZ basis sets. These data are plotted in Fig. 2.6.

| $R$ | B3LYP | SCAN | TPSS | PBE0 | PBE | rPW86-PBE | PW91 | LDA |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1.80 | 0.8822 | 1.0574 | 0.9894 | 1.0526 | 1.0708 | 0.9101 | 1.1152 | 1.7686 |
| 2.00 | 0.8134 | 1.0477 | 0.8934 | 0.9854 | 0.9667 | 0.8448 | 1.0248 | 1.7797 |
| 2.50 | 0.6676 | 1.0809 | 0.6309 | 0.8374 | 0.8013 | 0.7707 | 0.8928 | 1.8266 |
| 3.00 | 0.4819 | 1.1099 | 0.4489 | 0.7430 | 0.7769 | 0.7037 | 0.9479 | 1.8309 |
| 3.40 | 0.2606 | 1.0803 | 0.4788 | 0.7107 | 0.8345 | 0.6029 | 1.1818 | 1.7323 |
| 3.50 | 0.1965 | 1.0633 | 0.5061 | 0.7058 | 0.8534 | 0.5722 | 1.2669 | 1.6902 |
| 3.60 | 0.1301 | 1.0408 | 0.5372 | 0.7006 | 0.8716 | 0.5397 | 1.3599 | 1.6411 |
| 4.00 | -0.1360 | 0.9028 | 0.6574 | 0.6622 | 0.9138 | 0.4016 | 1.7590 | 1.3832 |
| 4.50 | -0.3786 | 0.6768 | 0.6895 | 0.5511 | 0.8438 | 0.2411 | 2.0710 | 0.9959 |
| 5.00 | -0.4556 | 0.4650 | 0.5638 | 0.3934 | 0.6511 | 0.1202 | 1.8717 | 0.6460 |
| 6.00 | -0.3102 | 0.1722 | 0.2338 | 0.1490 | 0.2632 | 0.0166 | 0.6064 | 0.2277 |
| 7.00 | -0.1277 | 0.0657 | 0.0838 | 0.0610 | 0.0945 | 0.0168 | 0.0969 | 0.0864 |
| 8.00 | -0.0366 | 0.0287 | 0.0310 | 0.0280 | 0.0353 | 0.0142 | 0.0267 | 0.0375 |
| 9.00 | 0.0004 | 0.0172 | 0.0211 | 0.0205 | 0.0219 | 0.0141 | 0.0229 | 0.0258 |
| 10.00 | 0.0162 | 0.0181 | 0.0216 | 0.0211 | 0.0207 | 0.0152 | 0.0262 | 0.0234 |

Table B.15: Exchange energy contributions $\Delta E_{\mathrm{x}}(\mathrm{kcal} / \mathrm{mol})$ to the interaction energy of the water dimer in the CBS limit. The basis sets utilized are aug-cc-pVTZ and aug-cc-pVQZ with midbond functions (3s3p2d2f). These data are not discussed in chapter 2 but are included for compatibility with $\mathrm{Ar}_{2}$ molecule.

| $R$ | B3LYP | SCAN | TPSS | PBE0 | PBE | rPW86-PBE | LDA |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2.50 | -17.3215 | -20.9318 | -21.3237 | -15.9164 | -21.5999 | -21.4286 | -28.4036 |
| 3.00 | -3.7223 | -4.2101 | -4.6845 | -3.7246 | -5.0762 | -4.9145 | -6.8863 |
| 3.50 | -0.5982 | -0.4791 | -1.1390 | -0.9042 | -1.1455 | -0.8773 | -1.2363 |
| 4.00 | -0.1067 | 0.0178 | -0.3832 | -0.2887 | -0.2897 | -0.1546 | -0.1393 |
| 4.50 | -0.1004 | -0.0370 | -0.1606 | -0.1413 | -0.1112 | -0.0947 | -0.0582 |
| 5.00 | -0.1177 | -0.0960 | -0.0991 | -0.0999 | -0.0836 | -0.1042 | -0.1026 |
| 5.50 | -0.1090 | -0.1104 | -0.0874 | -0.0835 | -0.0842 | -0.1023 | -0.1216 |
| 6.00 | -0.0900 | -0.1034 | -0.0818 | -0.0714 | -0.0819 | -0.0908 | -0.1163 |
| 6.50 | -0.0718 | -0.0898 | -0.0733 | -0.0601 | -0.0742 | -0.0768 | -0.1018 |
| 7.00 | -0.0575 | -0.0759 | -0.0633 | -0.0502 | -0.0645 | -0.0640 | -0.0860 |
| 7.50 | -0.0467 | -0.0636 | -0.0539 | -0.0419 | -0.0549 | -0.0533 | -0.0719 |
| 8.00 | -0.0385 | -0.0534 | -0.0456 | -0.0351 | -0.0465 | -0.0446 | -0.0602 |
| 8.50 | -0.0321 | -0.0450 | -0.0386 | -0.0295 | -0.0394 | -0.0376 | -0.0506 |
| 9.00 | -0.0272 | -0.0382 | -0.0329 | -0.0251 | -0.0336 | -0.0320 | -0.0429 |
| 10.00 | -0.0200 | -0.0282 | -0.0244 | -0.0185 | -0.0249 | -0.0237 | -0.0315 |

Table B.16: Correlation energy contributions $\Delta E_{\mathrm{c}}$ ( $\mathrm{kcal} / \mathrm{mol}$ )in the interaction energy of the water dimer in the CBS limit. The basis sets utilized are aug-cc-pVTZ and aug-cc-pVQZ with midbond functions (3s3p2d2f). These data are not discussed in chapter 2 but are included for compatibility with $\mathrm{Ar}_{2}$ molecule.

| $R$ | B3LYP | SCAN | TPSS | PBE0 | PBE | rPW86-PBE | LDA |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2.50 | -4.7657 | -5.1481 | -4.7401 | -4.9369 | -5.1019 | -5.1013 | -2.3759 |
| 3.00 | -2.0517 | -1.9237 | -1.5564 | -1.5729 | -1.6790 | -1.6895 | -0.7898 |
| 3.50 | -0.8015 | -0.6477 | -0.4380 | -0.4120 | -0.4536 | -0.4513 | -0.2291 |
| 4.00 | -0.2866 | -0.2054 | -0.1153 | -0.0964 | -0.1029 | -0.1044 | -0.0609 |
| 4.50 | -0.0993 | -0.0655 | -0.0288 | -0.0248 | -0.0202 | -0.0283 | -0.0186 |
| 5.00 | -0.0389 | -0.0234 | -0.0103 | -0.0118 | -0.0067 | -0.0148 | -0.0096 |
| 5.50 | -0.0199 | -0.0105 | -0.0078 | -0.0095 | -0.0063 | -0.0115 | -0.0077 |
| 6.00 | -0.0128 | -0.0061 | -0.0073 | -0.0083 | -0.0067 | -0.0095 | -0.0067 |
| 6.50 | -0.0092 | -0.0043 | -0.0067 | -0.0070 | -0.0064 | -0.0077 | -0.0058 |
| 7.00 | -0.0070 | -0.0033 | -0.0058 | -0.0058 | -0.0056 | -0.0062 | -0.0050 |
| 7.50 | -0.0055 | -0.0026 | -0.0049 | -0.0048 | -0.0048 | -0.0051 | -0.0042 |
| 8.00 | -0.0044 | -0.0022 | -0.0041 | -0.0040 | -0.0040 | -0.0042 | -0.0035 |
| 8.50 | -0.0037 | -0.0018 | -0.0034 | -0.0033 | -0.0034 | -0.0035 | -0.0030 |
| 9.00 | -0.0031 | -0.0015 | -0.0029 | -0.0028 | -0.0028 | -0.0029 | -0.0026 |
| 10.00 | -0.0022 | -0.0011 | -0.0021 | -0.0020 | -0.0021 | -0.0021 | -0.0019 |

Table B.17: The ratio $E_{\text {extra }} / E_{\text {dispx }}$ for water dimer in the CBS limit. The basis sets utilized are aug-cc-pVTZ and aug-cc-pVQZ with midbond functions (3s3p2d2f) added in each case. These data are plotted in Fig. 2.6.

