DISPERSION ENERGY IN DENSITY-FUNCTIONAL THEORY

by

Muhammad Shahbaz

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics

Winter 2019

© 2019 Muhammad Shahbaz All Rights Reserved

DISPERSION ENERGY IN DENSITY-FUNCTIONAL THEORY

by

Muhammad Shahbaz

Approved: _____

Edmund Nowak, Ph.D. Chair of the Department of Physics and Astronomy

Approved: _

John Pelesko, Ph.D. Interim Dean of the College of Arts and Science

Approved: _

Douglas J. Doren, Ph.D. Interim Vice Provost for Graduate and Professional Education I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed: _____

Krzysztof Szalewicz, D.Sc. Professor in charge of dissertation

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed: _

Branislav Nikolic, Ph.D. Member of dissertation committee

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed: _____

John Morgan, Ph.D. Member of dissertation committee

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed:

Marianna Safronova, Ph.D. Member of dissertation committee I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed:

Anderson Janotti, Ph.D. Member of dissertation committee

ACKNOWLEDGEMENTS

I would like to thank my advisor Krzysztof Szalewicz for helping me all these years, keeping me motivated, and being so kind and patient. I appreciate the faculty members of the Department of Physics and Astronomy at UD for being available for insightful discussions. I am also very grateful to Michael Metz for helping me acquire the programming skills necessary to complete my study. Finally, I would like to thank my parents and family for their love and support.

TABLE OF CONTENTS

L] L] A	IST (IST (BST)	OF TABLES v OF FIGURES v RACT v	'iii cvi cix
\mathbf{C}	hapte	er	
1	INT	FRODUCTION	1
	$\begin{array}{c} 1.1 \\ 1.2 \end{array}$	Density Functional Theory	5 14
2	DO API SM	SEMILOCAL DENSITY-FUNCTIONAL PROXIMATIONS RECOVER DISPERSION ENERGIES AT ALL INTERMONOMER SEPARATIONS?	17
3	DIS DE	SPERSION ENERGY FROM LOCAL POLARIZABILITY NSITY	29
4	EVA ENI CAI	ALUATION OF METHODS FOR OBTAINING DISPERSION ERGIES USED IN DENSITY-FUNCTIONAL LCULATIONS OF INTERMOLECULAR INTERACTIONS .	38
	4.1	Introduction	39
	4.2	Benchmark dispersion energies	44
	4.3	Nonlocal Correlation Functionals	45
	4.4	Asymptotics-based atom-atom dispersion functions	48
	4.5	Exchange-hole dipole moment model	50
	4.6	Many-Body Dispersion	51
	4.7	Computational Details	52
	4.8	Results	54
		4.8.1 Asymptotics-based methods	57
		4.8.2 Nonlocal functionals	59

	4.8.3 Atoms-in-molecules methods	61
	4.9 Summary and Conclusions	62
5	POLARIZABILITY DENSITY FROM TIME DEPENDENT DENSITY-FUNCTIONAL THEORY AND FURTHER DEVELOPMENT OF DADE	70
6	POTENTIAL ENERGY SURFACE DEVELOPMENT FOR CRYSTAL STRUCTURE PREDICTION	75
BI	BLIOGRAPHY	79
Aj	opendix	
A B	LIST OF PUBLICATIONS	95 96
	B.1Basis sets and CBS ExtrapolationB.2Level of SAPT TheoryB.3Uncertainties of SAPT ResultsB.4SAPT at small R 'sB.5Physical DampingB.6"Antidamping" in D3BJB.7Argon-protonB.8Argon-Lithium Cation $(Ar - Li^+)$ B.9 E_{extra} for Wave Function MethodsB.10RSH FunctionalsB.11Dependence of non-xc interaction energy on densityB.13SCAN at small R 's	96 97 97 100 102 104 105 107 108 108 108 109 111 112
C D	APPENDIX FOR CHAPTER 3	$\frac{135}{145}$

LIST OF TABLES

3.1	MAPEs of dispersion energies for the investigated dimers with respect to the benchmark dispersion energies E_{dispx} .	34
3.2	MedAPEs of interaction energies for the investigated dimers with respect to the benchmark interaction energies.	36
4.1	MAPEs of dispersion energy from investigated methods relative to E_{dispx} . DADE results are from Ref. [29]	55
4.2	MAPEs of dispersion energy from investigated methods relative to E_{disp} . DADE results are from Ref. [29].	56
6.1	The combinations of monomers, number of atoms, number of electrons, number of grid points, and corresponding RMSEs of the PESs	77
B.1	The interaction energies (kcal/mol) of the argon dimer 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 plotted in Fig. 2.1 except for LRC- ω PBEh and ω B97 which are used for Figs. B.4 and B.5	118
B.2	The interaction energies (kcal/mol) of Ar–HF in the CBS limit. The midbond functions (3s3p2d2f1g) were added to aug-cc-pVTZ and aug-cc-pVQZ basis sets. These data are used to construct Table B.14.	119
B.3	Ar–Li ⁺ interaction energy (kcal/mol) in the CBS limit. The midbond functions (3s3p2d2f1g) were added to basis sets aug-cc-pVTZ and aug-cc-pVQZ. These data are used to construct Table B.8	120
B.4	Water dimer interaction energies (kcal/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	191
	used to construct Table D.11	141

B.5	The dispersion correction multiplied by R^6 (Å ⁶ kcal/mol) 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 $E_{\text{disp,as}}$, SAPT(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.	122
B.6	The antidamping effect for D3BJ(revPBE) at $R = 6$ Å 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.	123
B.7	Ar-proton interaction energy (kcal/mol) in the CBS limit. The midbond functions were not used. These data are used to calculate $E_{\text{int}}^{\text{DFT}}/E_{\text{int}}^{\text{CCSD(T)}}$ plotted in Fig. B.1.	124
B.8	The ratio $E_{\text{int}}^{\text{DFT}}/E_{\text{int}}^{\text{CCSD}(T)}$ and $E_{\text{dispx}}/E_{\text{int}}^{\text{CCSD}(T)}$ for Ar–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 in Fig. 2.3.	125
B.9	The ratio $E_{\text{extra}}/E_{\text{dispx}}$ for the argon dimer. These data are plotted in Fig. 2.4.	126
B.10	Exchange energy contributions ΔE_x (kcal/mol) in the interaction energy of the argon dimer in the CBS limit. These data are used in Fig. 2.5	127
B.11	Correlation energy contributions ΔE_c (kcal/mol) in the interaction energy of the argon dimer in the CBS limit. These data are used in Fig. 2.5	128
B.12	Exchange energy contributions ΔE_x (kcal/mol) in the interaction energy of Ar–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 Ar ₂ molecule.	129
B.13	Correlation energy contributions ΔE_c (kcal/mol) in the interaction energy of Ar–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 Ar ₂ molecule.	130

B.14	The ratio $E_{\text{extra}}/E_{\text{dispx}}$ for Ar–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.	131
B.15	Exchange energy contributions ΔE_x (kcal/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 Ar ₂ molecule	132
B.16	Correlation energy contributions ΔE_c (kcal/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 Ar ₂ molecule	133
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.	134
C.1	Dispersion and interaction energies $(kcal/mol)$ at various separations of monomers (angstrom) for the benzene-methane dimer	136
C.2	Dispersion and interaction energies (kcal/mol) at various separations of monomers (angstrom) for the benzene-water dimer	136
C.3	Dispersion and interaction energies (kcal/mol) at various separations of monomers (angstrom) for the diamino-dinitroethylene (FOX-7) dimer.	136
C.4	Dispersion and interaction energies (kcal/mol) at various separations of monomers (angstrom) for the ethanol dimer.	137
C.5	Dispersion and interaction energies (kcal/mol) at various separations of monomers (angstrom) for the ethylenedinitramine (EDNA) dimer.	137
C.6	Dispersion and interaction energies (kcal/mol) at various separations of monomers (angstrom) for the imidazole dimer.	137
C.7	Dispersion and interaction energies (kcal/mol) at various separations of monomers (angstrom) for the methylformate dimer.	138

C.8	Dispersion and interaction energies (kcal/mol) at various separations of monomers (angstrom) for the nitrobenzene dimer.	138
C.9	Dispersion and interaction energies (kcal/mol) at various separations of monomers (angstrom) for the nitromethane dimer	138
C.10	Dispersion and interaction energies (kcal/mol) at various separations of monomers (angstrom) for the water dimer.	139
C.11	Dispersion and interaction energies (kcal/mol) at various separations of monomers (angstrom) for the argon dimer.	139
C.12	Dispersion and interaction energies (kcal/mol) at various separations of monomers (angstrom) for the Ar-HF dimer	139
C.13	APEs and MedAPEs relative to CCSD(T) values for the benzene-methane dimer.	140
C.14	APEs and MedAPEs relative to CCSD(T) values for the benzene-water dimer.	140
C.15	APEs and MedAPEs relative to CCSD(T) values for the diamino-dinitroethylene (FOX-7) dimer.	140
C.16	APEs and MedAPEs relative to CCSD(T) values for the ethanol dimer.	141
C.17	APEs and MedAPEs relative to CCSD(T) values for the ethylenedinitramine (EDNA) dimer.	141
C.18	APEs and MedAPEs relative to CCSD(T) values for the imidazole dimer.	141
C.19	APEs and MedAPEs relative to CCSD(T) values for the methylformate dimer	142
C.20	APEs and MedAPEs relative to CCSD(T) values for the nitrobenzene dimer.	142
C.21	APEs and MedAPEs relative to CCSD(T) values for the nitromethane dimer.	142
C.22	APEs and MedAPEs relative to CCSD(T) values for the water dimer.	143

C.23	APEs and MedAPEs relative to $CCSD(T)$ values for the argon dimer.	143
C.24	APEs and MedAPEs relative to CCSD(T) values for the Ar-HF dimer.	144
D.1	Dispersion energies (kcal/mol) from various methods for the benzene-methane at various monomer separations (angstrom)	146
D.2	Dispersion energies (kcal/mol) from various methods for the benzene-water at various monomer separations (angstrom)	146
D.3	Dispersion energies (kcal/mol) from various methods for the diamino-dinitroethylene (FOX-7) dimer at various monomer separations (angstrom).	146
D.4	Dispersion energies (kcal/mol) from various methods for the ethanol dimer at various monomer separations (angstrom).	147
D.5	Dispersion energies (kcal/mol) from various methods for the ethylenedinitramine (EDNA) dimer at various monomer separations (angstrom).	147
D.6	Dispersion energies (kcal/mol) from various methods for the imidazole dimer at various monomer separations (angstrom)	147
D.7	Dispersion energies (kcal/mol) from various methods for the methyl formate dimer at various monomer separations (angstrom)	148
D.8	Dispersion energies (kcal/mol) from various methods for the nitrobenzene dimer at various monomer separations (angstrom)	148
D.9	Dispersion energies (kcal/mol) from various methods for the nitromethane dimer at various monomer separations (angstrom)	148
D.10	Dispersion energies (kcal/mol) from various methods for the water dimer at various monomer separations (angstrom).	149
D.11	Dispersion energies (kcal/mol) from various methods for the argon dimer at various monomer separations (angstrom).	149
D.12	Dispersion energies (kcal/mol) from various methods for the Ar-HF dimer at various monomer separations (angstrom).	149

D.13	Ratio of dispersion energy from various methods to the E_{dispx} values for the benzene-methane at various monomer separations (angstrom).	150
D.14	Ratio of dispersion energy from various methods to the E_{dispx} values for the benzene-water at various monomer separations (angstrom).	150
D.15	Ratio of dispersion energy from various methods to the E_{dispx} values for the diamino-dinitroethylene (FOX-7) at various monomer separations (angstrom).	150
D.16	Ratio of dispersion energy from various methods to the $E_{\rm dispx}$ values for the ethanol dimer at various monomer separations (angstrom).	151
D.17	Ratio of dispersion energy from various methods to the E_{dispx} values for the ethylenedinitramine (EDNA) dimer at various monomer separations (angstrom).	151
D.18	Ratio of dispersion energy from various methods to the E_{dispx} values for the imidazole dimer at various monomer separations (angstrom).	151
D.19	Ratio of dispersion energy from various methods to the E_{dispx} values for the methylformate dimer at various monomer separations (angstrom)	152
D.20	Ratio of dispersion energy from various methods to the E_{dispx} values for the nitrobenzene dimer at various monomer separations (angstrom)	152
D.21	Ratio of dispersion energy from various methods to the E_{dispx} values for the nitromethane dimer at various monomer separations (angstrom)	152
D.22	Ratio of dispersion energy from various methods to the $E_{\rm dispx}$ values for the water dimer at various monomer separations (angstrom)	153
D.23	Ratio of dispersion energy from various methods to the $E_{\rm dispx}$ values for the argon dimer at various monomer separations (angstrom)	153
D.24	Ratio of dispersion energy from various methods to the $E_{\rm dispx}$ values for the Ar-HF dimer at various monomer separations (angstrom).	153
D.25	APEs at various monomer separations (angstrom) relative to the E_{dispx} values and MAPEs for the benzene-methane	154

D.26	APEs at various monomer separations (angstrom) relative to the E_{dispx} values and MAPEs for the benzene-water	154
D.27	APEs at various monomer separations (angstrom) relative to the E_{dispx} values and MAPEs for the diamino-dinitroethylene (FOX-7) dimer.	154
D.28	APEs at various monomer separations (angstrom) relative to the E_{dispx} values and MAPEs for the ethanol dimer	155
D.29	APEs at various monomer separations (angstrom) relative to the E_{dispx} values and MAPEs for the ethylenedinitramine (EDNA) dimer.	155
D.30	APEs at various monomer separations (angstrom) relative to the E_{dispx} values and MAPEs for the imidazole dimer	155
D.31	APEs at various monomer separations (angstrom) relative to the E_{dispx} values and MAPEs for the methylformate dimer	156
D.32	APEs at various monomer separations (angstrom) relative to the E_{dispx} values and MAPEs for the nitrobenzene dimer	156
D.33	APEs at various monomer separations (angstrom) relative to the E_{dispx} values and MAPEs for the nitromethane dimer	156
D.34	APEs at various monomer separations (angstrom) relative to the E_{dispx} values and MAPEs for the water dimer	157
D.35	APEs at various monomer separations (angstrom) relative to the E_{dispx} values and MAPEs for the argon dimer	157
D.36	APEs at various monomer separations (angstrom) relative to the E_{dispx} values and MAPEs for the Ar-HF dimer.	157
D.37	APEs at various monomer separations (angstrom) relative to the E_{disp} values and MAPEs for the benzene-methane dimer	158
D.38	APEs at various monomer separations (angstrom) relative to the E_{disp} values and MAPEs for the benzene-water dimer	158
D.39	APEs at various monomer separations (angstrom) relative to the E_{disp} values and MAPEs for the diamino-dinitroethylene (FOX-7) dimer.	158

D.40	APEs at various monomer separations (angstrom) relative to the E_{disp} values and MAPEs for the ethanol dimer.	159
D.41	APEs at various monomer separations (angstrom) relative to the $E_{\rm disp}$ values and MAPEs for the ethylenedinitramine (EDNA) dimer.	159
D.42	APEs at various monomer separations (angstrom) relative to the E_{disp} values and MAPEs for the imidazole dimer.	159
D.43	APEs at various monomer separations (angstrom) relative to the E_{disp} values and MAPEs for the methylformate dimer.	160
D.44	APEs at various monomer separations (angstrom) relative to the E_{disp} values and MAPEs for the nitrobenzene dimer.	160
D.45	APEs at various monomer separations (angstrom) relative to the E_{disp} values and MAPEs for the nitromethane dimer	160
D.46	APEs at various monomer separations (angstrom) relative to the E_{disp} values and MAPEs for the water dimer.	161
D.47	APEs at various monomer separations (angstrom) relative to the E_{disp} values and MAPEs for the argon dimer.	161
D.48	APEs at various monomer separations (angstrom) relative to the E_{disp} values and MAPEs for the Ar-HF dimer	161