| $R$ | B3LYP | SCAN | TPSS | PBE0 | PBE | rPW86-PBE | LDA |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2.50 | 0.8793 | 1.1538 | 0.9121 | 1.0574 | 1.0239 | 0.9285 | 1.9512 |
| 3.00 | 0.7544 | 1.1059 | 0.7156 | 0.9494 | 0.9587 | 0.9285 | 2.1265 |
| 3.50 | 0.5064 | 0.9602 | 0.4979 | 0.8389 | 0.8968 | 0.7600 | 2.0947 |
| 4.00 | 0.1426 | 0.7089 | 0.4333 | 0.7501 | 0.8163 | 0.4217 | 1.8414 |
| 4.50 | -0.2244 | 0.3852 | 0.3521 | 0.6354 | 0.6156 | -0.0005 | 1.4350 |
| 5.00 | -0.4921 | 0.0450 | 0.0705 | 0.4574 | 0.2225 | -0.4606 | 1.0011 |
| 5.50 | -0.6138 | -0.2937 | -0.3912 | 0.2578 | -0.3059 | -0.9277 | 0.6338 |
| 6.00 | -0.6260 | -0.6310 | -0.9219 | 0.0874 | -0.8779 | -1.3930 | 0.3653 |
| 6.50 | -0.6058 | -0.9746 | -1.4704 | -0.0425 | -1.4595 | -1.8808 | 0.1810 |
| 7.00 | -0.5982 | -1.3292 | -2.0406 | -0.1433 | -2.0588 | -2.4201 | 0.0501 |
| 7.50 | -0.6047 | -1.6953 | -2.6397 | -0.2173 | -2.6851 | -3.0199 | -0.0411 |
| 8.00 | -0.6348 | -2.0894 | -3.2888 | -0.2765 | -3.3615 | -3.6996 | -0.1108 |
| 8.50 | -0.7008 | -2.5355 | -4.0158 | -0.3400 | -4.1175 | -4.4822 | -0.1826 |
| 9.00 | -0.8088 | -3.0488 | -4.8407 | -0.4218 | -4.9740 | -5.3818 | -0.2738 |
| 10.00 | -1.1146 | -4.2711 | -6.7791 | -0.6244 | -6.9868 | -7.5143 | -0.5057 |

## Appendix C APPENDIX FOR CHAPTER 3

The data used in chapter 3 is partly given here. The absolute percentage errors (APEs) and median absolute percentage errors (MedAPEs) of the interaction energies relative to $\operatorname{CCSD}(\mathrm{T})$ results that are listed in Table 3.2 are also given. The ratios of DADE and disp(vdW-DF2) to $E_{\text {dispx }}$ plotted in Fig. 3.1 and mean absolute percentage errors (MAPEs) given in Table 3.1 are given in Appendix D. See chapter 3 for other details of these results.

Table C.1: Dispersion and interaction energies ( $\mathrm{kcal} / \mathrm{mol}$ ) at various separations of monomers (angstrom) for the benzene-methane dimer.

| $R$ | $E_{\text {disp }}$ | $E_{\text {exch-disp }}$ | $E_{\text {dispx }}$ | CCSD(T) | DADE | disp(vdW-DF2) | dlDF | dlDF+DADE | dlDF+disp(vdWDF2) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 3.2800 | -6.9226 | 1.3290 | -5.5936 | 0.1194 | -5.8932 | -3.7809 | 6.4498 | 0.5566 | 2.6689 |
| 3.8000 | -2.9475 | 0.3844 | -2.5631 | -1.4280 | -2.8173 | -2.0961 | 1.1997 | -1.6176 | -0.8964 |
| 4.8000 | -0.6508 | 0.0282 | -0.6226 | -0.6383 | -0.6549 | -0.5968 | -0.0354 | -0.6903 | -0.6322 |
| 5.8000 | -0.1851 | 0.0017 | -0.1834 | -0.2157 | -0.1872 | -0.1520 | -0.0423 | -0.2295 | -0.1943 |
| 6.8000 | -0.0662 | 0.0001 | -0.0661 | -0.0828 | -0.0646 | -0.0417 | -0.0195 | -0.0840 | -0.0612 |
| 7.8000 | -0.0279 | 0.0000 | -0.0279 | -0.0364 | -0.0256 | -0.0154 | -0.0080 | -0.0336 | -0.0234 |
| 8.8000 | -0.0132 | 0.0000 | -0.0132 | -0.0177 | -0.0115 | -0.0069 | -0.0038 | -0.0153 | -0.0107 |

Table C.2: Dispersion and interaction energies (kcal/mol) at various separations of monomers (angstrom) for the benzene-water dimer.

| $R$ | $E_{\text {disp }}$ | $E_{\text {exch-disp }}$ | $E_{\text {dispx }}$ | CCSD(T) | DADE | disp(vdW-DF2) | dlDF | dlDF+DADE | dlDF+disp(vdWDF2) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2.5000 | -12.9665 | 3.0565 | -9.9100 | 5.4577 | -9.2485 | -5.3623 | 17.7185 | 8.4701 | 12.3562 |
| 3.0000 | -5.3002 | 0.8814 | -4.4188 | -2.6842 | -4.7651 | -3.1561 | 2.4843 | -2.2808 | -0.6718 |
| 3.5000 | -2.2270 | 0.2328 | -1.9942 | -2.8021 | -2.2675 | -1.7751 | -0.6428 | -2.9103 | -2.4179 |
| 4.0000 | -0.9882 | 0.0580 | -0.9302 | -1.9127 | -1.0548 | -0.9630 | -0.9113 | -1.9661 | -1.8743 |
| 4.5000 | -0.4703 | 0.0139 | -0.4564 | -1.2346 | -0.5113 | -0.5055 | -0.7237 | -1.2350 | -1.2292 |
| 5.0000 | -0.2408 | 0.0032 | -0.2376 | -0.8148 | -0.2658 | -0.2576 | -0.5412 | -0.8070 | -0.7988 |
| 6.0000 | -0.0766 | 0.0002 | -0.0764 | -0.3978 | -0.0839 | -0.0683 | -0.2989 | -0.3829 | -0.3673 |
| 7.0000 | -0.0296 | 0.0000 | -0.0296 | -0.2199 | -0.0306 | -0.0239 | -0.1733 | -0.2039 | -0.1972 |
| 8.0000 | -0.0131 | 0.0000 | -0.0131 | -0.1323 | -0.0127 | -0.0110 | -0.1076 | -0.1203 | -0.1186 |

Table C.3: Dispersion and interaction energies ( $\mathrm{kcal} / \mathrm{mol}$ ) at various separations of monomers (angstrom) for the diamino-dinitroethylene (FOX-7) dimer.

| $R$ | $E_{\text {disp }}$ | $E_{\text {exch-disp }}$ | $E_{\text {dispx }}$ | CCSD(T) | DADE | disp(vdW-DF2) | dlDF | dlDF+DADE | dlDF+disp(vdWDF2) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 6.3790 | -10.6981 | 1.7913 | -8.9068 | -10.9250 | -6.5088 | -4.7574 | -2.1349 | -8.6438 | -6.8924 |
| 6.5790 | -7.4265 | 1.0524 | -6.3741 | -12.4044 | -4.8760 | -3.7798 | -6.3064 | -11.1824 | -10.0862 |
| 7.5790 | -1.4311 | 0.0582 | -1.3729 | -7.6001 | -1.0781 | -1.0728 | -6.7080 | -7.7861 | -7.7808 |
| 8.5790 | -0.4006 | 0.0026 | -0.3980 | -4.2065 | -0.2955 | -0.2629 | -4.1699 | -4.4654 | -4.4328 |
| 9.5790 | -0.1502 | 0.0001 | -0.1501 | -2.6672 | -0.1033 | -0.0732 | -2.7658 | -2.8691 | -2.8390 |
| 10.5790 | -0.0675 | 0.0000 | -0.0675 | -1.8430 | -0.0424 | -0.0282 | -1.9553 | -1.9976 | -1.9835 |

Table C.4: Dispersion and interaction energies ( $\mathrm{kcal} / \mathrm{mol}$ ) at various separations of monomers (angstrom) for the ethanol dimer.

| $R$ | $E_{\text {disp }}$ | $E_{\text {exch-disp }}$ | $E_{\text {dispx }}$ | CCSD(T) | DADE | disp(vdW-DF2) | dlDF | dlDF+DADE | dlDF+disp(vdWDF2) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 3.2560 | -8.8101 | 1.5662 | -7.2439 | -1.2469 | -7.4522 | -4.9447 | 6.4891 | -0.9631 | 1.5445 |
| 3.5580 | -5.1426 | 0.7110 | -4.4316 | -2.7159 | -4.8290 | -3.5174 | 1.9281 | -2.9009 | -1.5893 |
| 4.5580 | -1.0289 | 0.0454 | -0.9835 | -1.3517 | -1.0934 | -1.0126 | -0.3382 | -1.4316 | -1.3508 |
| 5.5580 | -0.2766 | 0.0025 | -0.2741 | -0.4930 | -0.2988 | -0.2537 | -0.2226 | -0.5213 | -0.4763 |
| 6.5580 | -0.0953 | 0.0001 | -0.0952 | -0.2146 | -0.0995 | -0.0666 | -0.1207 | -0.2202 | -0.1873 |
| 7.5580 | -0.0390 | 0.0000 | -0.0390 | -0.1110 | -0.0381 | -0.0226 | -0.0708 | -0.1088 | -0.0933 |
| 8.5580 | -0.0181 | 0.0000 | -0.0181 | -0.0651 | -0.0166 | -0.0096 | -0.0460 | -0.0626 | -0.0556 |

Table C.5: Dispersion and interaction energies ( $\mathrm{kcal} / \mathrm{mol}$ ) at various separations of monomers (angstrom) for the ethylenedinitramine (EDNA) dimer.

| $R$ | $E_{\text {disp }}$ | $E_{\text {exch-disp }}$ | $E_{\text {dispx }}$ | CCSD(T) | DADE | disp(vdW-DF2) | dlDF | dlDF+DADE | dlDF+disp(vdWDF2) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 4.4980 | -23.9854 | 4.0908 | -19.8946 | -6.2616 | -17.7126 | -14.4684 | 15.3192 | -2.3934 | 0.8508 |
| 4.7980 | -16.3291 | 2.3052 | -14.0239 | -10.9089 | -12.9756 | -11.2365 | 3.9595 | -9.0162 | -7.2771 |
| 5.7980 | -4.9909 | 0.3423 | -4.6486 | -8.3537 | -4.4335 | -4.4677 | -3.8909 | -8.3244 | -8.3586 |
| 6.7980 | -1.7678 | 0.0554 | -1.7124 | -4.2986 | -1.5959 | -1.6030 | -2.8256 | -4.4215 | -4.4286 |
| 7.7980 | -0.6965 | 0.0090 | -0.6875 | -2.2874 | -0.6214 | -0.5279 | -1.7853 | -2.4067 | -2.3132 |
| 8.7980 | -0.2944 | 0.0011 | -0.2933 | -1.2750 | -0.2553 | -0.1698 | -1.1018 | -1.3572 | -1.2716 |
| 9.7980 | -0.1340 | 0.0001 | -0.1339 | -0.7283 | -0.1105 | -0.0600 | -0.6698 | -0.7803 | -0.7298 |
| 10.7980 | -0.0657 | 0.0000 | -0.0657 | -0.4271 | -0.0509 | -0.0242 | -0.4099 | -0.4608 | -0.4341 |

Table C.6: Dispersion and interaction energies (kcal/mol) at various separations of monomers (angstrom) for the imidazole dimer.

| $R$ | $E_{\text {disp }}$ | $E_{\text {exch-disp }}$ | $E_{\text {dispx }}$ | CCSD(T) | DADE | disp(vdW-DF2) | dlDF | dlDF+DADE | dlDF+disp(vdWDF2) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 4.9250 | -11.1155 | 2.5149 | -8.6006 | -5.7778 | -5.5920 | -2.9359 | 1.6914 | -3.9005 | -1.2445 |
| 5.2470 | -5.8871 | 1.1944 | -4.6927 | -10.0238 | -3.5851 | -2.1125 | -5.3519 | -8.9370 | -7.4644 |
| 6.2470 | -0.9901 | 0.0781 | -0.9120 | -5.3982 | -0.7904 | -0.6812 | -4.3977 | -5.1881 | -5.0790 |
| 7.2470 | -0.2457 | 0.0041 | -0.2416 | -2.4642 | -0.1979 | -0.1878 | -2.1527 | -2.3505 | -2.3405 |
| 8.2470 | -0.0852 | 0.0002 | -0.0850 | -1.3334 | -0.0656 | -0.0538 | -1.2039 | -1.2695 | -1.2578 |
| 9.2470 | -0.0365 | 0.0000 | -0.0365 | -0.8177 | -0.0261 | -0.0203 | -0.7516 | -0.7777 | -0.7719 |
| 10.2470 | -0.0178 | 0.0000 | -0.0178 | -0.5438 | -0.0120 | -0.0098 | -0.5063 | -0.5183 | -0.5161 |

Table C.7: Dispersion and interaction energies ( $\mathrm{kcal} / \mathrm{mol}$ ) at various separations of monomers (angstrom) for the methylformate dimer.

| $R$ | $E_{\text {disp }}$ | $E_{\text {exch-disp }}$ | $E_{\text {dispx }}$ | CCSD(T) | DADE | disp(vdW-DF2) | dlDF | dlDF+DADE | dlDF+disp(vdWDF2) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 4.2430 | -5.5211 | 0.9202 | -4.6009 | -2.7780 | -4.2640 | -2.9155 | 1.7343 | -2.5298 | -1.1812 |
| 4.4340 | -3.8547 | 0.5398 | -3.3149 | -3.3172 | -3.1936 | -2.3321 | -0.0838 | -3.2774 | -2.4159 |
| 5.4340 | -0.7280 | 0.0293 | -0.6987 | -1.5655 | -0.6894 | -0.6490 | -0.8792 | -1.5686 | -1.5282 |
| 6.4340 | -0.1976 | 0.0015 | -0.1961 | -0.5693 | -0.1884 | -0.1594 | -0.3863 | -0.5747 | -0.5457 |
| 7.4340 | -0.0702 | 0.0001 | -0.0701 | -0.2335 | -0.0638 | -0.0440 | -0.1674 | -0.2313 | -0.2115 |
| 8.4340 | -0.0298 | 0.0000 | -0.0298 | -0.1055 | -0.0251 | -0.0161 | -0.0771 | -0.1021 | -0.0932 |

Table C.8: Dispersion and interaction energies ( $\mathrm{kcal} / \mathrm{mol}$ ) at various separations of monomers (angstrom) for the nitrobenzene dimer.

| $R$ | $E_{\text {disp }}$ | $E_{\text {exch-disp }}$ | $E_{\text {disp }}$ | CCSD(T) | DADE | disp(vdW-DF2) | dlDF | dlDF+DADE | dlDF+disp(vdWDF2) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2.9000 | -31.1856 | 6.3583 | -24.8273 | 0.8073 | -26.5027 | -19.3432 | 31.3840 | 4.8813 | 12.0408 |
| 3.2000 | -18.6056 | 2.9529 | -15.6527 | -6.5251 | -17.5432 | -13.6700 | 11.6672 | -5.8760 | -2.0028 |
| 4.2000 | -3.9495 | 0.1932 | -3.7563 | -4.5104 | -4.1479 | -3.9044 | -0.7785 | -4.9264 | -4.6829 |
| 5.2000 | -1.1270 | 0.0107 | -1.1163 | -1.8406 | -1.1731 | -1.0211 | -0.8572 | -2.0302 | -1.8783 |
| 6.2000 | -0.4084 | 0.0006 | -0.4078 | -0.9102 | -0.4066 | -0.2833 | -0.6241 | -1.0307 | -0.9074 |
| 7.2000 | -0.1739 | 0.0000 | -0.1739 | -0.5400 | -0.1612 | -0.1038 | -0.4530 | -0.6142 | -0.5569 |
| 8.2000 | -0.0827 | 0.0000 | -0.0827 | -0.3607 | -0.0721 | -0.0469 | -0.3438 | -0.4159 | -0.3906 |

Table C.9: Dispersion and interaction energies ( $\mathrm{kcal} / \mathrm{mol}$ ) at various separations of monomers (angstrom) for the nitromethane dimer.

| $R$ | $E_{\text {disp }}$ | $E_{\text {exch-disp }}$ | $E_{\text {dispx }}$ | CCSD(T) | DADE | disp(vdW-DF2) | dlDF | dlDF+DADE | dlDF+disp(vdWDF2) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2.8130 | -13.0887 | 2.4216 | -10.6671 | -2.7945 | -8.6551 | -7.4249 | 8.7503 | 0.0952 | 1.3254 |
| 3.1310 | -7.2632 | 1.0156 | -6.2476 | -6.1538 | -5.4106 | -4.9847 | 0.1512 | -5.2593 | -4.8335 |
| 4.1310 | -1.3376 | 0.0553 | -1.2823 | -3.4767 | -1.1759 | -1.2792 | -2.4832 | -3.6591 | -3.7624 |
| 5.1310 | -0.3359 | 0.0026 | -0.3333 | -1.5789 | -0.3192 | -0.2831 | -1.4328 | -1.7520 | -1.7159 |
| 6.1310 | -0.1103 | 0.0001 | -0.1102 | -0.8461 | -0.1049 | -0.0717 | -0.8376 | -0.9425 | -0.9093 |
| 7.1310 | -0.0437 | 0.0000 | -0.0437 | -0.5120 | -0.0394 | -0.0256 | -0.5293 | -0.5687 | -0.5549 |
| 8.1310 | -0.0197 | 0.0000 | -0.0197 | -0.3355 | -0.0169 | -0.0114 | -0.3564 | -0.3733 | -0.3678 |