LIST OF FIGURES

2.1	Performance of various DFT methods for 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_{dispx} . For details of calculations, see Appendix B	18
2.2	The dispersion corrections D3BJ [multiplied by R^6] for Ar ₂	10
	corresponding to various DFT functionals compared to $E_{disp}^{(2)} + E_{exch-disp}^{(2)}$ and to the dispersion energy from the asymptotic expansion, $E_{disp,as}^{(2)}$. The latter quantities were computed using SAPT(DFT) to be at the same level of theory as D3, see Appendix B.	20
2.3	Ratio of DFT interaction energies and E_{dispx} to $\text{CCSD}(T)$ interaction energy for the Ar – Li ⁺ complex	22
2.4	Comparison of $E_{\text{extra}}/E_{\text{dispx}}$ for Ar ₂	23
2.5	The ratios $E_{\text{extra}}/E_{\text{dispx}}$, $\Delta E_{\text{x}}/E_{\text{dispx}}$, $\Delta E_{\text{c}}/E_{\text{dispx}}$, and $\Delta E_{\text{xc}}/E_{\text{dispx}}$ for the argon dimer.	24
2.6	The ratios $E_{\text{extra}}/E_{\text{dispx}}$ for Ar–HF and $(H_2O)_2$	26
3.1	Ratios of the approximate dispersion energies from DADE and vdW-DF2 to SAPT(DFT) benchmarks for ethylenedinitramine dimer (top-left), 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	33
4.1	The mean absolute percentage errors of dispersion energies from the considered methods relative to E_{dispx}	66

4.2	The ratios of dispersion energies from investigated methods to E_{dispx} for 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.	67
4.3	The ratios of dispersion energies from investigated methods to E_{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.	68
4.4	The ratios of dispersion energies from investigated methods to E_{dispx} for homogeneous dimers of imidazole, nitrobenzene, FOX-7, and EDNA. For other details, see Figs. 4.2 and 4.3.	69
5.1	Comparison of the polarizability density $\alpha(\mathbf{r}, iu)$ for the argon atom in the case $x = z, y = 0.0$, and $u = 0.79$ in atomic units	72
5.2	Comparison of polarizability density $\alpha(\mathbf{r}, iu)$ for the argon atom from vdW-DF2 (bottom-right), VV09/10 (top-right), and DADE (bottom-left) with the one obtained from TD-DFT (top-left) for $y = 0.0$ and $u = 0.79$ in atomic units.	73
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.	77
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.	78
6.3	PES for 4-amino-2,3,6-trinitrophenol with 4,4-bipyridine compared with SAPT(DFT) for the the orientation corresponding to first minimum.	78
B.1	The ratio of the interaction energies from DFT to the corresponding $CCSD(T)$ values for the Ar-proton complex	102

B.2	The ratio of the DFT interaction energies and the dispersion energies to the $CCSD(T)$ interaction energies for the Ar–Li ⁺ complex	103
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	104
B.4	The ratios $E_{\text{extra}}/E_{\text{dispx}}$, $\Delta E_{\text{x}}/E_{\text{dispx}}$, $\Delta E_{\text{c}}/E_{\text{dispx}}$, and $\Delta E_{\text{xc}}/E_{\text{dispx}}$ for the argon dimer using LRC- ω PBEh (Ref. [71]).	106
B.5	The ratios $E_{\text{extra}}/E_{\text{dispx}}$, $\Delta E_{\text{x}}/E_{\text{dispx}}$, $\Delta E_{\text{c}}/E_{\text{dispx}}$, and $\Delta E_{\text{xc}}/E_{\text{dispx}}$ for the argon dimer using ω B97 (Ref. [72])	107
B.6	The non-xc part of the 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 Ar ₂	113
B.7	Ratios of SCAN Ar ₂ interaction energy components to E_{dispx} computed with KS and HF densities.	114
B.8	Ratios of PBE Ar ₂ interaction energy components to E_{dispx} computed with KS and HF densities	115
B.9	Ratios of B3LYP Ar ₂ interaction energy components to E_{dispx} computed with KS and HF densities.	116
B.10	Total interaction energy from SCAN, PBE, and B3LYP functionals computed with KS versus HF orbitals and densities	117

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 [CCSD(T)]. The computational cost of WF-based methods scales so steeply (for example, it scales as $O(N^7)$ for SAPT and CCSD(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 3N-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 Hartree-Fock (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 CCSD(T), and the benchmark dispersion energy using SAPT. The dispersionless part of the interaction energy is then

computed by taking the difference of the CCSD(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_{extra}) would give us the dispersion energy recovered by a given DFT method. We performed DFT calculations for the Ar-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_{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_{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_{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_{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 Ar_2 and Ar-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 (D_{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 vdW-DF2 [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 TD-DFT 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 SAPT(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]

$$\hat{H} = \hat{T} + \hat{\mathscr{W}} + \hat{V}_{\text{ext}} = -\sum_{j=1}^{N} \frac{1}{2} \nabla_{j}^{2} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\boldsymbol{r}_{i} - \boldsymbol{r}_{j}|} - \sum_{j,J} \frac{Z_{J}}{|\boldsymbol{r}_{j} - \boldsymbol{R}_{J}|}, \quad (1.1)$$

where \hat{T} is kinetic energy operator, $\hat{\mathscr{W}}$ is electron-electron repulsion energy, and \hat{V}_{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 Jth nucleus, respectively and values of i, j run over all electrons. The external potential can be written as $\hat{V}_{\text{ext}} = \sum_i v_{\text{ext}}(\boldsymbol{r}_i)$ where $v_{\text{ext}}(\boldsymbol{r}_i) = -\sum_J \frac{Z_J}{|\boldsymbol{r}_i - \boldsymbol{R}_J|}$ is the total external potential for the *i*th electron. The electron-density operator is defined as $\hat{n}(\boldsymbol{r}) = \sum_i \delta(\boldsymbol{r} - \boldsymbol{r}_i)$, which allows us to write $\hat{V}_{\text{ext}} = \int d^3 \boldsymbol{r} v(\boldsymbol{r}) \hat{n}(\boldsymbol{r})$.

The time independent Schrödinger wave equation for the systems discussed is

$$\hat{H}\Psi_j(\boldsymbol{x}_1, \boldsymbol{x}_2, \boldsymbol{x}_3, ..., \boldsymbol{x}_N) = E_j \Psi_j(\boldsymbol{x}_1, \boldsymbol{x}_2, \boldsymbol{x}_3, ..., \boldsymbol{x}_N),$$
 (1.2)

where Ψ_j is the wave function of the *j*th eigenstate of \hat{H} with energy E_j and $\boldsymbol{x}_i \equiv (\boldsymbol{r}_i, \sigma_i)$ 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 Rayleigh-Ritz principle, can be found by minimizing the expectation value of the Hamiltonian with respect to the wave function [39], i.e.,

$$E_{0} = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle = \min_{\Psi} \langle \Psi | \hat{T} + \hat{\mathscr{W}} + \hat{V}_{\text{ext}} | \Psi \rangle$$
$$= \min_{\Psi} \left[\langle \Psi | \hat{\mathscr{F}} | \Psi \rangle + \langle \Psi | \hat{V}_{\text{ext}} | \Psi \rangle \right], \qquad (1.3)$$

where $\langle \Psi | \hat{\mathscr{F}} | \Psi \rangle = \langle \Psi | \hat{T} + \hat{\mathscr{W}} | \Psi \rangle$ and Ψ 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

$$n_0(\boldsymbol{r}) = N \sum_{\sigma} \int d^3 \boldsymbol{r}_2 \cdots \int d^3 \boldsymbol{r}_N |\Psi_0(\boldsymbol{r}, \sigma_1, \boldsymbol{x}_2, \boldsymbol{x}_3, \dots, \boldsymbol{x}_N)|^2, \qquad (1.4)$$

where Ψ_0 is the ground-state wave function and the integral of the density is the total number of electrons in the system, i.e., $\int d^3 \mathbf{r} n_0(\mathbf{r}) = N$.

The basic idea of DFT is that we can completely describe the system if we know its ground state density $n_0(\mathbf{r})$. In a system of N electrons, \hat{T} and $\hat{\mathcal{W}}$ are fixed and hence the wave function is a functional of the external potential \hat{V}_{ext} . Thus, the ground state density is a functional of the external potential, i.e., $n_0[v](\mathbf{r})$, 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, $v[n_0](\mathbf{r})$. 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, $\hat{H}[n_0]$. Consequently, via Schrödinger's wave equation, the wave function of the system is a functional of the ground state density ($\Psi_j[n_0](\mathbf{r})$) and so is the energy of the system ($E_j[n_0]$) [38].

The variational principle in terms of the density becomes

$$E_0 = \min_{n(\mathbf{r})} \{ \mathscr{F}[n] + E_{\text{ext}}[n] \}, \qquad (1.5)$$

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 $n(\mathbf{r}), f = f[n]$, then its functional derivative with respect to $n(\mathbf{r}), \frac{\delta f[n]}{\delta n(\mathbf{r})}$, is defined by [39]

$$\lim_{\eta \to 0} \frac{f[n+\eta \delta n] - f[n]}{\eta} = \int d^3 \boldsymbol{r} \, \frac{\delta f[n]}{\delta n(\boldsymbol{r})} \delta n(\boldsymbol{r}) \,, \tag{1.6}$$

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

$$\frac{\delta}{\delta n(\boldsymbol{r})} \left[\mathscr{F}[n] + E_{\text{ext}}[n] - \mu \int d^3 \boldsymbol{r} n(\boldsymbol{r}) \right] = \frac{\delta \mathscr{F}[n]}{\delta n(\boldsymbol{r})} + v_{\text{ext}}(\boldsymbol{r}) - \mu = 0, \qquad (1.7)$$

where μ is a Lagrange multiplier ensuring that $\int d^3 \mathbf{r} n(\mathbf{r}) = N$. The density $n(\mathbf{r})$ 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]

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

where $\hat{V}_s = \sum_j v_s(\mathbf{r}_j)$ 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

$$\left[-\frac{1}{2}\nabla^2 + v_{\rm s}(\boldsymbol{r})\right]\psi_j(\boldsymbol{x}) = \varepsilon_j\psi_j(\boldsymbol{x}), \qquad (1.9)$$

where ψ_j is a spin-orbital. The corresponding electron density is

$$n(\mathbf{r}) = \sum_{s,j=1}^{N_{\text{occ}}} |\psi_j(\mathbf{x})|^2, \qquad (1.10)$$

where N_{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

$$T_{\rm s}[n] = -\frac{1}{2} \sum_{s,j} \langle \psi_j | \nabla^2 | \psi_j \rangle.$$
(1.11)

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

$$E_{\rm s}[n] = T_{\rm s}[n] + \int d^3 \boldsymbol{r} \, n(\boldsymbol{r}) v_{\rm s}(\boldsymbol{r})$$
(1.12)

The variational principle for the KS system becomes

$$\frac{\delta}{\delta n} \left[T_{\rm s}[n] + \int d^3 \boldsymbol{r} \, v_{\rm s}(\boldsymbol{r}) n(\boldsymbol{r}) - \mu \int d^3 \boldsymbol{r} n(\boldsymbol{r}) \right] = \frac{\delta T_{\rm s}[n]}{\delta n} + v_{\rm s} - \mu = 0, \qquad (1.13)$$

where again the Lagrange multiplier μ 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 $E_{\rm s}[n] = \sum_{j=1}^{N_{\rm occ}} \varepsilon_j$. Now one can write $\mathscr{F}[n]$ for the fully interacting system as

$$\mathscr{F}[n] = T[n] + \mathscr{W}[n]$$

= $T_{\rm s}[n] + E_{\rm H}[n] + T[n] - T_{\rm s}[n] + \mathscr{W}[n] - E_{\rm H}[n]$
= $T_{\rm s}[n] + E_{\rm H}[n] + E_{\rm xc},$ (1.14)

where $E_{\rm H}[n] = \frac{1}{2} \iint d^3 \mathbf{r} d^3 \mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$ is the so-called Hartree energy, and defining in this way the exchange-correlation energy $E_{\rm xc} = T[n] - T_{\rm s}[n] + \mathscr{W}[n] - E_{\rm H}[n]$. Thus, $E_{\rm xc}[n]$

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 $\mathscr{F}[n]$. $E_{\rm xc}$ turns out to be small as compared to $T_{\rm s}[n] + E_{\rm H}[n]$, so even if it is approximated in a crude way, the resulting method may work reasonably well. However, although $E_{\rm xc}$ 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 $E_{\rm xc}$ in KS DFT. The total energy of the interacting system can be written as

$$E[n] = T[n] + \mathscr{W}[n] + E_{\text{ext}}[n] = T_{\text{s}}[n] + E_{\text{H}}[n] + E_{\text{xc}}[n] + E_{\text{ext}}[n].$$
(1.15)

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

$$\frac{\delta T_{\rm s}[n]}{\delta n(\boldsymbol{r})} + \frac{\delta E_{\rm H}[n]}{\delta n(\boldsymbol{r})} + \frac{\delta E_{\rm xc}[n]}{\delta n(\boldsymbol{r})} + v_{\rm ext}(\boldsymbol{r}) - \mu = 0.$$
(1.16)

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

$$v_{\rm s}(\boldsymbol{r}) = \frac{\delta E_{\rm H}[n]}{\delta n} + \frac{\delta E_{\rm xc}[n]}{\delta n} + v_{\rm ext}(\boldsymbol{r}) = v_{\rm H}(\boldsymbol{r}) + v_{\rm xc}(\boldsymbol{r}) + v_{\rm ext}(\boldsymbol{r}), \qquad (1.17)$$

where $v_{\rm H}(\mathbf{r}) = \frac{\delta E_{\rm H}[n]}{\delta n} = \int d^3\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$ is the Hartree potential and $v_{\rm xc}(\mathbf{r}) = \frac{\delta E_{\rm xc}[n]}{\delta n}$ 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 $v_{\rm xc}(\mathbf{r})$, the DFT results would be exact. While the exact $v_{\rm xc}(\mathbf{r})$ is not known, several approximations for it has been developed. The approximations which represent $E_{\rm xc}$ 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 $E_{\rm xc}$ is always local, i.e., it is an integral of the exchange-correlation energy density $\varepsilon_{\rm xc}(\mathbf{r})$ [that $E_{\rm xc} = \int d\mathbf{r} n(\mathbf{r})\varepsilon_{\rm xc}(\mathbf{r})$] which depends on the density at a point \mathbf{r} (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, λ 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 λ is

$$\hat{H}^{\lambda} = \hat{T} + \hat{V}^{\lambda}_{\text{ext}} + \lambda \hat{\mathscr{W}}, \qquad (1.18)$$

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

$$E_0^{\lambda=1} = E_0^{\lambda=0} + \int_0^1 d\lambda \frac{dE_0^{\lambda}}{d\lambda} = E_0^{\lambda=0} + \int_0^1 d\lambda \left[\langle \Psi^{\lambda} | \frac{d\hat{V}_{\text{ext}}^{\lambda}}{d\lambda} | \Psi^{\lambda} \rangle + \langle \Psi^{\lambda} | \hat{\mathscr{W}} | \Psi^{\lambda} \rangle \right], \quad (1.19)$$

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

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

It should be noticed that $E_0^{\lambda=0} = E_s$ is the ground-state energy of the KS system, $v_{\text{ext}}^{\lambda=0} = v_{\text{s}}$ 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

$$E_{0} = E_{s} - \int d^{3}\boldsymbol{r} \, n(\boldsymbol{r}) v_{s}(\boldsymbol{r}) + \int d^{3}\boldsymbol{r} \, n(\boldsymbol{r}) v_{ext}(\boldsymbol{r}) + \int_{0}^{1} d\lambda \, \langle \Psi^{\lambda} | \hat{\mathscr{W}} | \Psi^{\lambda} \rangle$$

$$= T_{s} + E_{ext} + \int_{0}^{1} d\lambda \, \langle \Psi^{\lambda} | \hat{\mathscr{W}} | \Psi^{\lambda} \rangle, \qquad (1.21)$$

where we used the fact that $T_s = E_s - \int d^3 \mathbf{r} n(\mathbf{r}) v_s(\mathbf{r})$. Now comparing Eq. (1.15) and Eq. (1.21), we get

$$E_{\rm xc}[n] = \int_0^1 d\lambda \, \langle \Psi^\lambda | \hat{\mathscr{W}} | \Psi^\lambda \rangle - E_{\rm H}[n].$$
(1.22)

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

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

$$g(\boldsymbol{r},\boldsymbol{r}') = \frac{1}{n(\boldsymbol{r})n(\boldsymbol{r}')} \langle \Psi_0 | \sum_{i \neq j} \delta(\boldsymbol{r} - \boldsymbol{r}_i) \delta(\boldsymbol{r}' - \boldsymbol{r}_j) | \Psi_0 \rangle.$$
(1.23)

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

$$\hat{\mathscr{W}} = \frac{1}{2} \sum_{i \neq j} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} = \frac{1}{2} \iint d^3 \boldsymbol{r} d^3 \boldsymbol{r}' \sum_{i \neq j} \frac{\delta(\boldsymbol{r} - \boldsymbol{r}_i)\delta(\boldsymbol{r}' - \boldsymbol{r}_j)}{|\boldsymbol{r} - \boldsymbol{r}'|}, \quad (1.24)$$

the expectation value of this operator can be written as

$$\langle \Psi_0 | \hat{\mathscr{W}} | \Psi_0 \rangle = \frac{1}{2} \iint d^3 \mathbf{r} d^3 \mathbf{r}' \sum_{i \neq j} \frac{\langle \Psi_0 | \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) | \Psi_0 \rangle}{|\mathbf{r} - \mathbf{r}'|}$$
(1.25)

$$= \frac{1}{2} \iint d^3 \boldsymbol{r} d^3 \boldsymbol{r}' \, \frac{n(\boldsymbol{r})n(\boldsymbol{r}')g(\boldsymbol{r},\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|},\tag{1.26}$$

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

$$E_{\rm xc}[n] = \frac{1}{2} \iint d^3 \boldsymbol{r} d^3 \boldsymbol{r}' \int_0^1 d\lambda \, \frac{n(\boldsymbol{r})n(\boldsymbol{r}')[g^\lambda(\boldsymbol{r},\boldsymbol{r}')-1]}{|\boldsymbol{r}-\boldsymbol{r}'|},\tag{1.27}$$

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

$$n_{\rm xc}^{\lambda}(\boldsymbol{r},\boldsymbol{r}') = n(\boldsymbol{r}')[g^{\lambda}(\boldsymbol{r},\boldsymbol{r}') - 1].$$
(1.28)

The average exchange-correlation hole function $n_{\rm xc}(\mathbf{r}, \mathbf{r}')$ of the system is defined as [48]

$$n_{\rm xc}(\boldsymbol{r},\boldsymbol{r}') = \int_0^1 d\lambda \, n_{\rm xc}^{\lambda}(\boldsymbol{r},\boldsymbol{r}') = \int_0^1 d\lambda \, n(\boldsymbol{r}') [g^{\lambda}(\boldsymbol{r},\boldsymbol{r}') - 1]. \tag{1.29}$$

This function represents the reduction in the probability of finding an electron at \mathbf{r}' in the presence of another electron at \mathbf{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 $n_{\rm xc}(\mathbf{r}, \mathbf{r}')$ as

$$E_{\rm xc}[n] = \frac{1}{2} \iint d^3 \boldsymbol{r} d^3 \boldsymbol{r}' \, \frac{n(\boldsymbol{r}) n_{\rm xc}(\boldsymbol{r}, \boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}.$$
(1.30)

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 $\int d^3 \mathbf{r}' n_{\rm xc}(\mathbf{r}, \mathbf{r}') = -1$. 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

$$\hat{H} = \hat{F} + \hat{V} + \hat{W},\tag{1.31}$$

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 $E_{\rm int}$ as

$$E_{\rm int} = \sum_{n=1}^{\infty} \sum_{j=0}^{\infty} \left(E_{\rm RS}^{(nj)} + E_{\rm exch}^{(nj)} \right), \tag{1.32}$$

where the superscripts n and j denote the orders in \hat{V} and \hat{W} respectively. The corrections $E_{\rm RS}^{(nj)}$ are defined in the Rayleigh-Schrödinger perturbation theory, while

 $E_{\text{exch}}^{(nj)}$ 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]

$$E_{\rm disp}^{(2)} = \sum_{k \neq 0} \sum_{l \neq 0} \frac{|\langle \Phi_0^A \Phi_0^B | \hat{V} | \Phi_k^A \Phi_l^B \rangle|^2}{E_0^A + E_0^B - E_k^A - E_l^B},\tag{1.33}$$

where \hat{V} is intermonomer interaction operator and Φ_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]

$$E_{\rm disp}^{(2)} = -\frac{1}{2\pi} \int_0^\infty du \int \int \int \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_1' d\mathbf{r}_2' \frac{\chi_A(\mathbf{r}_1, \mathbf{r}_1', iu) \chi_B(\mathbf{r}_2, \mathbf{r}_2'), iu}{|\mathbf{r}_1 - \mathbf{r}_2| |\mathbf{r}_1' - \mathbf{r}_2'|}, \qquad (1.34)$$

where χ_A and χ_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 α is used instead of χ in this context, with $\alpha(\mathbf{r}, \mathbf{r}', iu) = -\chi(\mathbf{r}, \mathbf{r}', iu)$. Eq. (1.34) is often called the generalized Casimir-Polder expression. The second-order dispersion energy can also be written as

$$E_{\rm disp}^{(2)} = \langle \Phi_0 | V | \Phi_{\rm disp}^{(1)} \rangle, \qquad (1.35)$$

where $|\Phi_0\rangle = |\Phi_0^A \Phi_0^B\rangle$ and $\Phi_{disp}^{(1)}$ is the first-order dispersion wave function of the system, given by

$$|\Phi_{\rm disp}^{(1)}\rangle = \sum_{k \neq 0, l \neq 0} \frac{|\Phi_k^A \Phi_l^B\rangle \langle \Phi_k^A \Phi_l^B| V | \Phi_0^A \Phi_0^B\rangle}{E_0^A + E_0^B - E_k^A - E_l^B}.$$
 (1.36)

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

$$E_{\rm exch-disp}^{(2)} = -\langle \Phi_0 | (V - \bar{V}) (P_1 - \bar{P}_1) | \Phi_{\rm disp}^{(1)} \rangle, \qquad (1.37)$$

where $\bar{V} = \langle \Phi_0 | V | \Phi_0 \rangle$ and $\bar{P}_1 = \langle \Phi_0 | P_1 | \Phi_0 \rangle$ with the antisymmetrization limited to single pair exchanges of electrons between the monomers denoted by P_1 .

It should be mentioned that CCSD(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 CCSD(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 Å [18]. One can say that these methods are myopic with the range of vision of about 1 Å. 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 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 Ar₂: 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, $E_{\rm dispx}$. 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 [CCSD(T)]. We have also plotted the dispersion energy

$$E_{\rm dispx} = E_{\rm disp}^{(2)} + E_{\rm exch-disp}^{(2)} + E_{\rm disp}^{(3)} + E_{\rm exch-disp}^{(3)}, \qquad (2.1)$$

where $E_{\text{disp}}^{(i)}$ ($E_{\text{exch-disp}}^{(i)}$) 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 Å, 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 Å, DFT interaction energies start to agree with the benchmark. However, this is mainly because E_{dispx} becomes a small fraction of the total interaction energy, only 12% in magnitude at R = 1.5 Å.

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 Ar₂ corresponding to various DFT functionals compared to $E_{disp}^{(2)} + E_{exch-disp}^{(2)}$ and to the dispersion energy from the asymptotic expansion, $E_{disp,as}^{(2)}$. The latter quantities were computed using SAPT(DFT) to be at the same level of theory as D3, see Appendix B.

D3BJ(PBE) is reduced in magnitude by a factor of almost 2 at the vdW minimum, $R_{\rm vdW} = 3.76$ Å, as compared to D3(no-switching). This reduction is strikingly different from the physical damping of the asymptotic dispersion energy, $E_{\rm disp,as}^{(2)}$, as shown by the ratio of this quantity to $E_{\rm disp}^{(2)}$ amounting to about 1.06. The D3BJ switching is also too large to account for the exchange-dispersion effects, included in the curve $E_{\rm disp}^{(2)} + E_{\rm exch-disp}^{(2)}$. 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 Å, 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 dimens 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 CCSD(T)interaction energies as well as the ratio $E_{\rm dispx}/E_{\rm int}^{\rm CCSD(T)}$ for Ar–Li⁺. Surprisingly, all DFT methods overestimate the magnitude of interaction energy by about 10-25% at $R_{\rm vdW}$ (2.4 Å) where the dispersion energy amounts to only 5% of $E_{\rm int}^{\rm CCSD(T)}$. Thus, if one accepts the hypothesis that DFT approximations recover a part of the dispersion energy near $R_{\rm vdW}$, for Ar–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 dispersion*less* 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

$$E_{\rm dl} = E_{\rm int}^{\rm CCSD(T)} - E_{\rm dispx}.$$
 (2.2)



Figure 2.3: Ratio of DFT interaction energies and E_{dispx} to CCSD(T) interaction energy for the Ar – Li⁺ complex.

 $E_{\rm dl}$ does not contain any of the intermonomer electron correlation effects as these are, by definition, included in $E_{\rm dispx}$. However, it still contains some intramonomer correlation effects on interaction energies. Another quantity, $E_{\rm extra}$, is defined as

$$E_{\text{extra}} = E_{\text{int}}^{\text{DFT}} - E_{\text{dl}}.$$
(2.3)

Thus, E_{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 Ar₂ 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 Ar₂.



Figure 2.5: The ratios $E_{\text{extra}}/E_{\text{dispx}}$, $\Delta E_{\text{x}}/E_{\text{dispx}}$, $\Delta E_{\text{c}}/E_{\text{dispx}}$, and $\Delta E_{\text{xc}}/E_{\text{dispx}}$ for the argon dimer.

is a considerable spread in the values of this ratio near $R_{\rm vdW}$, the values are again very close to each other for the shortest separations shown (except for HF, LDA and dlDF [20]); (c) The ratio $E_{\rm extra}/E_{\rm dispx}$ reaches the value of 1 near R = 2 Å 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 $E_{\rm extra}$ larger in magnitude than $E_{\rm dispx}$ 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 $R_{\rm vdW}$ 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, $E_{\rm int}^{\rm HF}$ is not equal to $E_{\rm dl}$ 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 Å. Clearly, all these findings indicate that $E_{\rm extra}$ 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 $E_{\rm extra}$ computed using wave-function methods is approximately constant with R.

To get insights into the origin of E_{extra} , we plot in Fig. 2.5 the ratios $E_{\text{extra}}/E_{\text{dispx}}$, $\Delta E_{\rm c}/E_{\rm dispx}$, $\Delta E_{\rm x}/E_{\rm dispx}$, and $\Delta E_{\rm xc}/E_{\rm dispx} = (\Delta E_{\rm x} + \Delta E_{\rm c})/E_{\rm dispx}$, where $\Delta E_{\rm x}$ ($\Delta E_{\rm c}$) 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 ΔE_x). One may assume that if any component of DFT reproduces the dispersion energy, it should be mainly $\Delta E_{\rm c}$, but $\Delta E_{\rm x}$ can also contribute [69, 70]. Let us discuss these ratios for the SCAN functional. The behavior of $\Delta E_{\rm c}$ is reasonably physical as the ratio $\Delta E_{\rm c}/E_{\rm dispx}$ increases gradually with the decrease of R from zero to about 1 near R = 2.5 Å (but then starts to decrease). However, $\Delta E_{\rm c}/E_{\rm dispx}$ 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 $\Delta E_{\rm c}/E_{\rm dispx}$, $\Delta E_{\rm x}/E_{\rm dispx}$ changes rapidly with R, ranging from -1 to 3.5, the behavior clearly rooted in LDA. The negative sign for separations somewhat larger than $R_{\rm vdw}$, i.e., positive $\Delta E_{\rm x}$, means that the notion that $\Delta E_{\rm x}$ 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 Ar–HF and $(H_2O)_2$.

where $\Delta E_{\rm x}$ is positive, $\Delta E_{\rm c}$ is almost zero, but $E_{\rm extra}/E_{\rm dispx}$ reaches values as high as 0.5. This means that the non-exchange-correlation (non-xc) components of $E_{\rm extra}$ "reproduce" dispersion. For other functionals in Fig. 2.5, the relations are generally more chaotic and in particular $\Delta E_{\rm c}/E_{\rm dispx}$ and $E_{\rm extra}/E_{\rm dispx}$ 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 $\Delta E_{\rm xc}/E_{\rm dispx}$ and $E_{\rm extra}/E_{\rm dispx}$. In Appendix B we present similar results for LRC- ω PBEh [71] and ω B97 [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 Ar–HF and $(H_2O)_2$. The results for Ar–HF are

very similar to 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 CCSD(T) ones) could be several times larger than E_{dispx} , as the latter quantity amounts to only 1% of E_{int} at R = 10 Å.

If semilocal DFT approximations do not recover E_{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 $E_{\rm dl}$, 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 $E_{\rm dl}$, 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_{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_{extra} changes from zero at $R \to \infty$ to a value close to E_{dispx} at some R somewhat smaller than $R_{\rm vdW}$. We show, however, that $E_{\rm extra}$ does not have physical characteristics expected of dispersion energy. A major failure is that after becoming equal to $E_{\rm dispx}$, $E_{\rm extra}$ continues to increase in magnitude as R decreases. Furthermore, $E_{\rm extra}$ originates only in a small part from $\Delta E_{\rm c}$, whereas the major contributions come from $\Delta E_{\rm x}$ 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 Ar-proton and Ar-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]

$$E_{\rm disp}^{(2)} = -\int_0^\infty \frac{du}{2\pi} \iiint d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 d^3 \mathbf{r}_3 d^3 \mathbf{r}_4 \\ \times \chi_A(\mathbf{r}_1, \mathbf{r}_2, iu) \chi_B(\mathbf{r}_3, \mathbf{r}_4, iu) w(r_{14}) w(r_{23}),$$
(3.1)

where $w(r_{ij}) = 1/r_{ij} = 1/|\mathbf{r}_i - \mathbf{r}_j|$ is the inverse of the interelectronic distance and χ_X , X = A, B is the density-density response function of system X at imaginary frequency iu. This response function can be written in terms of the polarizability-density tensor $\alpha_X^{ij}(\mathbf{r}_1, \mathbf{r}_2, \mathrm{i}u)$ [79, 80]

$$\chi_X(\boldsymbol{r}_1, \boldsymbol{r}_2, \mathrm{i}u) = -\sum_{i,j=1}^3 \frac{\partial^2}{\partial x_{1\,i} \,\partial x_{2\,j}} \,\alpha_X^{ij}(\boldsymbol{r}_1, \boldsymbol{r}_2, \mathrm{i}u), \qquad (3.2)$$

where x_{ki} are the components of \mathbf{r}_k . If one assumes that α_X^{ij} can be approximated by a diagonal and local quantity,

$$\alpha_X^{ij}(\boldsymbol{r}_1, \boldsymbol{r}_2, \mathrm{i}u) = \delta_{ij} \,\alpha_X(\boldsymbol{r}_1, \mathrm{i}u) \,\delta(\boldsymbol{r}_1 - \boldsymbol{r}_2), \tag{3.3}$$

where $\alpha_X(\mathbf{r}_1, iu)$ is called the local polarizability density, Eq. (3.1) becomes

$$E_{\rm disp}^{(2)} = -\frac{3}{\pi} \int_0^\infty du \iint d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 \times \frac{\alpha_A(\mathbf{r}_1, iu) \alpha_B(\mathbf{r}_2, iu)}{r_{12}^6}.$$
 (3.4)