Table C.10: Dispersion and interaction energies ( $\mathrm{kcal} / \mathrm{mol}$ ) at various separations of monomers (angstrom) for the water dimer.

| $R$ | $E_{\text {disp }}$ | $E_{\text {exch-disp }}$ | $E_{\text {dispx }}$ | CCSD(T) | DADE | disp(vdW-DF2) | dlDF | dlDF+DADE | dlDF+disp(vdWDF2) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2.3100 | -11.7208 | 3.1567 | -8.5641 | 8.3579 | -4.1889 | -2.0923 | 15.9488 | 11.7599 | 13.8565 |
| 2.6100 | -5.9090 | 1.4370 | -4.4720 | -3.0752 | -2.7503 | -1.4609 | 1.4020 | -1.3483 | -0.0589 |
| 2.9100 | -3.0150 | 0.6097 | -2.4053 | -5.0051 | -1.7297 | -1.0167 | -2.5873 | -4.3170 | -3.6040 |
| 3.2100 | -1.5692 | 0.2487 | -1.3205 | -4.4021 | -1.0493 | -0.7062 | -3.1479 | -4.1972 | -3.8542 |
| 3.5100 | -0.8386 | 0.0991 | -0.7395 | -3.3870 | -0.6221 | -0.4874 | -2.7231 | -3.3452 | -3.2105 |
| 4.0100 | -0.3176 | 0.0206 | -0.2970 | -2.0610 | -0.2605 | -0.2529 | -1.8081 | -2.0686 | -2.0610 |
| 4.5100 | -0.1336 | 0.0041 | -0.1295 | -1.2887 | -0.1174 | -0.1229 | -1.1893 | -1.3067 | -1.3122 |
| 5.0100 | -0.0625 | 0.0008 | -0.0617 | -0.8512 | -0.0582 | -0.0570 | -0.8103 | -0.8685 | -0.8673 |
| 5.5100 | -0.0321 | 0.0002 | -0.0319 | -0.5921 | -0.0309 | -0.0268 | -0.5723 | -0.6033 | -0.5991 |
| 6.0100 | -0.0178 | 0.0000 | -0.0178 | -0.4297 | -0.0172 | -0.0136 | -0.4190 | -0.4362 | -0.4325 |
| 6.5100 | -0.0104 | 0.0000 | -0.0104 | -0.3225 | -0.0100 | -0.0077 | -0.3166 | -0.3266 | -0.3243 |
| 7.0100 | -0.0064 | 0.0000 | -0.0064 | -0.2487 | -0.0060 | -0.0047 | -0.2457 | -0.2517 | -0.2504 |
| 7.5050 | -0.0041 | 0.0000 | -0.0041 | -0.1966 | -0.0038 | -0.0031 | -0.1953 | -0.1991 | -0.1984 |
| 8.0050 | -0.0027 | 0.0000 | -0.0027 | -0.1579 | -0.0025 | -0.0022 | -0.1575 | -0.1600 | -0.1597 |
| 8.5050 | -0.0019 | 0.0000 | -0.0019 | -0.1289 | -0.0016 | -0.0016 | -0.1291 | -0.1307 | -0.1307 |
| 9.0050 | -0.0013 | 0.0000 | -0.0013 | -0.1066 | -0.0011 | -0.0012 | -0.1072 | -0.1083 | -0.1084 |

Table C.11: Dispersion and interaction energies (kcal/mol) at various separations of monomers (angstrom) for the argon dimer.

| $R$ | $E_{\text {disp }}$ | $E_{\text {exch-disp }}$ | $E_{\text {dispx }}$ | CCSD(T) | DADE | disp(vdW-DF2) | dlDF | dlDF+DADE | dlDF+disp(vdWDF2) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 3.2000 | -1.9126 | 0.2370 | -1.6756 | 0.5257 | -1.4119 | -1.0385 | 2.2528 | 0.8409 | 1.2143 |
| 3.5000 | -1.0335 | 0.0878 | -0.9457 | -0.1739 | -0.8396 | -0.6870 | 0.7430 | -0.0966 | 0.0560 |
| 3.7600 | -0.6232 | 0.0362 | -0.5870 | -0.2765 | -0.5327 | -0.4749 | 0.2771 | -0.2556 | -0.1977 |
| 4.2500 | -0.2597 | 0.0066 | -0.2531 | -0.1968 | -0.2349 | -0.2296 | 0.0404 | -0.1945 | -0.1893 |
| 4.5000 | -0.1729 | 0.0027 | -0.1702 | -0.1462 | -0.1601 | -0.1554 | 0.0105 | -0.1496 | -0.1449 |
| 5.0000 | -0.0826 | 0.0005 | -0.0821 | -0.0774 | -0.0799 | -0.0680 | -0.0072 | -0.0871 | -0.0753 |
| 6.0000 | -0.0241 | 0.0000 | -0.0241 | -0.0238 | -0.0239 | -0.0198 | -0.0027 | -0.0266 | -0.0226 |
| 7.0000 | -0.0089 | 0.0000 | -0.0089 | -0.0088 | -0.0084 | -0.0059 | -0.0003 | -0.0087 | -0.0062 |
| 8.0000 | -0.0038 | 0.0000 | -0.0038 | -0.0038 | -0.0034 | -0.0024 | 0.0000 | -0.0034 | -0.0025 |
| 9.0000 | -0.0019 | 0.0000 | -0.0019 | -0.0018 | -0.0016 | -0.0011 | 0.0000 | -0.0016 | -0.0011 |
| 10.0000 | -0.0010 | 0.0000 | -0.0010 | -0.0010 | -0.0008 | -0.0005 | 0.0000 | -0.0008 | -0.0005 |

Table C.12: Dispersion and interaction energies (kcal/mol) at various separations of monomers (angstrom) for the Ar-HF dimer.

| $R$ | $E_{\text {disp }}$ | $E_{\text {exch-disp }}$ | $E_{\text {dispx }}$ | CCSD(T) | DADE | disp(vdW-DF2) | dlDF | dlDF+DADE | dlDF+disp(vdWDF2) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 3.0000 | -1.4120 | 0.1601 | -1.2519 | 0.2846 | -1.0066 | -0.7749 | 1.5059 | 0.4993 | 0.7310 |
| 3.5000 | -0.4923 | 0.0271 | -0.4652 | -0.2229 | -0.4104 | -0.3805 | 0.2057 | -0.2047 | -0.1748 |
| 4.0000 | -0.1922 | 0.0044 | -0.1878 | -0.1534 | -0.1744 | -0.1785 | 0.0119 | -0.1625 | -0.1666 |
| 4.5000 | -0.0842 | 0.0007 | -0.0835 | -0.0806 | -0.0821 | -0.0781 | -0.0143 | -0.0964 | -0.0924 |
| 5.0000 | -0.0409 | 0.0001 | -0.0408 | -0.0417 | -0.0422 | -0.0334 | -0.0115 | -0.0537 | -0.0448 |
| 6.0000 | -0.0121 | 0.0000 | -0.0121 | -0.0129 | -0.0129 | -0.0103 | -0.0025 | -0.0154 | -0.0128 |
| 7.0000 | -0.0045 | 0.0000 | -0.0045 | -0.0049 | -0.0046 | -0.0033 | -0.0006 | -0.0051 | -0.0038 |
| 8.0000 | -0.0020 | 0.0000 | -0.0020 | -0.0021 | -0.0019 | -0.0012 | -0.0002 | -0.0021 | -0.0014 |
| 9.0000 | -0.0009 | 0.0000 | -0.0009 | -0.0010 | -0.0009 | -0.0005 | -0.0001 | -0.0010 | -0.0006 |

Table C.13: APEs and MedAPEs relative to $\operatorname{CCSD}(\mathrm{T})$ values for the benzenemethane dimer.

| $R$ |  | dlDF + DADE |
| :---: | :---: | :---: |
| dlDF + disp(vdWDF2) |  |  |
| 3.2800 | 366.0720 | 2134.7953 |
| 3.8000 | 13.2749 | 37.2278 |
| 4.8000 | 8.1479 | 0.9534 |
| 5.8000 | 6.3760 | 9.9421 |
| 6.8000 | 1.4706 | 26.1361 |
| 7.8000 | 7.6615 | 35.6093 |
| 8.8000 | 13.2646 | 39.2619 |
| MedAPE | 8.1479 | 35.6093 |

Table C.14: APEs and MedAPEs relative to $\operatorname{CCSD}(\mathrm{T})$ values for the benzene-water dimer.