This expression is singular if α_A and α_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 α_A and α_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)

$$E_{\text{disp}}^{\text{DADE}} = -\frac{3}{\pi} \int_0^\infty du \iint d^3 \boldsymbol{r}_1 d^3 \boldsymbol{r}_2 f_8(\beta(r_{12}), r_{12}) \\ \times \frac{\alpha_A(\boldsymbol{r}_1, \mathrm{i}u)\alpha_B(\boldsymbol{r}_2, \mathrm{i}u)}{r_{12}^6}, \qquad (3.5)$$

where $f(\beta, r_{12})$ 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 $\lim_{x\to 0} f_8(\beta, x)/(\beta x)^6 = (\beta x)^3/9!$ 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: $\alpha(\mathbf{r}_1, iu) = 1/4\pi \int d^3\mathbf{r}_2 S(\mathbf{r}_1, \mathbf{r}_2, iu)$ [81]. The formula for the S-function assumed in Ref. [25] leads to the following expression for the local polarizability density [82, 83]:

$$\alpha(\mathbf{r}, iu) = \frac{n(\mathbf{r})}{\omega_0^2(\mathbf{r}) + u^2},$$
(3.6)

where $n(\mathbf{r})$ is the electron density and $\omega_0(\mathbf{r})$ is a local excitation frequency. This frequency was assumed in Ref. [25] to be of the form

$$\omega_{0}(\boldsymbol{r}) = \frac{9}{8\pi} \Biggl[k_{\rm F}(\boldsymbol{r}) \Biggl(1 - \frac{Z_{ab}}{9} \Biggl(\frac{|\boldsymbol{\nabla}n(\boldsymbol{r})|}{2k_{\rm F}(\boldsymbol{r})n(\boldsymbol{r})} \Biggr)^{2} \Biggr) - \frac{4\pi}{3} \varepsilon_{c}^{\rm LDA}(\boldsymbol{r}) \Biggr]^{2}, \qquad (3.7)$$

where $k_{\rm F}(\mathbf{r}) = [3\pi^2 n(\mathbf{r})]^{1/3}$ is the length of the Fermi wave vector, $\varepsilon_c^{\rm LDA}(\mathbf{r})$ is the LDA correlation energy density, and Z_{ab} is a parameter which was interpreted in Ref. [25] as originating from screened exchange. The excitation frequency ω_0 is a special value of a more general function $\omega_q(\mathbf{r})$ defined in Ref. [25]: $\omega_0(\mathbf{r}) = \omega_q(\mathbf{r})|_{q=0}$. The choice of $\omega_0(\mathbf{r})$ given by Eq. (3.7) ensures that the polarizability density decays like $n(\mathbf{r})^{7/3}$, which leads to finite static polarizabilities and avoids nonphysical contribution from low density regions present in ALL. Using $\alpha(\mathbf{r}, iu)$ given by Eq. (3.6) in Eq. (3.5) and integrating over the frequency, we get

$$E_{\rm disp}^{\rm DADE} = -\frac{3}{2} \iint d^3 \boldsymbol{r}_1 d^3 \boldsymbol{r}_2 \times \frac{f_8(\beta(r_{12}), r_{12}) n_A(\boldsymbol{r}_1) n_B(\boldsymbol{r}_2)}{\omega_0^A(\boldsymbol{r}_1) \omega_0^B(\boldsymbol{r}_2) \left[\omega_0^A(\boldsymbol{r}_1) + \omega_0^B(\boldsymbol{r}_2)\right] r_{12}^6}.$$
(3.8)

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_{ab} has been chosen to have a value between those used in vdW-DF1 [25] and vdW-DF2 [26], i.e., $Z_{ab} = -1.1972$. The function $\beta(r_{12})$ has been chosen of the form $\beta(r_{12}) = \beta_0 + \beta_1 e^{-\beta_2 r_{12}^2}$, where $\beta_0 = 1.70$, $\beta_1 = 1.90$, and $\beta_2 = \beta_0/10$. The values of Z_{ab} and β_i were roughly adjusted to achieve the best agreement with dispersion energies from symmetry-adapted perturbation theory (SAPT) based on DFT description of monomers [SAPT(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 Ar₂ data [84] to fit its parameters. Thus, our approach is non-empirical in this sense.

To perform the integration over \mathbf{r}_1 and \mathbf{r}_2 in Eq. (3.8), we rewrite this equation as

$$E_{\rm disp}^{\rm DADE} = -\frac{3}{2} \iint d^3 \boldsymbol{r}_1 \, d^3 \boldsymbol{r}_2 \, F(\boldsymbol{r}_1, \boldsymbol{r}_2) \tag{3.9}$$

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

$$E_{\text{disp}}^{\text{DADE}} = -\frac{3}{2} \sum_{a \in A} \sum_{b \in B} \sum_{i,j} \Delta^3 \boldsymbol{r}_i^a \Delta^3 \boldsymbol{r}_j^b \\ \times W^a(\boldsymbol{r}_i^a) W^b(\boldsymbol{r}_j^b) F(\boldsymbol{r}_i^a, \boldsymbol{r}_j^b), \qquad (3.10)$$

where W^c is Becke's atomic weight for atom c and $\Delta^3 \mathbf{r}_i^c$ is the volume of the grid cell at the grid point \mathbf{r}_i^c . This point is defined as $\mathbf{r}_i^c = \mathbf{R}^c + \mathbf{r}_i$, where \mathbf{R}^c is the position of atom c and \mathbf{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 A(B) since the density $n_A(n_B)$ 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_{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 vdW-DF2 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.

	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

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

SAPT(DFT). The benchmark interaction energies are CCSD(T) values in the complete basis set (CBS) limit. The SAPT(DFT) and CCSD(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 CCSD(T) benchmarks are at CBS limits, SAPT(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 Ar_2 and Ar-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 vdW-DF2 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_{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_{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 Rs 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_{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 dlDF 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

	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

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

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 dlDF+DADE is 4.4 times smaller than that of dlDF+disp(vdW-DF2). Similarly large ratios are found for Ar₂ and Ar-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], dlDF 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 Ar_2 and Ar-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_{ab} was adjusted, in DADE the parameters of the function β_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

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 Å, 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 DFT+D fashion.

The most popular DFT+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^{ab} 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^{ab} 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 DFT+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 $R \to 0$). 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 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 DFT+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

$$E_{\rm dispx} = E_{\rm disp}^{(20)} + E_{\rm disp}^{(21)} + E_{\rm disp}^{(22)} + E_{\rm exch-disp}^{(20)} + E_{\rm disp}^{(30)} + E_{\rm exch-disp}^{(30)}, \tag{4.1}$$

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_{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]

$$E_{\rm disp}^{(2)} = -\frac{1}{2\pi} \int_0^\infty du \iiint d^3 \mathbf{r} d^3 \mathbf{r}' d^3 \mathbf{r}'' d^3 \mathbf{r}''' \frac{\chi_a(\mathbf{r}, \mathbf{r}', iu)\chi_b(\mathbf{r}'', \mathbf{r}''', iu)}{|\mathbf{r} - \mathbf{r}''||\mathbf{r}' - \mathbf{r}'''|}, \qquad (4.2)$$

where χ_a and χ_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

$$E_{\text{dispx}} = E_{\text{disp}}^{(2)}(\text{CKS}) + E_{\text{exch-disp}}^{(2)}(\text{CKS}).$$
(4.3)

The values of E_{dispx} defined by this equation have been taken from the calculations in Taylor *et al.* [33], except for the Ar₂ 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 $E_{\rm c}$ 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 $E_{\rm c}$ 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 r-dependent pole frequency which was assumed to be a simple function depending also on the magnitude of the wave vector q

$$\omega_q(\mathbf{r}) = \frac{q^2}{2} \left[1 - e^{-\frac{4\pi}{9} \left(\frac{q}{q_0(\mathbf{r})}\right)^2} \right]^{-1}.$$
(4.4)

where

$$q_0(\boldsymbol{r}) = k_{\rm F}(\boldsymbol{r}) \left[1 - \frac{Z_{ab}}{9} \left(\frac{|\boldsymbol{\nabla}\rho(\boldsymbol{r})|}{2k_F(\boldsymbol{r})\rho(\boldsymbol{r})} \right)^2 \right] - \frac{4\pi}{3} \varepsilon_{\rm c}^{\rm LDA}(\boldsymbol{r}).$$
(4.5)

The quantities appearing in Eq. (4.5) are the same as used in semilocal DFTs: $\rho(\mathbf{r})$ is the ground-state electron density, $k_{\rm F}(\mathbf{r}) = [3\pi^2\rho(\mathbf{r})]^{1/3}$ is the magnitude of the Fermi vector, and $\varepsilon_{\rm c}^{\rm LDA}(\mathbf{r})$ is the correlation energy density in LDA. The value of the parameter Z_{ab} 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 $\omega_q(\mathbf{r})$ as

$$E_{\rm c}^{\rm nl} \approx \frac{1}{2} \iint d^3 \boldsymbol{r} d^3 \boldsymbol{r}' \,\rho(\boldsymbol{r}) \Phi(\boldsymbol{r}, \boldsymbol{r}') \rho(\boldsymbol{r}'), \tag{4.6}$$

with the so-called nonlocal correlation kernel $\Phi(\mathbf{r}, \mathbf{r}')$ given by

$$\Phi(\mathbf{r},\mathbf{r}') = \frac{2}{\pi^2} \int_0^\infty da \int_0^\infty db \, a^2 b^2 \, W(a,b) \, T(\nu(a),\nu(b),\nu'(a),\nu'(b)), \tag{4.7}$$

where

$$T(w, x, y, z) = \frac{1}{2} \left[\frac{1}{w+x} + \frac{1}{y+z} \right] \left[\frac{1}{(w+y)(x+z)} + \frac{1}{(w+x)(y+z)} \right], \quad (4.8)$$
$$W(a, b) = \left[(a^2 + b^2 - 3) \sin a \sin b - 3ab \cos a \cos b \right]$$

$$(a^{2} + b^{2} - 3) \sin a \sin b - 3ab \cos a \cos b + a(3 - b^{2}) \cos a \sin b + b(3 - a^{2}) \sin a \cos b \left[\frac{2}{a^{3}b^{3}},$$

$$(4.9)$$

and the auxiliary variables are $\nu(a) = \omega_q(\mathbf{r})|\mathbf{r} - \mathbf{r}'|^2$ and $\nu'(a) = \omega_q(\mathbf{r}')|\mathbf{r} - \mathbf{r}'|^2$ with $q = a/|\mathbf{r} - \mathbf{r}'|$ and similarly for b. Thus, E_c^{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_{ab} 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 revPBE-PW92 [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_{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_{ab} .

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 $\omega_0^2(\mathbf{r}) = C \left| \frac{\nabla \rho(\mathbf{r})}{\rho(\mathbf{r})} \right|^4 + 4\pi \rho(\mathbf{r})/3$. 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

$$\Phi_{\rm VV10}(\boldsymbol{r}, \boldsymbol{r}') = -\frac{3}{2} \frac{1}{g(\boldsymbol{r})g(\boldsymbol{r}') \left[g(\boldsymbol{r}) + g(\boldsymbol{r}')\right]},\tag{4.10}$$

where $g(\mathbf{r}) = \sqrt{\omega_0^2(\mathbf{r})} |\mathbf{r} - \mathbf{r}'|^2 + \kappa(\mathbf{r})$. The term $\kappa(\mathbf{r}) = b k_{\rm F}^2(\mathbf{r})/(2\pi\rho(\mathbf{r}))$ controls here the short-range damping where b is a constant determined by fitting to benchmark data of ab 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 $E_{\rm dispx}$. 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 $E_{\rm dispx}$ 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^{ab} 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^{ab} constants computed from the Casimir-Polder expression using TD-DFT FDDSs. The C_8^{ab} and higher constants were then computed from C_6^{ab} 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

$$E_{\text{disp}} = -\sum_{a \in A, b \in B} \sum_{n=6,8,10} s_n \frac{C_n^{ab}}{r_{ab}^n + \left[f_{\text{damp}}(a_1, a_2, R_0^{ab}) \right]^n},$$
(4.11)

where r_{ab} 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 $f_{\text{damp}} = a_1 R_0^{ab} + a_2$, where a_1 and a_2 are adjustable parameters and $R_0^{ab} = \sqrt{C_8^{ab}/C_6^{ab}}$. As discussed earlier, the damping/scaling parameters have been fitted to a set of *ab 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_{dispx} from SAPT. Such a dispersion function, D_{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

$$\boldsymbol{d}_{\mathbf{X}\sigma}(\boldsymbol{r}) = \frac{1}{\rho_{\sigma}(\boldsymbol{r})} \sum_{ij} \phi_{i\sigma}(\boldsymbol{r}) \phi_{j\sigma}(\boldsymbol{r}) \int \boldsymbol{r}' \phi_{i\sigma}(\boldsymbol{r}') \phi_{j\sigma}(\boldsymbol{r}') \, d^3 \boldsymbol{r}' - \boldsymbol{r}, \qquad (4.12)$$

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

$$\langle d_X^2 \rangle_a = \sum_{\sigma} \int \omega_a(\boldsymbol{r}) \, \rho_\sigma(\boldsymbol{r}) |\boldsymbol{d}_{\mathrm{X}\,\sigma}(\boldsymbol{r})|^2 \, d^3 \boldsymbol{r},$$
(4.13)

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

$$C_6^{ab} = \frac{\alpha_a \alpha_b \langle d_X^2 \rangle_a \langle d_X^2 \rangle_b}{\langle d_X^2 \rangle_a \alpha_b + \langle d_X^2 \rangle_b \alpha_a},\tag{4.14}$$

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

$$\alpha_a = \frac{\int r^3 w_a(\boldsymbol{r}) \rho(\boldsymbol{r}) d^3 \boldsymbol{r}}{\int r^3 \rho_a^{\text{free}}(\boldsymbol{r}) d^3 \boldsymbol{r}} \ \alpha_a^{\text{free}} = \frac{V_a^{\text{eff}}}{V_a^{\text{free}}} \alpha_a^{\text{free}}, \tag{4.15}$$

where $\rho_a^{\text{free}}(\mathbf{r})$ 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^{eff} , and of the free atom, V_a^{free} . The coefficients C_8^{ab} and C_{10}^{ab} 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^{ab} is replaced by $\frac{1}{3} \left[\left(\frac{C_8^{ij}}{C_6^{ij}} \right)^{1/2} + \left(\frac{C_{10}^{ij}}{C_6^{ij}} \right)^{1/4} + \left(\frac{C_{10}^{ij}}{C_8^{ij}} \right)^{1/2} \right]$ (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 polarizabilities 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]

$$\tau_{ab} = \sum_{i,j=1}^{3} \frac{\partial^2}{\partial x_a^i \partial x_b^j} \frac{1 - \exp[(r_{ab}/\bar{r}_{ab}^{\rm vdW})^\beta]}{r_{ab}},\tag{4.16}$$

where $\bar{r}_{ab}^{vdW} = \bar{r}_{a}^{vdW} + \bar{r}_{b}^{vdW}$ is sum of van der Waals radii. The term in the numerator introduces damping in the MBD method and the parameter β is fitted to match DFT+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_{dispx} defined by Eq. (4.3) were taken from Ref. [33] except for those for Ar₂ 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 $/\sim$ 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 sensitivity 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- ω PBE [71] RSH functional. The VV10 calculations were done with 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^{ab}/r_{ab}^6 and C_8^{ab}/r_{ab}^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[PW86-PBE] the approach that uses terms involving C_6^{ab} and C_8^{ab} , while XDM10[PW86-PBE] uses C_{10}^{ab} 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_{dispx} are listed in Table 4.1 and shown as scatter plots in Fig. 4.1. The ratios of the dispersion energies to E_{dispx} as functions of intermonomer separation Rare 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 Å, 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

XDM10[No-	switching]	7.56	10.33	454.81	70.55	38.63	57.31	60.59	123.01	309.59	39.73	127.65	55.51	119.07
disp(vdW-	DF1)	49.20	79.19	76.26	51.69	44.62	42.49	44.08	69.46	34.97	39.21	21.58	32.65	48.78
XDM8[No-	switching]	12.21	5.36	101.96	32.13	10.41	18.80	28.90	57.49	73.23	15.98	43.70	20.70	25, 07
XDM8	[PW86-PBE]	35.91	27.24	36.17	29.77	30.37	30.72	29.00	37.99	35.41	28.72	44.87	34.76	33.41
D3MBJ	[PBE]	28.38	29.68	37.85	26.18	32.42	33.55	22.68	27.09	40.10	21.19	41.73	36.52	21.45
XDM10	[PW86-PBE]	30.13	22.89	34.59	28.91	26.52	26.22	27.34	37.34	30.55	26.80	39.70	28.48	90.06
D3BJ[PBE]		27.73	27.20	34.94	23.25	29.94	30.49	21.14	27.12	37.70	21.87	41.73	33.95	90.76
disp(MBD)		39.13	32.38	36.11	22.18	27.29	28.89	26.41	26.03	31.40	22.06	34.39	26.79	90.49
disp(VV09)		24.82	27.40	48.77	31.34	34.50	23.83	25.22	23.86	23.99	42.18	19.81	26.24	90.22
-Wbv(vdW-	DF2)	26.98	23.56	29.40	25.96	26.31	29.20	28.75	17.14	42.10	23.05	42.08	30.14	98 79
disp(VV10)		21.05	19.33	31.46	21.19	22.15	23.05	19.90	27.28	30.69	23.92	34.04	17.35	94.98
D3[No-	switching]	3.79	9.36	50.73	6.21	5.14	7.32	6.80	25.08	46.19	7.06	27.95	14.74	17 53
DADE		9.55	6.86	15.03	6.77	10.52	6.85	6.58	9.06	24.89	7.82	27.68	11.55	11 02
D3BJ[HF]		8.94	13.24	14.21	4.76	9.62	9.83	4.81	10.01	21.46	6.79	18.35	13.13	11 96
D_{as}		8.45	3.81	4.86	1.53	4.51	7.39	4.65	12.72	8.62	12.56	8.84	10.12	7 2.1
Dimer		Argon dimer	Ar-HF	Water dimer	Ethanol dimer	Nitromethane dimer	Methylformate dimer	Benzene-methane	Benzene-water	Imidazole dimer	Nitrobenzene dimer	FOX-7 dimer	EDNA dimer	Arona of MADEe

<u> </u>
29
lef
Ц
Ш
frc
e
ബ
ts
sul
re
Ē
Ą
Q
Ц.
хd
dis
Ы
$_{\mathrm{to}}$
ē
tiv
la,
re
ds
ĮÕ
etł
Ĕ
Ŋ
ate
. <u>60</u>
Sct
IV
E.
E
frc
Σ
gre
ш
пe
ioi
SIS
βD€
dis
f
C S
Ĕ
$^{\rm AF}$
Μ
-
÷
4
\mathbf{le}
qε
Ĥ

XDM10[No-	switching]	5.10	7.51	336.71	56.89	28.00	43.81	47.88	97.79	235.25	28.91	103.23	42.69	86.15
- disp(vdW-	DF1)	47.91	78.84	78.06	50.50	44.06	43.74	43.16	68.94	36.84	37.40	24.84	31.21	48.79
XDM8[PW86	PBE]	36.72	27.92	37.34	31.41	31.82	32.76	30.93	40.06	37.38	30.91	46.46	36.68	35.03
D3MBJ	[PBE]	29.64	30.49	39.22	28.42	34.30	35.97	25.32	30.17	42.37	24.35	43.75	38.87	33.57
disp(vdW-	DF2)	29.05	25.19	32.50	29.20	30.44	33.34	32.84	20.30	45.55	27.04	45.58	34.45	32.12
D3BJ[PBE]		28.77	27.97	36.38	25.56	31.78	32.96	23.80	30.13	40.02	24.86	43.75	36.32	31.86
XDM10	[PW86-PBE]	31.13	23.72	35.93	30.94	28.26	28.57	29.74	39.21	32.88	29.23	41.60	30.78	31.83
disp(MBD)		39.87	33.06	37.62	24.76	29.18	31.57	29.02	29.11	33.82	25.01	36.66	29.35	31.59
disp(VV09)		26.27	28.25	49.74	33.04	36.35	27.00	27.12	26.36	26.90	45.46	22.78	27.31	31.38
disp(VV10)		22.52	20.49	33.52	23.96	24.90	26.08	22.72	30.50	33.41	27.21	36.70	20.57	26.88
-on] 8mdx	switching]	14.63	7.43	72.06	23.71	3.65	10.46	20.78	43.83	50.78	8.60	32.46	13.84	25.19
D3BJ[HF]		11.22	14.81	18.78	9.50	14.04	14.82	9.80	11.55	26.49	12.03	23.19	17.93	15.35
DADE		12.07	8.71	19.75	7.29	15.06	12.48	6.39	9.13	30.40	7.20	32.14	16.46	14.76
D3[No-	switching]	6.48	11.20	33.56	2.87	6.38	4.77	4.86	15.18	33.04	8.92	20.70	11.24	13.27
D_{as}		10.34	5.16	11.41	6.30	2.24	12.89	9.83	11.63	11.60	8.31	9.65	4.42	8.65
Dimer		Argon dimer	Ar-HF	Water dimer	Ethanol dimer	Nitromethane dimer	Methylformate dimer	Benzene-methane	Benzene-water	Imidazole dimer	Nitrobenzene dimer	FOX-7 dimer	EDNA dimer	Average of MAPEs

•
29]
<u> </u>
ef
щ
ш
fro
e
ສາ
lts
sul
r_{e}
Ē
Ą
Q V
Ξ.
isp
$E_{\rm d}$
Ö
e t
ive
at
rel
S
00
$^{\mathrm{th}}$
ne
ц Ц
te
ga
sti
Ve
in
n
fro
y f
L 00
ne
l e
ior
[S]
pe
\lim
f
0
Ĕ
ЧЪ
Μ
ñ
4
le
ab
Ĥ

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_{disp} (i.e., it is E_{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 D_{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 D_{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_{dispx} values and therefore includes the physical damping of asymptotic expansion. However, the training set used to fit D_{as} was [20, 21], with a couple exceptions, completely different from our test set, so our results do confirm robustness of D_{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 D3BJ[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 $1/r_{ab}^8$.

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 D3BJ[HF]. At small R, it overstimates the magnitude of dispersion energy (except for Ar₂ and Ar–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_{disp} rather than to E_{dispx} , see Table 4.2. This is an expected improvement since D3[No-switching] does not include exchange-dispersion effects.

The D3BJ[PBE] and D3MBJ[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 D3BJ[PBE] is quite different from D3[Noswitching] not only at short, but also at large R's. The reason is the scaling parameter for C_8^{ab} 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 D_{as} and D3BJ(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_{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_{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_{ab} 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_{ab} , 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[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 $E_{\rm disp}$, 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 $E_{\rm disp}$). 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 Rs 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 disp(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 D_{as} and D3BJ[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_{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 Rincluded 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 vdW-DF1 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_{dispx} values remain approximately constant. This is not the case in general and the ratios change dramatically for most methods except for D_{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_{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 dipoledipole-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 D_{as} and D3BJ[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_{dispx} .



Figure 4.2: The ratios of dispersion energies from investigated methods to E_{dispx} for Ar₂, 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_{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_{dispx} for homogeneous dimers of imidazole, nitrobenzene, FOX-7, and EDNA. For other details, see Figs. 4.2 and 4.3.

Chapter 5

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 $\chi(\boldsymbol{r}, \boldsymbol{r}', \mathrm{i}u)$ in terms of the polarizability-density tensor $\alpha_{ij}(\boldsymbol{r}, \boldsymbol{r}', \mathrm{i}u)$ [79, 80] as

$$\chi(\boldsymbol{r}, \boldsymbol{r}', \mathrm{i}u) = -\sum_{i,j=1}^{3} \frac{\partial^2}{\partial x_i \, \partial x'_j} \, \alpha_{ij}(\boldsymbol{r}, \boldsymbol{r}', \mathrm{i}u), \qquad (5.1)$$

where x_i are the components of \mathbf{r} . Furthermore, we introduced an approximate α_{ij} , a local and isotropic quantity by

$$\alpha_{ij}(\boldsymbol{r}, \boldsymbol{r}', iu) = \delta_{ij} \,\alpha(\boldsymbol{r}, iu) \,\delta(\boldsymbol{r} - \boldsymbol{r}'), \qquad (5.2)$$

where $\alpha(\mathbf{r}, iu)$ is called the local polarizability density.

The Cartesian dipole-dipole polarizability can be obtained from the densitydensity response function $\chi(\mathbf{r}, \mathbf{r}', iu)$ of time-dependent DFT (TD-DFT) as [167]

$$\alpha_{ij}(\mathbf{i}u) = -\iint d^3 \mathbf{r} d^3 \mathbf{r}' \, x_i x_j' \chi(\mathbf{r}, \mathbf{r}', \mathbf{i}u)$$
(5.3)

where x_i are components of r. Plugging Eq. (5.1) into Eq. (5.3) we get

$$\alpha_{ij}(\mathbf{i}u) = \sum_{i',j'=1}^{3} \iint d^3 \mathbf{r} d^3 \mathbf{r}' \, x_i x_j' \frac{\partial^2}{\partial x_{i'} \, \partial x_{j'}'} \, \alpha_{i'j'}(\mathbf{r}, \mathbf{r}', \mathbf{i}u), \tag{5.4}$$

Now integrating by parts and assuming α_{ij} and its gradient vanish when coordinates go to infinity we get

$$\alpha_{ij}(iu) = \iint d^3 \boldsymbol{r} d^3 \boldsymbol{r}' \, \alpha_{ij}(\boldsymbol{r}, \boldsymbol{r}', iu).$$
(5.5)

Thus, $\alpha_{ij}(\mathbf{r}, \mathbf{r}', iu)$ can be called two-electron dipole-dipole polarizability density at points \mathbf{r} and \mathbf{r}' since integration of this quantity over all coordinates gives us dipole-dipole polarizability of the system. Comparing Eq. (5.5) and Eq. (5.3) we get

$$\alpha_{ij}(\boldsymbol{r}, \boldsymbol{r}', \mathrm{i}u) = -x_i x'_j \chi(\boldsymbol{r}, \boldsymbol{r}', \mathrm{i}u)$$
(5.6)

Although the knowledge of χ gives α_{ij} in a trivial way, it does not allow us to find $\alpha(\mathbf{r}, iu)$ in Eq. (5.2). The polarizability density $\alpha_{ij}(\mathbf{r}, iu)$ can be defined from Eq. (5.6) as

$$\alpha_{ij}(\boldsymbol{r}, \mathrm{i}u) = \int d^3 \boldsymbol{r}' \,\alpha_{ij}(\boldsymbol{r}, \boldsymbol{r}', \mathrm{i}u) = -x_i \int d^3 \boldsymbol{r}' \,x'_j \chi(\boldsymbol{r}, \boldsymbol{r}', \mathrm{i}u). \tag{5.7}$$

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

$$\int d^{3}\boldsymbol{r}\alpha_{ij}(\boldsymbol{r},\boldsymbol{r}',\mathrm{i}u) = \delta_{ij} \int d^{3}\boldsymbol{r} \,\alpha(\boldsymbol{r},\mathrm{i}u)\delta(\boldsymbol{r}-\boldsymbol{r}'),$$
$$\alpha_{ij}(\boldsymbol{r}',\mathrm{i}u) = \delta_{ij}\alpha(\boldsymbol{r}',\mathrm{i}u), \qquad (5.8)$$

Therefore, the polarizability density given in Eq. (5.2) is $\alpha(\mathbf{r}, iu) = \sum_i \alpha_{ii}(\mathbf{r}, iu)/3$ 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]

$$\chi(\boldsymbol{r}, \boldsymbol{r}', \mathrm{i}u) = -\sum_{iv, i'v'} C_{iv, i'v'}(\mathrm{i}u)\phi_i(\boldsymbol{r})\phi_v(\boldsymbol{r})\phi_{i'}(\boldsymbol{r}')\phi_{v'}(\boldsymbol{r}'), \qquad (5.9)$$



Figure 5.1: Comparison of the polarizability density $\alpha(\mathbf{r}, iu)$ for the argon atom in the case x = z, y = 0.0, and u = 0.79 in atomic units.

where ϕ_i and ϕ_v are occupied and virtual orbitals of the considered system and $C_{iv,i'v'}(iu)$ linear coefficients determined by equations of TD-DFT. Using Eq. (5.9) in Eq. (5.7), the polarizability density can be written as

$$\alpha_{jk}(\boldsymbol{r}, \mathrm{i}u) = \sum_{iv, i'v'} C_{iv, i'v'}(\mathrm{i}u) \, x_j \, \phi_i(\boldsymbol{r}) \phi_v(\boldsymbol{r}) \int d^3 \boldsymbol{r}' \, x'_k \, \phi_{i'}(\boldsymbol{r}') \phi_{v'}(\boldsymbol{r}').$$
(5.10)

We computed polarizability density $\alpha(\mathbf{r}, iu)$ 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 α_{vdWDF2} and α_{DADE} , are obtained from Eqs. (3.6) and (3.7) with values of Z_{ab} taken to be -1.887 and -1.1972, respectively. For VV09 and VV10 cases, the polarizability density is same, denoted as α_{VV} and given by Eq. (3.6) with $\omega_0(\mathbf{r}) = \sqrt{4\pi n(\mathbf{r})/3 + 0.0089 \left|\frac{\nabla n(\mathbf{r})}{n(\mathbf{r})}\right|^4}$ 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 $\alpha(\mathbf{r}, iu)$ for the argon atom from vdW-DF2 (bottom-right), VV09/10 (top-right), and DADE (bottom-left) with the one obtained from TD-DFT (top-left) for y = 0.0 and u = 0.79 in atomic units.

The polarizability densities $\alpha_{vdW-DF2}(\mathbf{r}, iu)$ and $\alpha_{DADE}(\mathbf{r}, iu)$ agree reasonably

closely with $\alpha_{\text{TD}-\text{DFT}}(\mathbf{r}, iu)$, in particular when compared to $\alpha_{\text{VV}}(\mathbf{r}, iu)$ 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_{ab} . 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 $\delta(\mathbf{r} - \mathbf{r'})$ 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 SAPT(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

$$V = \sum_{a \in A, b \in B} u_{ab}(r_{ab}) = V_{\text{elst}} + V_{\text{exp}} + V_{\text{asymp}}^{(2)}$$
$$= \sum_{a \in A, b \in B} \left[u_{\text{elst}, ab}(r_{ab}) + u_{\text{exp}, ab}(r_{ab}) + u_{\text{asymp}, ab}^{(2)}(r_{ab}) \right]$$
(6.1)

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

$$u_{\text{elst},ab}(r_{ab}) = \frac{q_a q_b}{r_{ab}}$$

$$u_{\text{exp},ab}(r_{ab}) = \left[1 + \sum_{i=1}^k a_i^{ab}(r_{ab})^i\right] e^{\alpha^{ab} - \beta^{ab}r_{ab}} + \frac{A_{12}^{ab}}{(r_{ab})^{12}}$$

$$u_{\text{asymp},ab}^{(2)}(r_{ab}) = -\sum_{n=6,8} f_n(\delta_n^{ab}, r_{ab}) \frac{C_n^{ab}}{(r_{ab})^n},$$
(6.2)

where f_n are Tang-Toennies damping functions [66]

$$f_n(\delta_n^{ab}, r_{ab}) = 1 - e^{-\delta r} \sum_{m=0}^n \frac{(\delta r)^m}{m!}.$$
 (6.3)

The partial charges q_x and induction plus dispersion coefficients C_n^{ab} are fitted on asymptotic data and then keeping them fixed, parameters α^{ab} , β^{ab} , δ_n^{ab} , a_i^{ab} , and A_{12}^{ab} 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	$N_{\rm atoms}$	$N_{\text{electrons}}$	$N_{\rm grid}$	RMSE	RMSE
				-	E < 0	E < 10
					(kcal/mol)	(kcal/mol)
4-amino-2,3,6-trinitrophenol	4-amino-2,3,6-	21 + 21	124 + 124	1132	0.3	0.52
	trinitrophenol					
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-	2,4,6-Trinitrophenol	18 + 19	114 + 116	2100	0.32	0.58
triazole	_					



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 SAPT(DFT) for the the orientation corresponding to first minimum.