| $R$ | dlDF+DADE | dlDF + disp(vdWDF2) |
| :---: | :---: | :---: |
| 2.5000 | 55.1955 | 126.4001 |
| 3.0000 | 15.0304 | 74.9720 |
| 3.5000 | 3.8613 | 13.7117 |
| 4.0000 | 2.7897 | 2.0092 |
| 4.5000 | 0.0348 | 0.4387 |
| 5.0000 | 0.9549 | 1.9631 |
| 6.0000 | 3.7602 | 7.6800 |
| 7.0000 | 7.2654 | 10.3119 |
| 8.0000 | 9.0246 | 10.3406 |
| MedAPE | 3.8613 | 10.3119 |

Table C.15: APEs and MedAPEs relative to $\operatorname{CCSD}(\mathrm{T})$ values for the diaminodinitroethylene (FOX-7) dimer.

| $R$ | dlDF+DADE | dlDF+disp(vdWDF2) |
| :---: | :---: | :---: |
| 6.3790 | 20.8808 | 36.9121 |
| 6.5790 | 9.8510 | 18.6880 |
| 7.5790 | 2.4466 | 2.3767 |
| 8.5790 | 6.1551 | 5.3790 |
| 9.5790 | 7.5726 | 6.4426 |
| 10.5790 | 8.3912 | 7.6252 |
| MedAPE | 7.9819 | 7.0339 |

Table C.16: APEs and MedAPEs relative to $\operatorname{CCSD}(\mathrm{T})$ values for the ethanol dimer.

| $R$ | dlDF+DADE | dlDF+disp(vdWDF2) |
| :---: | :---: | :---: |
| 3.2560 | 22.7622 | 223.8660 |
| 3.5580 | 6.8115 | 41.4824 |
| 4.5580 | 5.9137 | 0.0644 |
| 5.5580 | 5.7441 | 3.3870 |
| 6.5580 | 2.6030 | 12.7285 |
| 7.5580 | 1.9563 | 15.9070 |
| 8.5580 | 3.8580 | 14.5239 |
| MedAPE | 5.7441 | 14.5239 |

Table C.17: APEs and MedAPEs relative to $\operatorname{CCSD}(\mathrm{T})$ values for the ethylenedinitramine (EDNA) dimer.

| $R$ | dlDF+DADE | dlDF + disp(vdWDF2) |
| :---: | :---: | :---: |
| 4.4980 | 61.7770 | 113.5879 |
| 4.7980 | 17.3499 | 33.2923 |
| 5.7980 | 0.3514 | 0.0582 |
| 6.7980 | 2.8600 | 3.0254 |
| 7.7980 | 5.2165 | 1.1303 |
| 8.7980 | 6.4462 | 0.2634 |
| 9.7980 | 7.1353 | 0.2035 |
| 10.7980 | 7.8887 | 1.6240 |
| MedAPE | 6.7908 | 1.3772 |

Table C.18: APEs and MedAPEs relative to $\operatorname{CCSD}(\mathrm{T})$ values for the imidazole dimer.

| $R$ | dlDF + DADE | dlDF + disp(vdWDF2) |
| :---: | :---: | :---: |
| 4.9250 | 32.4905 | 78.4610 |
| 5.2470 | 10.8427 | 25.5332 |
| 6.2470 | 3.8919 | 5.9133 |
| 7.2470 | 4.6135 | 5.0201 |
| 8.2470 | 4.7916 | 5.6720 |
| 9.2470 | 4.8901 | 5.6049 |
| 10.2470 | 4.6983 | 5.1000 |
| MedAPE | 4.7916 | 5.6720 |

Table C.19: APEs and MedAPEs relative to $\operatorname{CCSD}(\mathrm{T})$ values for the methylformate dimer.

| $R$ | dlDF + DADE | dlDF + disp(vdWDF2) |
| :---: | :---: | :---: |
| 4.2430 | 8.9368 | 57.4806 |
| 4.4340 | 1.2007 | 27.1712 |
| 5.4340 | 0.2009 | 2.3821 |
| 6.4340 | 0.9548 | 4.1374 |
| 7.4340 | 0.9639 | 9.4393 |
| 8.4340 | 3.1756 | 11.6488 |
| MedAPE | 1.0823 | 10.5440 |

Table C.20: APEs and MedAPEs relative to $\operatorname{CCSD}(\mathrm{T})$ values for the nitrobenzene dimer.

| $R$ | dlDF + DADE | dlDF + disp(vdWDF2) |
| :---: | :---: | :---: |
| 2.9000 | 504.6461 | 1391.4795 |
| 3.2000 | 9.9476 | 69.3057 |
| 4.2000 | 9.2239 | 3.8249 |
| 5.2000 | 10.3029 | 2.0476 |
| 6.2000 | 13.2458 | 0.3025 |
| 7.2000 | 13.7483 | 3.1328 |
| 8.2000 | 15.2844 | 8.2896 |
| MedAPE | 13.2458 | 3.8249 |

Table C.21: APEs and MedAPEs relative to $\operatorname{CCSD}(\mathrm{T})$ values for the nitromethane dimer.

| $R$ | dlDF+DADE | dlDF+disp(vdWDF2) |
| :---: | :---: | :---: |
| 2.8130 | 103.4063 | 147.4279 |
| 3.1310 | 14.5350 | 21.4549 |
| 4.1310 | 5.2454 | 8.2161 |
| 5.1310 | 10.9604 | 8.6766 |
| 6.1310 | 11.3959 | 7.4688 |
| 7.1310 | 11.0776 | 8.3782 |
| 8.1310 | 11.2466 | 9.6234 |
| MedAPE | 11.2466 | 8.6766 |

Table C.22: APEs and MedAPEs relative to $\operatorname{CCSD}(\mathrm{T})$ values for the water dimer.

| $R$ | dlDF+DADE | dlDF + disp(vdWDF2) |
| :---: | :---: | :---: |
| 2.3100 | 40.7042 | 65.7892 |
| 2.6100 | 56.1541 | 98.0841 |
| 2.9100 | 13.7481 | 27.9924 |
| 3.2100 | 4.6536 | 12.4472 |
| 3.5100 | 1.2348 | 5.2124 |
| 4.0100 | 0.3680 | 0.0037 |
| 4.5100 | 1.3980 | 1.8263 |
| 5.0100 | 2.0310 | 1.8924 |
| 5.5100 | 1.8790 | 1.1737 |
| 6.0100 | 1.5124 | 0.6565 |
| 6.5100 | 1.2738 | 0.5474 |
| 7.0100 | 1.2043 | 0.6727 |
| 7.5050 | 1.2560 | 0.9144 |
| 8.0050 | 1.3177 | 1.1400 |
| 8.5050 | 1.4277 | 1.3811 |
| 9.0050 | 1.5861 | 1.6382 |
| MedAPE | 1.4700 | 1.5097 |

Table C.23: APEs and MedAPEs relative to $\operatorname{CCSD}(\mathrm{T})$ values for the argon dimer.

| $R$ | dlDF + DADE | dlDF + disp(vdWDF2) |
| :---: | :---: | :---: |
| 3.2000 | 59.9569 | 130.9812 |
| 3.5000 | 44.4562 | 132.1916 |
| 3.7600 | 7.5636 | 28.4900 |
| 4.2500 | 1.1407 | 3.8197 |
| 4.5000 | 2.2863 | 0.9170 |
| 5.0000 | 12.6289 | 2.7128 |
| 6.0000 | 11.9913 | 5.0739 |
| 7.0000 | 1.5176 | 29.5157 |
| 8.0000 | 9.5346 | 34.5668 |
| 9.0000 | 14.0281 | 38.6664 |
| 10.0000 | 16.6972 | 47.9597 |
| MedAPE | 11.9913 | 29.5157 |

Table C.24: APEs and MedAPEs relative to $\operatorname{CCSD}(\mathrm{T})$ values for the Ar-HF dimer.

| R | dlDF+DADE | dlDF+disp(vdWDF2) |
| :---: | :---: | :---: |
| 3.0000 | 75.4079 | 156.8348 |
| 3.5000 | 8.1584 | 21.5795 |
| 4.0000 | 5.8969 | 8.6167 |
| 4.5000 | 19.6502 | 14.7148 |
| 5.0000 | 28.6668 | 7.5273 |
| 6.0000 | 18.7991 | 0.7818 |
| 7.0000 | 5.2974 | 21.9431 |
| 8.0000 | 2.3270 | 33.2879 |
| 9.0000 | 5.9300 | 43.1671 |
| MedAPE | 8.1584 | 21.5795 |

## Appendix D

## APPENDIX FOR CHAPTERS 3 AND 4

In the following tables we give dispersion energies from various methods used in chapter 3 and 4 . We also listed ratios of the dispersion energies from these methods to $E_{\text {dispx }}$ values which are plotted in Fig. 3.1 and Figs. 4.2, 4.3, and 4.2. The absolute percentage errors (APEs) at the different monomer separations are also given which are used to calculate mean absolute percentage errors (MAPEs) for the given dimers which are listed in Table 3.1 and plotted in Fig.4.1. The APEs and MAPEs relative to $E_{\text {disp }}$ are also given which are listed in Table 4.2. All energy values are given in (kcal/mol) and all separations are given in angstrom. See chapter 3 and 4 for the computational details of these results.