BIBLIOGRAPHY

- K. Szalewicz and B. Jeziorski, "Symmetry-adapted double-perturbation analysis of intramolecular correlation effects in weak intermolecular interactions," *Mol. Phys.*, vol. 38, pp. 191–208, 1979.
- [2] S. Rybak, B. Jeziorski, and K. Szalewicz, "Many-body symmetry-adapted perturbation theory of intermolecular interactions - H₂O and HF dimers," J. Chem. Phys., vol. 95, pp. 6576–6601, 1991.
- [3] B. Jeziorski, R. Moszyński, and K. Szalewicz, "Perturbation theory approach to intermolecular potential energy surfaces of van der Waals complexes," *Chem. Rev.*, vol. 94, pp. 1887–1930, 1994.
- [4] K. Patkowski, K. Szalewicz, and B. Jeziorski, "Third-order interactions in symmetry-adapted perturbation theory," J. Chem. Phys., vol. 125, pp. 154107– (1:20), 2006.
- [5] W. Kohn and L. J. Sham, "Self-consistent equations including exchange and correlation effects," *Phys. Rev.*, vol. 140, pp. 1133–1138, 1965.
- [6] P. Hohenberg and W. Kohn, "Inhomogeneous electron gas," *Phys. Rev.*, vol. 136, pp. B864–B871, 1964.
- [7] L. Hedin and B. I. Lundqvist, "Explicit local exchange-correlation potentials," J. Phys. C: Solid State Physics, vol. 4, no. 14, p. 2064, 1971.
- [8] U. von Barth and L. Hedin, "A local exchange-correlation potential for the spin polarized case. i," J. Phys. C: Solid State Phys., vol. 5, no. 13, p. 1629, 1972.
- [9] O. Gunnarsson and B. I. Lundqvist, "Exchange and correlation in atoms, molecules, and solids by the spin-density-functional formalism," *Phys. Rev. B*, vol. 13, pp. 4274–4298, 1976.
- [10] R. O. Jones and O. Gunnarsson, "The density functional formalism, its applications and prospects," *Rev. Mod. Phys.*, vol. 61, pp. 689–746, 1989.
- [11] D. C. Langreth and M. Mehl, "Easily implementable nonlocal exchangecorrelation energy functional," *Phys. Rev. Lett.*, vol. 47, no. 6, pp. 446–450, 1981.

- [12] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, "Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation," *Phys. Rev. B*, vol. 46, pp. 6671–6687, 1992.
- [13] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," *Phys. Rev. Lett.*, vol. 77, pp. 3865–3868, 1996.
- [14] X. Wu, M. C. Vargas, S. Nayak, V. L. Lotrich, and G. Scoles, "Towards extending the applicability of density functional theory to weakly bound systems," J. Chem. Phys., vol. 115, pp. 8748–8757, 2001.
- [15] Q. Wu and W. Yang, "Empirical correction to density functional theory for van der Waals interactions," J. Chem. Phys., vol. 116, pp. 515–524, 2002.
- [16] S. Grimme, J. Antony, S. Elrich, and H. Krieg, "A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu," J. Chem. Phys., vol. 132, pp. 154104–(1:19), 2010.
- [17] A. Tkatchenko, R. A. DiStasio, R. Car, and M. Scheffler, "Accurate and efficient method for many-body van der waals interactions," *Phys. Rev. Lett.*, vol. 108, p. 236402, 2012.
- [18] O. Gunnarsson, M. Jonson, and B. I. Lundqvist, "Descriptions of exchange and correlation effects in inhomogeneous electron systems," *Phys. Rev. B*, vol. 20, no. 8, p. 3136, 1979.
- [19] S. Grimme, S. Ehrlich, and L. Goerigk, "Effect of the damping function in dispersion corrected density functional theory," J. Comp. Chem., vol. 32, no. 7, pp. 1456–1465, 2011.
- [20] K. Pernal, R. Podeszwa, K. Patkowski, and K. Szalewicz, "Dispersionless density functional theory," *Phys. Rev. Lett.*, vol. 103, pp. 263201–(1:4), 2009.
- [21] R. Podeszwa, K. Pernal, K. Patkowski, and K. Szalewicz, "An extension of the Hartree-Fock plus dispersion method for calculations of intermolecular interaction energies," J. Phys. Chem. Lett., vol. 1, pp. 550–555, 2010.
- [22] A. Tkatchenko and M. Scheffler, "Accurate molecular van der waals interactions from ground-state electron density and free-atom reference data," *Phys. Rev. Lett.*, vol. 102, p. 073005, 2009.
- [23] A. D. Becke and E. R. Johnson, "Exchange-hole dipole moment and the dispersion interaction," J. Chem. Phys., vol. 122, no. 15, p. 154104, 2005.
- [24] A. D. Becke and E. R. Johnson, "A density-functional model of the dispersion interaction," J. Chem. Phys., vol. 123, no. 15, p. 154101, 2005.

- [25] M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, and B. I. Lundqvist, "Van der Waals density functional for general geometries," *Phys. Rev. Lett.*, vol. 92, pp. 246401–(1:4), 2004.
- [26] K. Lee, E. D. Murray, L. Kong, B. I. Lundqvist, and D. C. Langreth, "Higheraccuracy van der Waals density functional," *Phys. Rev. B*, vol. 82, pp. 081101– (1:4), 2010.
- [27] O. A. Vydrov and T. Van Voorhis, "Nonlocal van der waals density functional made simple," *Phys. Rev. Lett.*, vol. 103, no. 6, p. 063004, 2009.
- [28] O. A. Vydrov and T. Van Voorhis, "Nonlocal van der waals density functional: The simpler the better," J. Chem. Phys., vol. 133, no. 24, p. 244103, 2010.
- [29] M. Shahbaz and K. Szalewicz, "Dispersion energy from local polarizability density." submitted, 2018.
- [30] J. Sun, A. Ruzsinszky, and J. P. Perdew, "Strongly constrained and appropriately normed semilocal density functional," *Phys. Rev. Lett.*, vol. 115, no. 3, p. 036402, 2015.
- [31] Y. Andersson, D. C. Langreth, and B. I. Lundqvist, "Van der waals interactions in density-functional theory," *Phys. Rev. Lett.*, vol. 76, pp. 102–105, 1996.
- [32] J. F. Dobson and B. P. Dinte, "Constraint satisfaction in local and gradient susceptibility approximations: Application to a van der Waals density functional," *Phys. Rev. Lett.*, vol. 76, pp. 1780–1783, 1996.
- [33] D. E. Taylor, J. G. Angyán, G. Galli, C. Zhang, F. Gygi, K. Hirao, J. W. Song, K. Rahul, O. A. von Lilienfeld, R. Podeszwa, *et al.*, "Blind test of densityfunctional-based methods on intermolecular interaction energies," *J. Chem. Phys.*, vol. 145, no. 12, p. 124105, 2016.
- [34] A. J. Misquitta, B. Jeziorski, and K. Szalewicz, "Dispersion energy from densityfunctional theory description of monomers," *Phys. Rev. Lett.*, vol. 91, pp. 033201– (1:4), 2003.
- [35] A. Hesselmann and G. Jansen, "Intermolecular dispersion energies from timedependent density functional theory," *Chem. Phys. Lett.*, vol. 367, pp. 778–784, 2003.
- [36] A. J. Misquitta, R. Podeszwa, B. Jeziorski, and K. Szalewicz, "Intermolecular potentials based on symmetry-adapted perturbation theory including dispersion energies from time-dependent density functional calculations," J. Chem. Phys., vol. 123, pp. 214103–(1:14), 2005.

- [37] A. Hesselmann, G. Jansen, and M. Schütz, "Density-functional theory-symmetryadapted intermolecular perturbation theory with density fitting: A new efficient method to study intermolecular interaction energies," J. Chem. Phys., vol. 122, pp. 014103–(1:17), 2005.
- [38] C. A. Ullrich, Time-Dependent Density-Functional Theory: Concepts and Applications. New York: Oxford University Press, 2010.
- [39] G. Giuliani and G. Vignale, *Quantum Theory of the Electron Liquid.* New York: Cambridge University Press, 2005.
- [40] J. P. Perdew and S. Kurth, "Density functionals for non-relativistic coulomb systems in the new century," in *A primer in density functional theory* (C. Fiolhais, F. Nogueira, and M. A. Marques, eds.), vol. 620, Springer Science & Business Media, 2003.
- [41] J. P. Perdew and Y. Wang, "Accurate and simple density functional for the electronic exchange energy: Generalized gradient approximation," *Phys. Rev. B*, vol. 33, pp. 8800–8802, 1986.
- [42] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," *Phys. Rev. Lett.*, vol. 77, no. 18, p. 3865, 1996.
- [43] E. D. Murray, K. Lee, and D. C. Langreth, "Investigation of exchange energy density functional accuracy for interacting molecules," J. Chem. Theory Comput., vol. 5, no. 10, pp. 2754–2762, 2009.
- [44] D. C. Langreth and J. P. Perdew, "The exchange-correlation energy of a mmetallic surface," *Solid State Commun.*, vol. 17, no. 11, pp. 1425–1429, 1975.
- [45] D. C. Langreth and J. P. Perdew, "Exchange-correlation energy of a metallic surface: Wave-vector analysis," *Phys. Rev. B*, vol. 15, no. 6, pp. 2884–2901, 1977.
- [46] M. Levy and J. P. Perdew, "Hellmann-feynman, virial, and scaling requisites for the exact universal density functionals. shape of the correlation potential and diamagnetic susceptibility for atoms," *Phys. Rev. A*, vol. 32, pp. 2010–2021, Oct 1985.
- [47] G. Giuliani and G. Vignale, *Quantum Theory of the Electron Liquid*. New York: Cambridge University Press, 2005.
- [48] K. Burke, "Digging into the exchange-correlation energy: The exchangecorrelation hole," in *Electronic Density Functional Theory: Recent Progress and New Directions* (G. V. J. F. Dobson and M. P. Das, eds.), pp. 19–23, Springer Science & Business Media, 1998.

- [49] M. Rasolt and D. J. W. Geldart, "Exchange and correlation energy in a nonuniform fermion fluid," *Phys. Rev. B*, vol. 34, pp. 1325–1328, Jul 1986.
- [50] D. C. Langreth and M. J. Mehl, "Beyond the local-density approximation in calculations of ground-state electronic properties," *Phys. Rev. A*, vol. 26, pp. 1809– 1834, 1983.
- [51] J. P. Perdew, "Accurate density functional for the energy: Real-space cutoff of the gradient expansion for the exchange hole," *Phys. Rev. Lett.*, vol. 55, pp. 2370– 2370, Nov 1985.
- [52] H. C. Longuet-Higgins, "Spiers memorial lecture. intermolecular forces," Discuss. Faraday Soc., vol. 40, pp. 7–18, 1965.
- [53] S. Kristyán and P. Pulay, "Can (semi) local density functional theory account for the london dispersion forces?," *Chem. Phys. Lett.*, vol. 229, no. 3, pp. 175–180, 1994.
- [54] A. D. Becke, "A new mixing of hartree–fock and local density-functional theories," J. Chem. Phys., vol. 98, no. 2, pp. 1372–1377, 1993.
- [55] J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, "Climbing the density functional ladder: Nonempirical meta-generalized gradient approximation designed for molecules and solids," *Phys. Rev. Lett.*, vol. 91, no. 14, p. 146401, 2003.
- [56] C. Adamo and V. Barone, "Toward reliable density functional methods without adjustable parameters: The pbe0 model," J. Chem. Phys., vol. 110, no. 13, pp. 6158–6170, 1999.
- [57] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, "Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation," *Phys. Rev. B*, vol. 46, no. 11, p. 6671, 1992.
- [58] J. P. Perdew and Y. Wang, "Accurate and simple analytic representation of the electron-gas correlation energy," *Phys. Rev. B*, vol. 45, pp. 13244–13249, Jun 1992.
- [59] J. P. Perdew in *Electronic Structure of Solids '91* (P. Ziesche and H. Eschrig, eds.), p. 11, Berlin: Akademie Verlag, 1991.
- [60] Y. Zhang and W. Yang, "Comment on "Generalized Gradient Approximation Made Simple"," Phys. Rev. Lett., vol. 80, no. 4, p. 890, 1998.

- [61] F. A. Gianturco, F. Paesani, M. F. Laranjeira, V. Vassilenko, M. A. Cunha, A. G. Shashkov, and A. F. Zolotoukhina, "Computed and measured transport coefficients for CO-He mixtures: Testing a density functional approach," *Mol. Phys.*, vol. 94, pp. 605–622, 1998.
- [62] S. Grimme, "Accurate description of van der Waals complexes by density functional theory including empirical corrections," J. Comput. Chem., vol. 25, pp. 1463–1473, 2004.
- [63] S. Grimme, "Semiempirical GGA-type density functional constructed with a long-range dispersion correction," J. Comput. Chem., vol. 27, pp. 1787–1799, 2006.
- [64] D. E. Taylor, J. G. ÅAngyÅan, G. Galli, C. Zhang, F. Gygi, K. Hirao, J. W. Song, K. Rahul, O. A. von Lilienfeld, R. Podeszwa, I. W. Bulik, T. M. Henderson, G. E. Scuseria, J. Toulouse, R. Peverati, D. G. Truhlar, and K. Szalewicz, "Blind test of density-functional-based methods on intermolecular interaction energies," J. Chem. Phys., vol. 145, no. 12, p. 124105, 2016.
- [65] M. Krauss and D. Neumann, "Charge overlap effects in dispersion energies," J. Chem. Phys., vol. 71, pp. 107–112, 1979.
- [66] K. Tang and J. P. Toennies, "An improved simple model for the van der waals potential based on universal damping functions for the dispersion coefficients," *J. Chem. Phys.*, vol. 80, no. 8, pp. 3726–3741, 1984.
- [67] P. J. Knowles and W. J. Meath, "Non-expanded dispersion and induction energies, and damping functions, for molecular-interactions with application to hfhe," *Mol. Phys.*, vol. 59, pp. 965–984, 1986.
- [68] P. J. Knowles and W. J. Meath, "A separable method for the calculation of dispersion and induction energy damping functions with applications to the dimers arising from he, ne and hf," *Mol. Phys.*, vol. 60, pp. 1143–1158, 1987.
- [69] N. C. Handy and A. J. Cohen, "Left-right correlation energy," Mol. Phys., vol. 99, no. 5, pp. 403–412, 2001.
- [70] H. Peng, Z.-H. Yang, J. P. Perdew, and J. Sun, "Versatile van der waals density functional based on a meta-generalized gradient approximation," *Phys. Rev. X*, vol. 6, no. 4, p. 041005, 2016.
- [71] M. A. Rohrdanz, K. M. Martins, and J. M. Herbert, "A long-range-corrected density functional that performs well for both ground-state properties and timedependent density functional theory excitation energies, including charge-transfer excited states," J. Chem. Phys., vol. 130, no. 5, p. 054112, 2009.

- [72] J.-D. Chai and M. Head-Gordon, "Systematic optimization of long-range corrected hybrid density functionals," J. Chem. Phys., vol. 128, p. 084106, 2008.
- [73] A. Austin, G. A. Petersson, M. J. Frisch, F. J. Dobek, G. Scalmani, and K. Throssell, "A density functional with spherical atom dispersion terms," J. Chem. Theory Comput., vol. 8, pp. 4989–5007, 2012.
- [74] A. D. Becke, "Density-functional exchange-energy approximation with correct asymptotic behavior," *Phys. Rev. A*, vol. 38, no. 6, p. 3098, 1988.
- [75] J. Pérez-Jordá and A. D. Becke, "A density-functional study of van der waals forces: rare gas diatomics," *Chem. Phys. Lett.*, vol. 233, no. 1-2, pp. 134–137, 1995.
- [76] J. M. Pérez-Jordá, E. San-Fabián, and A. J. Pérez-Jiménez, "Density-functional study of van der waals forces on rare-gas diatomics: Hartree–fock exchange," J. Chem. Phys., vol. 110, no. 4, pp. 1916–1920, 1999.
- [77] 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.
- [78] B. I. Lundqvist, "Single-particle spectrum of the degenerate electron gas," Phys. Kond. Mat., vol. 9, pp. 236–248, 1969.
- [79] K. L. C. Hunt, "Nonlocal polarizability densities and van der waals interactions," J. Chem. Phys., vol. 78, pp. 6149–55, 1983.
- [80] K. L. C. Hunt, "Nonlocal polarizability densities and the effects of short-range interactions on molecular dipoles, quadrupoles, and polarizabilities," J. Chem. Phys., vol. 80, no. 1, pp. 393–407, 1984.
- [81] O. A. Vydrov and T. Van Voorhis, "Improving the accuracy of the nonlocal van der waals density functional with minimal empiricism," J. Chem. Phys., vol. 130, no. 10, p. 104105, 2009.
- [82] O. A. Vydrov and T. Van Voorhis, "Dispersion interactions from a local polarizability model," *Phys. Rev. A*, vol. 81, no. 6, p. 062708, 2010.
- [83] O. A. Vydrov and T. Van Voorhis, "Nonlocal van der waals density functionals based on local response models," in *Fundamentals of Time-Dependent Density Functional Theory* (M. A. Marques, N. T. Maitra, F. M. Nogueira, E. K. Gross, and A. Rubio, eds.), vol. 837, Springer Science & Business Media, 2012.
- [84] K. Patkowski, G. Murdachaew, C.-M. Fou, and K. Szalewicz, "Accurate *ab initio* potential for argon dimer including highly repulsive region," *Mol. Phys.*, vol. 103, pp. 2031–2045, 2005.

- [85] A. D. Becke, "A multicenter numerical integration scheme for polyatomic molecules," J. Chem. Phys., vol. 88, no. 4, pp. 2547–2553, 1988.
- [86] C. W. Murray, N. C. Handy, and G. J. Laming, "Quadrature schemes for integrals of density functional theory," *Mol. Phys.*, vol. 78, no. 4, pp. 997–1014, 1993.
- [87] V. Lebedev, "Spherical quadrature formulas exact to orders 25–29," Siber. Math. J., vol. 18, no. 1, pp. 99–107, 1977.
- [88] F. Neese, "The orca program system," Wiley Interdiscip. Rev.: Comput. Mol. Sci., vol. 2, no. 1, pp. 73–78, 2012.
- [89] T. H. Dunning Jr., "Gaussian basis sets for use in correlated molecular calculations. i. the atoms boron through neon and hydrogen," J. Chem. Phys., vol. 90, no. 2, pp. 1007–1023, 1989.
- [90] R. A. Kendall, T. H. Dunning Jr., and R. J. Harrison, "Electron affinities of the first-row atoms revisited. systematic basis sets and wave functions," J. Chem. Phys., vol. 96, no. 9, pp. 6796–6806, 1992.
- [91] D. E. Woon and T. H. Dunning Jr, "Gaussian basis sets for use in correlated molecular calculations. iii. the atoms aluminum through argon," J. Chem. Phys., vol. 98, no. 2, pp. 1358–1371, 1993.
- [92] S. F. Boys and F. Bernardi, "The calculation of small molecular interactions by the differences of separate total energies. some procedures with reduced errors," *Mol. Phys.*, vol. 19, no. 4, pp. 553–566, 1970.
- [93] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, *et al.*, "Gaussian 09 Revision A.1." Gaussian Inc. Wallingford CT 2009.
- [94] R. Podeszwa, K. Pernal, K. Patkowski, and K. Szalewicz, "Extension of the hartreeâĹŠfock plus dispersion method by first-order correlation effects," J. Phys. Chem. Lett., vol. 1, no. 2, pp. 550–555, 2010.
- [95] J. P. Perdew, "Density-functional approximation for the correlation energy of the inhomogeneous electron gas," *Phys. Rev. B*, vol. 33, no. 12, p. 8822, 1986.
- [96] J. F. Dobson and T. Gould, "Calculation of dispersion energies," J. Phys. Cond. Mat., vol. 24, p. 073201, 2012.
- [97] R. Eisenschitz and F. London, "About the relationship of the van der Waals forces to the covalent bonding forces," Z. Phys., vol. 60, pp. 491–527, 1930.
- [98] K. Szalewicz, "Symmetry-adapted perturbation theory of intermolecular forces," Wiley Interdisc. Rev.-Comp. Mol. Sci., vol. 2, pp. 254–272, 2012.

- [99] E. Kochanski, "Calculation of the dispersion contribution to the interaction energy of two hydrogen molecules at large but finite distances," *Chem. Phys. Lett.*, vol. 10, p. 543, 1971.
- [100] B. Jeziorski and M. van Hemert, "Variation-perturbation treatment of hydrogenbond between water molecules," *Mol. Phys.*, vol. 31, pp. 713–729, 1976.
- [101] G. Chalasinski, B. Jeziorski, J. Andzelm, and K. Szalewicz, "On the multipole structure of exchange dispersion energy in the interaction of two helium atoms," *Mol. Phys.*, vol. 33, pp. 971–977, 1977.
- [102] H. L. Williams, K. Szalewicz, R. Moszyński, and B. Jeziorski, "Dispersion energy in the coupled pair approximation with noniterative inclusion of single and triple excitations," J. Chem. Phys., vol. 103, pp. 4586–4599, 1995.
- [103] R. Moszyński, B. Jeziorski, and K. Szalewicz, "Møller-Plesset expansion of the dispersion energy in the ring approximation," Int. J. Quantum Chem., vol. 45, pp. 409–432, 1993.
- [104] T. Korona and B. Jeziorski, "Dispersion energy from density-fitted density susceptibilities of singles and doubles coupled cluster theory," J. Chem. Phys., vol. 128, pp. 144107–(1:10), 2008.
- [105] A. J. Misquitta and K. Szalewicz, "Intermolecular forces from asymptotically corrected density functional description of monomers," *Chem. Phys. Lett.*, vol. 357, pp. 301–306, 2002.
- [106] A. J. Misquitta and K. Szalewicz, "Symmetry-adapted perturbation theory calculations of intermolecular forces employing density functional description of monomers," J. Chem. Phys., vol. 122, pp. 214109–(1:19), 2005.
- [107] R. Bukowski, R. Podeszwa, and K. Szalewicz, "Efficient calculations of coupled Kohn-Sham dynamic susceptibility functions and dispersion energies with density fitting," *Chem. Phys. Lett.*, vol. 414, pp. 111–116, 2005.
- [108] R. Podeszwa, W. Cencek, and K. Szalewicz, "Efficient calculations of dispersion energies for nanoscale systems from coupled density response functions," J. Chem. Theory Comput., vol. 8, pp. 1963–1969, 2012.
- [109] R. Podeszwa, R. Bukowski, and K. Szalewicz, "Density fitting methods in symmetry-adapted perturbation theory based on Kohn-Sham description of monomers," J. Chem. Theory Comput., vol. 2, pp. 400–412, 2006.
- [110] T. Thonhauser, V. R. Cooper, S. Li, A. Puzder, P. Hyldgaard, and D. C. Langreth, "Van der Waals density functional: Self-consistent potential and the nature of the van der Waals bond," *Phys. Rev. B*, vol. 76, no. 12, p. 125112, 2007.

- [111] K. Berland, V. R. Cooper, K. Lee, E. Schröder, T. Thonhauser, P. Hyldgaard, and B. I. Lundqvist, "Van der waals forces in density functional theory: A review of the vdw-df method," *Reports on Progress in Physics*, vol. 78, no. 6, p. 066501, 2015.
- [112] A. J. Stone, The Theory of Intermolecular Forces. Clarendon Press, Oxford, second ed., 2013.
- [113] J. G. Ángyán, G. Jansen, M. Loos, C. Hattig, and B. A. Hess, "Distributed polarizabilities using the topological theory of atoms in molecules," *Chem. Phys. Lett.*, vol. 219, pp. 267–273, 1994.
- [114] C. Hättig, G. Jansen, B. A. Hess, and J. G. Ángyán, "Intermolecular interaction energies by topologically partitioned electric properties. 2. Dispersion energies in one-centre and multicentre multipole expansions," *Mol. Phys.*, vol. 91, pp. 145– 160, 1997.
- [115] F. Rob and K. Szalewicz, "Asymptotic dispersion energies from distributed polarizabilities," Chem. Phys. Lett., vol. 572, pp. 146–149, 2013.
- [116] F. Rob and K. Szalewicz, "Distributed molecular polarizabilities and asymptotic intermolecular interaction energies," *Mol. Phys.*, vol. 111, pp. 1430–1455, 2013.
- [117] E. Caldeweyher, C. Bannwarth, and S. Grimme, "Extension of the d3 dispersion coefficient model," J. Chem. Phys., vol. 147, pp. 034112–(1:7), 2017.
- [118] T. Bucko, J. Hafner, S. Lebegue, and J. G. Ángyán, "Improved description of the structure of molecular and layered crystals: Ab initio DFT calculations with van der Waals corrections," J. Phys. Chem. A, vol. 114, pp. 11814–11824, 2010.
- [119] J. G. Ángyán, "On the exchange-hole model of London dispersion forces," J. Chem. Phys., vol. 127, p. 024108, 2007.
- [120] T. Bucko, S. Lebegue, J. Hafner, and J. G. Ángyán, "Tkatchenko-Scheffler van der Waals correction method with and without self-consistent screening applied to solids," *Phys. Rev. B*, vol. 87, p. 064110, 2013.
- [121] T. Bucko, S. Lebegue, J. Hafner, and J. G. Ángyán, "Improved density dependent correction for the description of London dispersion forces," J. Chem. Theory Comput., vol. 9, pp. 4293–4299, 2013.
- [122] T. Bucko, S. Lebegue, J. G. Ángyán, and J. Hafner, "Extending the applicability of the Tkatchenko-Scheffler dispersion correction via iterative Hirshfeld partitioning," J. Chem. Phys., vol. 141, p. 034114, 2014.
- [123] T. Bucko, S. Lebegue, T. Gould, and J. G. Ángyán, "Many-body dispersion corrections for periodic systems: an efficient reciprocal space implementation," J. Phys.-Cond. Mat., vol. 28, p. 045201, 2016.

- [124] J. G. Ángyán, I. C. Gerber, J. Toulouse, and A. Savin, "Van der Waals forces in density functional theory: Perturbational long-range electron-interaction corrections," *Phys. Rev. A*, vol. 72, pp. 012510–(1:9), 2005.
- [125] I. C. Gerber and J. G. Ángyán, "Potential curves for alkaline-earth dimers by density functional theory with long-range correlation corrections," *Chem. Phys. Lett.*, vol. 416, pp. 370–375, 2005.
- [126] I. C. Gerber and J. G. Ángyán, "London dispersion forces by range separated hybrid density functional with second order perturbational corrections (RSH+MP2): the case of rare gas complexes," J. Chem. Phys., vol. 126, p. 044103, 2007.
- [127] J. Toulouse, I. C. Gerber, G. Jansen, A. Savin, and J. G. Ángyán, "Adiabaticconnection fluctuation-dissipation density-functional theory based on range separation," *Phys. Rev. Lett.*, vol. 102, pp. 096404–(1:4), 2009.
- [128] S. Lebegue, J. Harl, T. Gould, J. G. Ángyán, G. Kresse, and J. F. Dobson, "Cohesive properties and asymptotics of the dispersion interaction in graphite by the random phase approximation," *Phys. Rev. Lett.*, vol. 105, p. 196401, 2010.
- [129] W. M. Zhu, J. Toulouse, A. Savin, and J. G. Ángyán, "Range-separated densityfunctional theory with random phase approximation applied to noncovalent intermolecular interactions," J. Chem. Phys., vol. 132, p. 244108, 2010.
- [130] J. Toulouse, W. Zhu, A. Savin, G. Jansen, and J. G. Ángyán, "Closed-shell ring coupled cluster doubles theory with range separation applied on weak intermolecular interactions," J. Chem. Phys., vol. 135, p. 084119, 2011.
- [131] S. Lebegue, J. Harl, T. Gould, J. G. Ángyán, G. Kresse, and J. F. Dobson, "Cohesive properties and asymptotics of the dispersion interaction in graphite by the random phase approximation," *Phys. Rev. Lett.*, vol. 105, p. 196401, 2012.
- [132] J. G. Angyán, R.-F. Liu, J. Toulouse, and G. Jansen, "Correlation energy expressions from the adiabatic-connection fluctuation-dissipation theorem approach," *J. Chem. Theory Comput.*, vol. 7, pp. 3116–3130, 2011.
- [133] B. Mussard, P. G. Szalay, and J. G. Ángyán, "Analytical energy gradients in range-separated hybrid density functional theory with random phase approximation," J. Chem. Theory Comput., vol. 10, pp. 1968–1979, 2014.
- [134] J. Claudot, W. J. Kim, A. Dixit, H. Kim, T. Gould, D. Rocca, and S. Lebègue, "Benchmarking several van der waals dispersion approaches for the description of intermolecular interactions," J. Chem. Phys., vol. 148, no. 6, p. 064112, 2018.
- [135] K. Patkowski, K. Szalewicz, and B. Jeziorski, "Orbital relaxation and the thirdorder induction energy in symmetry-adapted perturbation theory," *Theor. Chem. Acc.*, vol. 127, pp. 211–221, 2010.
- [136] J. Lindhard, "On the properties of a gas of charged particles," Kgl. Danske Videnskab. Selskab Mat.-Fys. Medd., vol. 28, 1954.
- [137] N. Bohr and J. Lindhard, "Electron capture and loss by heavy ions penetrating through matter," Mat. Fys. Medd. Dan. Vid. Selsk, vol. 28, 1954.
- [138] P. Nozieres and D. Pines, "Correlation energy of a free electron gas," *Physical Review*, vol. 111, no. 2, p. 442, 1958.
- [139] K. Rapcewicz and N. Ashcroft, "Fluctuation attraction in condensed matter: A nonlocal functional approach," *Phys. Rev. B*, vol. 44, no. 8, p. 4032, 1991.
- [140] B. I. Lundqvist, Y. Andersson, H. Shao, S. Chan, and D. Langreth, "Density functional theory including van der waals forces," *Int. J. Quantum Chem.*, vol. 56, no. 4, pp. 247–255, 1995.
- [141] E. Hult, Y. Andersson, B. I. Lundqvist, and D. C. Langreth, "Density functional for van der waals forces at surfaces," *Phys. Rev. Lett.*, vol. 77, no. 10, p. 2029, 1996.
- [142] Y. Andersson, E. Hult, P. Apell, D. Langreth, and B. Lundqvist, "Densityfunctional account of van der waals forces between parallel surfaces," *Solid state commun.*, vol. 106, no. 5, pp. 235–238, 1998.
- [143] Y. Andersson and H. Rydberg, "Dispersion coefficients for van der waals complexes, including c60–c60," *Physica Scripta*, vol. 60, no. 3, p. 211, 1999.
- [144] V. R. Cooper, L. Kong, and D. C. Langreth, "Computing dispersion interactions in density functional theory," *Phys. Proc.*, vol. 3, no. 3, pp. 1417–1430, 2010.
- [145] K. Berland and P. Hyldgaard, "Exchange functional that tests the robustness of the plasmon description of the van der waals density functional," *Phys. Rev. B*, vol. 89, no. 3, p. 035412, 2014.
- [146] K. Berland, C. A. Arter, V. R. Cooper, K. Lee, B. I. Lundqvist, E. Schröder, T. Thonhauser, and P. Hyldgaard, "Van der waals density functionals built upon the electron-gas tradition: Facing the challenge of competing interactions," J. Chem. Phys., vol. 140, no. 18, p. 18A539, 2014.
- [147] I. Hamada, "Van der waals density functional made accurate," Phys. Rev. B, vol. 89, no. 12, p. 121103, 2014.
- [148] D. C. Langreth and B. I. Lundqvist, "Comment on "nonlocal van der waals density functional made simple"," *Phys. Rev. Lett.*, vol. 104, p. 099303, 2010.