| Tab | D |  | $\begin{aligned} & \text { Dis } \\ & \text { (an } \end{aligned}$ | $\begin{aligned} & \text { spers } \\ & \text { gstr } \end{aligned}$ | $\begin{aligned} & \text { sion e } \\ & \text { om). } \end{aligned}$ |  | es (kca | $\mathrm{mol})$ | from | OUS |  |  | $\text { e } 6$ |  | e a | ious m | mer | parations |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 3.2800 | ${ }_{\text {E }}^{\text {Etap }}$ | 13290 | ${ }^{\text {catax }}$ | $\mathrm{D}_{\text {mas }}$ | DBBJJ HF | DADE | D3[No-switching | disp(V10) | disp(vdW-DF2) | disp (MBD) | disp(VV09) | D3BJPBE | XDM10 PW86-PBE] | D3MBJJPBE] | XDM 8 PW [6-PBE] | XDM8(No.switching] | disp(vdV-DFI) |  |
| 2800 |  |  |  |  | -5.297 | -5.8932 | ${ }^{-6.9535}$ | ${ }^{-2.3490}$ | ${ }^{-3.8809}$ | ${ }^{-2.1436}$ | -2.8191 | ${ }^{-2.1391}$ | ${ }^{-1.9841}$ | -2.2004 | ${ }^{-1.57}$ | -9.53 | -5.33 |  |
| 8000 | 9475 | 0.3844 | -2.5631 | -2.4594 | $-2.3686$ | $-2.8173$ | -2.6680 | $-1.431$ | ${ }^{-2.0961}$ | ${ }^{-1.3683}$ | $-1.8584$ | ${ }^{-1.3666}$ | ${ }^{1.46}$ | -1.34 | -1.13 | -3.4.4 | ${ }^{3.08}$ | 4.98 |
| 4.8000 |  | 0.0282 | 226 | 815 | ${ }^{-0.5726}$ | -0.0549 | -0.5949 | -0.496 | -0.596 | -0.438 | -0.653 | -0.488 | -0.5 | -0.45 | -0.5009 | -0.7330 | -1.0294 |  |
|  |  |  | -0.1834 |  | -0.1776 | ${ }^{-0.1872}$ | -0.1812 | -0.1732 | -0.1520 | -0.1464 | -0.22 | -0.1 |  |  | -0.1 | -0.2 | 0.3 |  |
|  |  |  |  |  |  |  |  | -0.066 | -0.0 | -0.0 |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 8000 |  | 0.0000 | -0.0132 |  | 139 | -0.0115 | -0.040 | ${ }_{0}^{0.0142}$ | 0.006 | 0.0125 | 0.0163 | 0.0138 | 0.0161 | 0.01 | -0.0158 | -0.0159 | -0.0171 | -0.0162 |



| Tab |  | 3 : |  | us | sion <br> mon | mer | gies (kc separa | $\begin{aligned} & \mathrm{al} / \mathrm{m} \\ & \text { ions } \end{aligned}$ | l) from angstro | vario m). | us 1 | hods | for the | diamino | -dinitro | ethylene | FOX-7) | dimer at |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\frac{R}{6,390}$ | ${ }_{\text {E }}^{\text {Etit) }}$ |  | ${ }_{\text {E }}^{\text {Etatax }}$ |  | ${ }_{\text {D } 3 \text { SJJIHF] }}$ | ${ }^{\text {DADE }}$ | D3[1/.oswitching] | $\frac{\text { disp }(\mathrm{VV10} 0}{3.301}$ | disp(dxW-DF2) | disp(MBD) | disp (V)099) | D3BJIPBE] | XDM10 [PW86-PBE] | D3MBJ [PBE] | XDM 8 PW 86 -PBE] | XDM8(No-switching | disp(vdW-DF | IIO[Noswitching] |
| ${ }^{6.3790}$ | ${ }^{-10.0981}$ | ${ }^{1.7913}$ | ${ }^{-8.9068}$ | ${ }^{-9.7622}$ | -6.9544 | ${ }^{-6.5088}$ | -14.8842 | ${ }^{-3.4051}$ | ${ }_{-}^{-4.7574}$ | ${ }^{-2.6593}$ | ${ }^{-3.9041}$ | ${ }^{-2.4131}$ | ${ }^{-2.11430}$ | ${ }^{-2.4131}$ | ${ }^{-1.7869}$ | ${ }^{-20.0337}$ | ${ }^{-7.0876}$ | ${ }^{-46.8788}$ |
| 6.5790 | -7.4265 | 1.0524 | ${ }^{-6.3741}$ | ${ }^{-6.8235}$ | ${ }^{-5.3136}$ | $-4.8760$ | -8.9846 | $-2.7952$ | ${ }^{-3.7798}$ | $-2.3194$ | $-3.3810$ | $-2.0662$ | $-1.8879$ | -2.0662 | $-1.5617$ | -11.6962 | $-5.71$ | -23. |
| 7.5790 | -1.4311 | 0.0582 | $-1.3729$ | -1.3451 | -1.1988 | -1.0781 | -1.3012 | -0.9452 | -1.0728 | -0.9641 | -1.2464 | -0.8338 | -0.8612 | -0.8338 | -0.7408 | -1.4909 | -1.8486 |  |
| 8.5790 | -0.4006 | 0.0026 | $-0.3880$ | ${ }^{-0.3685}$ | -0.3319 | ${ }^{-0.2955}$ | ${ }^{-0.3406}$ | ${ }^{0.3195}$ | -0.2629 | -0.3371 | $-0.4112$ | $-0.3000$ | $-0.3283$ | $-0.3000$ | $-0.2988$ | -0.3640 | ${ }^{-0.5701}$ | -0.4017 |
| 9.5790 | -0.1502 | 0.0001 | ${ }^{-0.1501}$ | ${ }^{-0.1324}$ | -0.1204 | ${ }^{-0.1033}$ | ${ }^{-0.1223}$ | ${ }^{-0.1238}$ | ${ }^{-0.0732}$ | ${ }^{-0.1306}$ |  | -0.1164 | ${ }^{-0.1248}$ | $-0.1164$ | -0.1192 | ${ }^{-0.1261}$ | ${ }^{-0.1788}$ | ${ }^{-0.1318}$ |
| 10.5790 | $-0.0675$ | 0.0000 | $-0.0675$ | $-0.0572$ | -0.0523 | ${ }^{-0.0424}$ | ${ }_{-0.0530}$ | -0.0554 | -0.0282 | ${ }_{-0.0577}$ | ${ }_{-0.0671}$ | ${ }_{-0.0516}$ | -0.0538 | -0.0516 | ${ }_{-0.0526}$ | ${ }_{-0.0536}$ | ${ }_{-0.0664}$ | $-0.0548$ |


Table D.5: Dispersion energies ( $\mathrm{kcal} / \mathrm{mol}$ ) from various methods for the ethylenedinitramine (EDNA) dimer at various



Table D.8: Dispersion energies ( $\mathrm{kcal} / \mathrm{mol}$ ) from various methods for the nitrobenzene dimer at various monomer sepa-










| dimer at various monomer separations (angstrom). |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\frac{R}{4.4080}$ | ${ }_{\text {D }}{ }_{\text {D }}^{\text {cem }}$ | $\frac{\mathrm{DB3JJHIH}}{0.8943}$ | ${ }_{\text {DADE }}$ |  | $\mathrm{d}^{\text {disp }(\mathrm{CV})}$ |  | $\frac{\text { dipe(MB1) }}{0.3514}$ |  |  |  | ${ }_{0}^{0.388}$ |  |  | (val-DF1 |  |
| 17880 |  |  |  |  |  |  |  |  |  |  | 0391 |  |  |  |  |
| 598 |  |  |  |  |  | , |  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  | , |  |  |  |  |  |  |  |  |  |
|  |  |  |  | 209 |  | Se9 | , | 120 | , |  |  |  |  |  |  |
|  |  |  |  |  |  | 0589 | - | S362 | 退 | 0130 |  |  |  |  |  |
| 9798 |  |  |  |  |  | 0481 | 0.9321 | 2088 | \% 0.8228 | 09091 |  |  |  |  |  |
| 10.7880 |  | 0.8388 | 0.7754 |  | ${ }_{0}^{0.9888}$ |  |  |  |  |  |  |  |  |  |  |





Table D.22: Ratio of dispersion energy from various methods to the $E_{\text {dispx }}$ values for the water dimer at various monomer

| R | $\mathrm{Das}_{\text {as }}$ | D3BJJHF] | DADE | D3(No-switching) | disp(VV10) | disp(vdW-DF2) | disp(MBD) | disp(VV09) | D3BJ [PBE] | XDM10[PW86-PBE] | D3MBJ [PBE] | XDM8[PW86-PBE | XDM8(No-switching) | disp(VdW-DF1) | XDM10\|No-switching] |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2.3100 | 1.0091 | 0.4176 | 0.4891 | 5.7139 | 0.1403 | ${ }_{0} .2443$ | 0.0579 | -0.0523 | 0.0637 | 0.0490 | 0.0629 | 0.0393 | 9.6265 | 0.3927 | 48.7233 |
| 2.6100 | 0.9900 | 0.5759 | 0.6150 | 2.7937 | 0.2046 | ${ }^{0.3267}$ | 0.1073 | ${ }^{0.0023}$ | 0.1080 | 0.0911 | 0.1053 | $0^{0.0730}$ | 4.3549 | ${ }^{0.5276}$ | 14.3777 |
| 2.9100 | 0.9532 | 0.7207 | 0.7191 | 1.7563 | 0.2785 | ${ }^{0.4227}$ | 0.1812 | ${ }^{0.0965}$ | ${ }^{0.1703}$ | 0.1554 | 0.1635 | 0.1245 | 2.5929 | 0.6811 | 6.2250 |
| 3.2100 | 0.9248 | 0.8197 | 0.7946 | 1.3123 | 0.3602 | 0.5348 | 0.2777 | 0.2165 | 0.2524 | 0.2433 | 0.2387 | 0.1960 | 1.8532 | 0.8620 | 3.5237 |
| 3.5100 | ${ }^{0.9109}$ | ${ }^{0.8607}$ | 0.8473 | 1.1024 | ${ }^{0.4462}$ | ${ }^{0.6591}$ | ${ }^{0.3914}$ | ${ }^{0.3470}$ | ${ }^{0.3518}$ | ${ }^{0.3533}$ | ${ }^{0.3292}$ | ${ }^{0.2883}$ | 1.4992 | 1.0764 | ${ }^{2.4073}$ |
| 4.0100 | 0.9156 | ${ }^{0.8744}$ | 0.8772 | ${ }^{0.9643}$ | 0.5875 | 0.8514 | ${ }^{0.5775}$ | ${ }^{0.5560}$ | ${ }^{0.5327}$ | ${ }^{0.5763}$ | ${ }^{0.4940}$ | 0.4809 | 1.2468 | 1.4929 | 1.6671 |
| 4.5100 | 0.9408 | 0.8875 | 0.9062 | 0.9313 | 0.7076 | 0.9489 | 0.7015 | 0.7199 | ${ }^{0.6871}$ | 0.8078 | 0.6374 | ${ }^{0.6895}$ | 1.1604 | 1.8917 | 1.3960 |
| 5.0100 | 0.9708 | 0.9066 | 0.9431 | 0.9327 | 0.7955 | 0.9240 | 0.7716 | ${ }^{0.8197}$ | ${ }^{0.7913}$ | 0.9721 | ${ }^{0.7393}$ | ${ }^{0.8593}$ | 1.1309 | 2.1403 | 1.2774 |
| 5.5100 | 0.9982 | 0.9255 | ${ }^{0.9696}$ | ${ }^{0.9433}$ | ${ }^{0.8561}$ | ${ }^{0.8387}$ | ${ }^{0.8166}$ | 0.8609 | ${ }^{0.8561}$ | 1.0558 | ${ }^{0.8071}$ | 0.9671 | 1.1209 | 2.1959 | 1.2182 |
| 6.0100 | 1.0139 | 0.9349 | 0.9681 | 0.9482 | ${ }^{0.8871}$ | ${ }^{0.7615}$ | 0.8444 | ${ }^{0.8549}$ | ${ }^{0.8909}$ | 1.0858 | ${ }^{0.8468}$ | 1.0212 | 1.1091 | 2.1104 | 1.1760 |
| 6.5100 | 1.0364 | 0.9521 | 0.9609 | ${ }^{0.9622}$ | 0.9148 | 0.7356 | ${ }^{0.8752}$ | 0.8282 | 0.9220 | 1.1065 | 0.8821 | 1.0591 | 1.1118 | 2.0325 | 1.1598 |
| 7.0100 | 1.0505 | 0.9619 | 0.9415 | 0.9700 | 0.9364 | 0.7348 | 0.8973 | 0.7758 | ${ }^{0.9403}$ | 1.1121 | ${ }^{0.9040}$ | 1.0771 | ${ }^{1.1096}$ | 1.9500 | 1.1449 |
| 7.5050 | 1.0653 | ${ }^{0.9719}$ | 0.9245 | ${ }^{0.9794}$ | ${ }^{0.9500}$ | ${ }^{0.7607}$ | 0.9184 | ${ }^{0.7039}$ | ${ }^{0.9566}$ | 1.1173 | ${ }^{0.9244}$ | 1.0907 | 1.1118 | 1.9172 | 1.1384 |
| 8.0050 | 1.0791 | 0.9831 | 0.9101 | 0.9888 | 0.9711 | ${ }^{0.8062}$ | ${ }^{0.9378}$ | ${ }^{0.6141}$ | 0.9715 | 1.1211 | ${ }^{0.9413}$ | 1.1007 | 1.1146 | 1.9316 | 1.1350 |
| 8.5050 | 1.0507 | 0.9545 | ${ }^{0.8652}$ | 0.9601 | ${ }^{0.9493}$ | ${ }^{0.8336}$ | ${ }^{0.9193}$ | ${ }^{0.4863}$ | ${ }^{0.9446}$ | 1.0824 | 0.9214 | 1.0671 | 1.0762 | 1.9110 | 1.0915 |
| 9.0050 | 1.0770 | 0.9799 | 0.8694 | 0.9818 | 0.9811 | 0.9122 | 0.9476 | 0.3667 | 0.9702 | 1.1014 | 0.9461 | 1.0890 | 1.0954 | 2.0155 | 1.1078 |



| able D.24: |  |  | Ratio of dispersion energ separations (angstrom). |  |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $R$ | $\mathrm{D}_{\text {ss }}$ | D3BJJHF] | DADE | D3/No-switching | disp(VV10) | disp(vdW-DF2) | disp(MBD) | disp(VV09) | D3BJJPBE] | XDM10[PW86-PBE] | D3MBJ [PBE] | XDM8[PW86-PBE] | XDM8(No-switching) | disp(vdW-DF1) | XDM10[(No-switching] |
| 3.0000 | 0.9630 | 0.6557 | 0.8041 | 0.8172 | 0.4113 | 0.6190 | 0.1917 | ${ }^{0.3238}$ | 0.2259 | 0.2250 | ${ }^{0.2593}$ | 0.1795 | 0.9356 | 0.9906 | ${ }^{1.3603}$ |
| 3.5000 | 1.0038 | 0.7154 | 0.8823 | 0.7946 | 0.5774 | 0.8180 | 0.3637 | 0.5895 | 0.3996 | 0.4446 | 0.4118 | 0.3572 | 0.8911 | 1.3944 | 1.1449 |
| 4.0000 | 1.0333 | 0.7778 | 0.9286 | 0.8254 | 0.7296 | 0.9508 | 0.5222 | 0.8402 | 0.5688 | 0.6676 | 0.5501 | 0.5577 | 0.9077 | 1.8342 | 1.0773 |
| 4.5000 | 1.0539 | 0.8373 | 0.9829 | 0.8699 | 0.8428 | 0.9353 | 0.6414 | 1.0288 | 0.7015 | 0.8252 | 0.6617 | 0.7239 | 0.9408 | 2.1551 | 1.0600 |
| 5.0000 | 1.0630 | 0.8859 | 1.0335 | 0.9102 | 0.9195 | 0.8175 | 0.7261 | 1.1512 | 0.7958 | 0.9196 | 0.7462 | 0.8389 | 0.9708 | 2.2333 | 1.0567 |
| 6.0000 | 1.0658 | 0.9564 | 1.0618 | 0.9720 | 1.0096 | 0.8531 | 0.8385 | 1.2597 | 0.9114 | 1.0124 | 0.8602 | 0.9656 | 1.0170 | 2.1683 | 1.0642 |
| 7.0000 | 1.0517 | 0.9925 | 1.0197 | 1.0036 | 1.0539 | 0.7242 | 0.9940 | 1.2766 | 0.9660 | 1.0431 | 0.9214 | 1.0156 | 1.0375 | 1.9462 | 1.0651 |
| 8.0000 | 1.0276 | 1.0043 | 0.9684 | 1.0128 | 1.0721 | 0.6325 | 0.9390 | 1.2609 | 0.9882 | 1.0453 | 0.9497 | 1.0284 | 1.0386 | 1.7731 | 1.05 |
| 9.0000 | 1.0065 | 1.0079 | 0.9310 | 1.0157 | 1.0845 | 0.5297 | 0.9590 | 1.2426 | 0.9947 | 1.0411 | 0.9681 | 1.0304 | 1.0355 | 1.6128 | 1.0463 |






Table D.30: APEs at various monomer separations (angstrom) relative to the $E_{\text {dispx }}$ values and MAPEs for the imidazole





|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 0.9114 | ${ }_{58}^{582366}$ | ${ }^{51.0874}$ | ${ }^{471.3856}$ | ${ }^{85.9670}$ | ${ }^{75.5684}$ | 94.2105 | 10.5 .2345 | ${ }^{93.35377}$ | ${ }^{95.0997}$ | ${ }^{93.7862}$ | ${ }^{96.0686}$ | ${ }^{862.554}$ | ${ }^{60.7288}$ |  |
| ${ }_{2}^{2,9100}$ |  | ${ }^{\substack{4274969 \\ 27.929}}$ | 38.8992 <br> 28.099 |  | ${ }_{72,1453}^{77.547}$ | ${ }_{\substack{6.7 .325 \\ 57.7301}}$ | ¢, | ${ }_{\text {90, }}$ |  |  |  | ${ }^{9827.5028}$ |  |  |  |
| 3.2100 | 7.517 | 18.032 | ${ }^{20.5359}$ | ${ }^{31.2329}$ | 63.9843 | 46.5173 | 72229 | ${ }^{78.303}$ | ${ }^{74.7632}$ | ${ }^{75.6673}$ | 76.1280 | 80.3951 | ${ }^{85.3232}$ | 13.78 | 252.3653 |
| 3.5100 | 8.919 | 13.330 | 15.8725 | ${ }^{10.2399}$ | ${ }^{55.3787}$ | ${ }^{34.0901}$ | 60.8571 | 65.2962 | ${ }^{61.8221}$ | ${ }^{64.6659}$ | 67.08 | ${ }^{71.1743}$ |  |  | 140.7 |
| 1500 |  | ${ }^{12.5259}$ | 122739 | 3.5724 | ${ }^{4.2231}$ | , | ${ }_{2028162}^{12214}$ | 20005 | ${ }^{4} .12251$ | 12.3235 |  |  |  |  |  |
| 50100 |  |  | 5 5880 | 67397 | 23154 | 76096 | 228234 | 18033 | 22.8878 | 22800 |  | 110718 |  | 114030 |  |
| 5.5100 | 0.1798 | 7.4773 | 3.0113 | ${ }_{5.6687}$ | 14.393 | ${ }^{16.1334}$ | 18.3371 | ${ }_{13.9096}$ | 14.3912 | 5.5769 | ${ }^{19.2983}$ | 3.2917 | ${ }^{12.0895}$ | 119.5906 | 21.8173 |
| 6.0100 | 1.3588 | 6.5081 | ${ }^{3.1877}$ | ${ }^{5.1823}$ | 11.2914 | ${ }^{23.8479}$ | ${ }^{15.5587}$ | ${ }^{14.5078}$ | 10.9148 | ${ }^{\text {8.5776 }}$ | ${ }^{15} 5.3215$ | 2.1187 | ${ }^{10.9143}$ | ${ }^{111.0442}$ | ${ }^{17,5}$ |
| 6.510 |  |  | ${ }^{3.9143}$ | 3.779 | ${ }^{8.5198}$ | 26.402 | 12.475 | 17.1766 | 7.8043 | ${ }^{10.6661}$ | ${ }^{11.7886}$ |  |  |  |  |
|  |  |  |  | 2060 | ${ }^{\text {40905 }}$ |  | ${ }_{8}^{11583}$ | 22,6072 | ${ }_{4}$ | ${ }^{1127319}$ |  | 9031 |  |  |  |
| 8.0050 | 7.9129 | 1.6900 | 8.9588 | ${ }_{1.1237}$ | ${ }_{2} .8906$ | ${ }_{193}^{29367}$ | ${ }_{6.2188}$ | 338.5854 | 2.8522 | 12.1084 | ${ }_{5.837}$ | ${ }^{10.0676}$ | 11.4576 | 93.1 | ${ }_{13.5010}$ |
| 8.5.550 | 5.0. |  | So | 边 | c.i.6099 | ${ }^{16.6368}$ | ${ }_{8}^{8.0731}$ | ${ }_{511.3746}$ | ${ }_{\text {, }}^{5.5132}$ | ${ }^{8.2424}$ | ${ }^{7} .8 .8538$ | ${ }_{6}^{6.7881}$ | ${ }_{7}^{7.6}$ | 91.0 |  |
| $\frac{9}{\text { M }}$ MPSE |  | ${ }_{1}^{20.2027}$ | ${ }_{\text {1.0.030 }}^{15031}$ | ${ }_{\text {che }}^{\text {50.7288 }}$ |  | ${ }^{8}$ |  | ${ }^{658.7295}$ | ${ }_{3}^{2.9415}$ | ${ }_{3} 10.50572$ |  | $\frac{8.8597}{36.164}$ | ${ }^{\text {a }}$ | ${ }_{76} 7$ 20263 |  |

Table D.35: APEs at various monomer separations (angstrom) relative to the $E_{\text {dispx }}$ values and MAPEs for the argon


\footnotetext{
Table D.36: APEs at various monomer separations (angstrom) relative to the $E_{\text {dispx }}$ values and MAPEs for the Ar-HF

| ${ }^{R}$ |  |  |  |  |  |  |  |  |  |  |  |  |  | (vdNW-D | N |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 3,0000 | 3.7001 | ${ }^{34.4294}$ | ${ }^{19.5921}$ | ${ }^{18.2803}$ | 58.8 | ${ }^{38.1049}$ | ${ }^{80.8314}$ | ${ }^{67,6211}$ | ${ }^{77.4127}$ | ${ }^{77.5029}$ | ${ }^{74.4 .668}$ | ${ }^{82.0793}$ | ${ }^{6.4382}$ | ${ }^{0.9374}$ |  |  |
| 5.000 | ${ }^{0.3}$ | 28,46 | 11.7 | ${ }^{20.3}$ | 42.2 | 18.1996 | ${ }^{63,2629}$ | 41099 |  | ${ }^{50.5143}$ |  | 61.2799 | 10.8908 | 305 | 14.4853 |  |
|  |  | 21726 | 1720 | 120135 |  | ${ }_{6}$ | ${ }_{3}^{358563}$ | ${ }^{12.5828}$ | ${ }^{29.12185}$ | ${ }^{3172898}$ |  | 27.612 | 52024 | 52070 |  |  |
| 5.0000 | ${ }_{6.3032}$ | 11.411 | 3.3553 | 8.9801 | 8.0504 | 18.22515 | ${ }_{27,333}$ | 15.11165 | 20.4191 | 8.0335 | ${ }_{25} 5.3813$ | 16.1121 | 2.9185 | ${ }^{123,3236}$ | 5.6656 |  |
| 6.0000 | ${ }^{6.5825}$ | 4.3643 | ${ }_{6} 6.1755$ | 2.8028 | 0.9557 | ${ }^{14.6939}$ | 16.1512 | ${ }^{25.9723}$ | ${ }^{8.8642}$ | 1.2339 | 13.9847 | 3.4375 | 1.695 | 116.8293 | 6.4226 |  |
| 7.0000 |  |  |  | ${ }^{0.35951}$ | ${ }_{5}^{5.3925}$ | ${ }^{27.5841}$ | ${ }^{9.5999}$ | ${ }^{27.6611}$ | ${ }^{3.3990}$ | 4.3110 | 7.5396 |  | 3.7508 | ${ }^{94,6225}$ |  |  |
| ( | ${ }_{0.6}^{2.6}$ | ${ }_{0}$ | ${ }_{6}$ | 691 | ${ }_{8}^{1.4148}$ | 5317 | ${ }_{4}^{6} 1.1018$ | ${ }_{\text {24, } 2 \text { 2092 }}^{20.105}$ |  | ${ }_{4}^{4.1447}$ |  |  | ${ }_{\substack{3.5617 \\ 3.5196}}$ | ${ }_{61}$ |  |  |
| MAPE | 3.8081 | 13.2360 | ${ }_{6.8619}$ | 9,3649 | ${ }^{0.3266}$ | ${ }^{23.5561}$ | 323826 | ${ }^{27,4033}$ | 27.2020 | ${ }_{22} 28891$ | 2.6824 | ${ }_{27}^{27.2390}$ | ${ }_{5.3616}$ | ${ }^{79.1857}$ |  |  |






Table D.42: APEs at various monomer separations (angstrom) relative to the $E_{\text {disp }}$ values and MAPEs for the imidazole