- [149] J. Hepburn, G. Scoles, and R. Penco, "A simple but reliable method for the prediction of intermolecular potentials," *Chem. Phys. Lett.*, vol. 36, no. 4, pp. 451– 456, 1975.
- [150] D. G. Smith, L. A. Burns, K. Patkowski, and C. D. Sherrill, "Revised damping parameters for the d3 dispersion correction to density functional theory," J. Phys. Chem. Lett., vol. 7, no. 12, pp. 2197–2203, 2016.
- [151] L. Salem, "The calculation of dispersion forces," Mol. Phys., vol. 3, pp. 441–452, 1960.
- [152] K. T. Tang and M. Karplus, "Padé approximant calculation of the nonretarded van der Waals coefficients for two and three helium atoms," *Phys. Rev.*, vol. 171, no. 1, p. 70, 1968.
- [153] F. L. Hirshfeld, "Bonded-atom fragments for describing molecular charge densities," *Theor. Chim. Acta.*, vol. 44, no. 2, pp. 129–138, 1977.
- [154] A. Otero-De-La-Roza and E. R. Johnson, "Non-covalent interactions and thermochemistry using XDm-corrected hybrid and range-separated hybrid density functionals," J. Chem. Phys., vol. 138, p. 204109, 2013.
- [155] A. Donchev, "Many-body effects of dispersion interaction," J. Chem. Phys., vol. 125, no. 7, p. 074713, 2006.
- [156] T. W. Whitfield and G. J. Martyna, "A unified formalism for many-body polarization and dispersion: The quantum drude model applied to fluid xenon," *Chem. Phys. Lett.*, vol. 424, no. 4, pp. 409–413, 2006.
- [157] A. Jones, A. Thompson, J. Crain, M. H. Müser, and G. J. Martyna, "Normconserving diffusion monte carlo method and diagrammatic expansion of interacting drude oscillators: Application to solid xenon," *Phys. Rev. B*, vol. 79, no. 14, p. 144119, 2009.
- [158] K. Szalewicz, R. Bukowski, and B. Jeziorski, "On the importance of many-body forces in clusters and condensed phase," in *Theory and Applications of Computational Chemistry: The First Fourty Years* (C. E. Dykstra, G. Frenking, K. S. Kim, and G. E. Scuseria, eds.), ch. 33, pp. 919–962, Elsevier, Amsterdam, 2005.
- [159] W. Jankiewicz, R. Podeszwa, and H. A. Witek, "Dispersion-corrected dft struggles with predicting three-body interaction energies," J. Chem. Theory Comput., vol. 14, no. 10, pp. 5079–5089, 2018.
- [160] T. H. Dunning Jr., "Gaussian basis sets for use in correlated molecular calculations. i. the atoms boron through neon and hydrogen," J. Chem. Phys., vol. 90, no. 2, pp. 1007–1023, 1989.

- [161] R. A. Kendall, T. H. Dunning Jr., and R. J. Harrison, "Electron affinities of the first-row atoms revisited. systematic basis sets and wave functions," J. Chem. Phys., vol. 96, no. 9, pp. 6796–6806, 1992.
- [162] H. L. Williams, E. M. Mas, K. Szalewicz, and B. Jeziorski, "On the effectiveness of monomer-, dimer-, and bond-centered basis functions in calculations of intermolecular interaction energies," J. Chem. Phys., vol. 103, pp. 7374–7391, 1995.
- [163] Y. Shao, L. F. Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S. T. Brown, A. T. Gilbert, L. V. Slipchenko, S. V. Levchenko, *et al.*, "Advances in methods and algorithms in a modern quantum chemistry program package," *Phys. Chem. Chem. Phys.*, vol. 8, pp. 3172–3191, 2006.
- [164] M. Modrzejewski, G. Chalasinski, and M. M. Szczesniak, "Range-separated meta-GGA functional designed for noncovalent interactions," J. Chem. Theory Comput., vol. 10, pp. 4297–4306, 2014.
- [165] M. Valiev, E. J. Bylaska, N. Govind, K. Kowalski, T. P. Straatsma, H. J. Van Dam, D. Wang, J. Nieplocha, E. Apra, T. L. Windus, *et al.*, "Nwchem: a comprehensive and scalable open-source solution for large scale molecular simulations," *Comp. Phys. Commun.*, vol. 181, no. 9, pp. 1477–1489, 2010.
- [166] J. P. Perdew and W. Yue, "Accurate and simple density functional for the electronic exchange energy: Generalized gradient approximation," *Phys. Rev. B*, vol. 33, pp. 8800–8802, 1986.
- [167] C. A. Ullrich, Time-Dependent Density-Functional Theory: Concepts and Applications. New York: Oxford University Press, 2010.
- [168] R. Bukowski, W. Cencek, P. Jankowski, M. Jeziorska, B. Jeziorski, S. A. Kucharski, V. F. Lotrich, M. P. Metz, A. J. Misquitta, R. Moszyński, K. Patkowski, R. Podeszwa, F. Rob, S. Rybak, K. Szalewicz, H. L. Williams, R. J. Wheatley, P. E. S. Wormer, and P. S. Żuchowski, "SAPT2016: An *ab initio* program for many-body symmetry-adapted perturbation theory calculations of intermolecular interaction energies." University of Delaware and University of Warsaw, 2016.
- [169] M. P. Metz, K. Piszczatowski, and K. Szalewicz, "Automatic generation of intermolecular potential energy surfaces," J. Chem. Theory Comput., vol. 12, no. 12, pp. 5895–5919, 2016.
- [170] 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.

- [171] 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.
- [172] T. Helgaker, W. Klopper, H. Koch, and J. Noga, "Basis-set convergence of correlated calculations on water," J. Chem. Phys., vol. 106, no. 23, pp. 9639–9646, 1997.
- [173] A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, and A. K. Wilson, "Basis-set convergence in correlated calculations on ne, n 2, and h 2 o," *Chem. Phys. Lett.*, vol. 286, no. 3, pp. 243–252, 1998.
- [174] R. Podeszwa, R. Bukowski, and K. Szalewicz, "Potential energy surface for the benzene dimer and perturbational analysis of π- π interactions," J. Phys. Chem. A, vol. 110, no. 34, pp. 10345–10354, 2006.
- [175] S. Lehtola, "Erkale hf/dft from hel," ERKALE HF/DFT from Hel, http://github.com/susilehtola/erkale, 2016.
- [176] Y. Shao, L. F. Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S. T. Brown, A. T. Gilbert, L. V. Slipchenko, S. V. Levchenko, D. P. O'Neill, R. A. DiStasio Jr, R. C. Lochan, T. Wang, G. J. Beran, N. A. Besley, J. M. Herbert, C. Yeh Lin, T. Van Voorhis, S. Hung Chien, A. Sodt, R. P. Steele, V. A. Rassolov, P. E. Maslen, P. P. Korambath, R. D. Adamson, B. Austin, J. Baker, E. F. C. Byrd, H. Dachsel, R. J. Doerksen, A. Dreuw, B. D. Dunietz, A. D. Dutoi, T. R. Furlani, S. R. Gwaltney, A. Heyden, S. Hirata, C.-P. Hsu, G. Kedziora, R. Z. Khalliulin, P. Klunzinger, A. M. Lee, M. S. Lee, W. Liang, I. Lotan, N. Nair, B. Peters, E. I. Proynov, P. A. Pieniazek, Y. Min Rhee, J. Ritchie, E. Rosta, C. David Sherrill, A. C. Simmonett, J. E. Subotnik, H. Lee Woodcock III, W. Zhang, A. T. Bell, A. K. Chakraborty, D. M. Chipman, F. J. Keil, A. Warshel, W. J. Hehre, H. F. Schaefer III, J. Kong, A. I. Krylov, P. M. W. Gill, and M. Head-Gordon, "Advances in methods and algorithms in a modern quantum chemistry program package," *Phys. Chem. Chem. Phys.*, vol. 8, pp. 3172–3191, 2006.
- [177] R. Bukowski, W. Cencek, P. Jankowski, M. Jeziorska, B. Jeziorski, S. A. Kucharski, V. F. Lotrich, M. P. Metz, A. J. Misquitta, R. Moszyński, K. Patkowski, R. Podeszwa, F. Rob, S. Rybak, K. Szalewicz, H. L. Williams, R. J. Wheatley, P. E. S. Wormer, and P. S. Żuchowski, "SAPT2016: An *ab initio* program for many-body symmetry-adapted perturbation theory calculations of intermolecular interaction energies." University of Delaware and University of Warsaw, 2016.
- [178] K. Szalewicz, K. Patkowski, and B. Jeziorski, "Intermolecular interactions via perturbation theory: from diatoms to biomolecules," *Structure and Bonding*, vol. 116, pp. 43–117, 2005.

- [179] T. Korona, "Exchange-dispersion energy: A formulation in terms of monomer properties and coupled cluster treatment of intramonomer correlation," J. Chem. Theory Comput., vol. 5, pp. 2663–2678, 2009.
- [180] T. M. Parker, L. A. Burns, R. M. Parrish, A. G. Ryno, and C. D. Sherrill, "Levels of symmetry adapted perturbation theory (SAPT). I. Efficiency and performance for interaction energies," J. Chem. Phys., vol. 140, p. 094106, 2014.
- [181] A. Hesselmann, "DFT-SAPT intermolecular interaction energies employing exact-exchange KohnâĹŠSham response methods," J. Chem. Theory Comput., vol. 14, pp. 1943–1959, 2018.
- [182] R. Schäffer and G. Jansen, "Single-determinant-based symmetry-adapted perturbation theory without single-exchange approximation," *Mol. Phys.*, vol. 111, no. 16-17, pp. 2570–2584, 2013.
- [183] P. E. S. Wormer and H. Hettema, "Many-body perturbation theory of frequencydependent polarizabilities and van der waals coefficients: Application to h2o-h2o and ar-nh3," J. Chem. Phys., vol. 97, no. 8, pp. 5592–5606, 1992.
- [184] R. Podeszwa, R. Bukowski, and K. Szalewicz, "Potential energy surface for the benzene dimer and perturbational analysis of π- π interactions," J. Phys. Chem. A, vol. 110, no. 34, pp. 10345–10354, 2006.
- [185] D. E. Taylor, F. Rob, B. M. Rice, R. Podeszwa, and K. Szalewicz, "A molecular dynamics study of 1, 1-diamino-2, 2-dinitroethylene (fox-7) crystal using a symmetry adapted perturbation theory-based intermolecular force field," *Phys. Chem. Chem. Phys.*, vol. 13, no. 37, pp. 16629–16636, 2011.
- [186] F. Rob and K. Szalewicz, "Distributed molecular polarisabilities and asymptotic intermolecular interaction energies," *Mol. Phys.*, vol. 111, no. 9-11, pp. 1430– 1455, 2013.
- [187] W. Cencek and K. Szalewicz, "On asymptotic behavior of density functional theory," J. Chem. Phys., vol. 139, pp. 024104–(1:27), 2013. Erratum: 140:149902, 2014.
- [188] K. Patkowski and K. Szalewicz, "Argon pair potential at basis and excitation limits," J. Chem. Phys., vol. 133, pp. 094304–(1:20), 2010.

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 CCSD(T) interaction energies, as well as the DFT interaction energies, were extrapolated using $E_{\rm Y} = E_{\rm CBS} + B e^{-\alpha Y}$, where Y is the cardinal number and B and α are constants. The constant α was chosen to be 1.63, as recommended in Refs. [172, 173]. The correlation parts of SAPT and CCSD(T) interaction energies were extrapolated using the formula $E_{\rm Y} = E_{\rm CBS} + A/Y^3$, 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 Ar–Ar, Ar–HF, and Ar–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 (DC^+BS) [162]. All listed energies are in kcal/mol and the distances between centers of mass, R, of the interacting monomers are given in angstroms. All electrons were correlated in CCSD(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

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

where $E^{(ij)}$ are corrections of the *i*th-order in intermolecular interaction operator Vand of the *j*th-order in the Møller-Plesset fluctuation operator W, and $\epsilon^{(1)}_{exch}(CCSD) = E^{(1)}_{exch}(CCSD) - E^{(10)}_{exch}$ 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 Ar₂ and Ar–HF at very small separations, see below.

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

$$E_{\rm disp}^{(2)} = E_{\rm disp}^{(20)} + E_{\rm disp}^{(21)} + E_{\rm disp}^{(22)}, \tag{B.2}$$

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_{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_{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 Ar₂, Ar–HF, Ar–Li⁺, and (H₂O)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_{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

$$\tilde{E}_{\rm disp}^{(2)} = E_{\rm disp}^{(2)}[\rm CCD] + E_{\rm disp}^{(2)}[\rm S(\rm CCD)] + E_{\rm disp}^{(2)}[\rm T(\rm CCD)].$$
(B.3)

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 $E_{\rm disp}^{(2)}$ 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 $\epsilon_{\text{exch-disp}}^{(n)} = E_{\text{exch-disp}}^{(n)} - E_{\text{exch-disp}}^{(n0)}$, 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 Ar₂ 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_{dispx} , the addition of $\epsilon_{\text{exch-disp}}^{(2)}$ would have changed E_{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_{dispx} has uncertainties of the order of 1%.

Another way to estimate uncertainies of E_{dispx} is provided by comparisons of SAPT results with CCSD(T) ones. For Ar_2 , Fig. (2.1) and Table B.1 here show that the two methods agree reasonably well. The relative discrepancies between SAPT and CCSD(T) interaction energies at the vdW minima are 4.9%, 5.4%, 1.7%, and 5.1% for Ar_2 , Ar-HF, $Ar-Li^+$, and $(H_2O)_2$, respectively (see Tables B.1, B.2, B.3, and B.4). [Many papers comparing SAPT and CCSD(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 CCSD(T)) of the accuracy of E_{dispx} suggest that its uncertainty is of the order of 1%. Thus, when subtracted from $E_{\text{int}}^{\text{CCSD}(T)}$, it will give equally accurate values of $E_{\rm dl}$. One more source of uncertainty of the latter quantity is, of course, the fact that CCSD(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_{dl} , they are unimportant relative to the differences between E_{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 Å, 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 $R \leq 2.4$ Å. 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 $\delta_{\text{int}}^{\text{HF}}$ correction effectively cures the S^2 problem for small R. The quantity $\delta_{\text{int}}^{\text{HF}}$ is defined as

$$\delta_{\rm int}^{\rm HF} = E_{\rm int}^{\rm HF} - E_{\rm elst}^{(10)} - E_{\rm exch}^{(10)} - E_{\rm ind,resp}^{(20)} - E_{\rm exch-ind,resp}^{(20)} - E_{\rm ind}^{(30)} - E_{\rm exch-ind}^{(30)}, \qquad (B.4)$$

where $E_{\text{int}}^{\text{HF}}$ is the supermolecular Hartree-Fock interaction energy. One should note, however, that the addition of $\delta_{\text{int}}^{\text{HF}}$ is not recommended for nonpolar systems, as emphasized in Ref. [135] where it was shown that such addition increases the SAPT error relative to CCSD(T) interaction energies (this behaviour is also seen in Table B.1 for R's down to 3.2 Å). This is because while the inclusion of δ_{int}^{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 δ_{int}^{HF} is not recommended for systems with small induction effects like Ar₂ at separations relevant in studies of intermolecular interactions. We have therefore decided to include δ_{int}^{HF} in Fig. 2.1 only at $R \leq 2.8$ Å. This results in a reasonably good agreement between the SAPT and CCSD(T) interaction energies for all separations, in particular, at R = 1.5 Å the two quantities differ by only 6%. This agreement indicates that the E_{dispx} contribution, a part of the SAPT interaction energy, also has to be similarly accurate. One may note that although the addition of δ_{int}^{HF} cannot improve over the S^2 approximation in the $E_{exch-disp}$ terms, this approximation works much better in this case than in the case of $E_{exch-disp}^{(i0)}$ contributions [182].

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

For Ar–Li⁺ and for the water dimer, the agreement between SAPT and CCSD(T) is reasonable even at the smallest R (see Tables B.3 and B.4), therefore we have not included δ_{int}^{HF} in the SAPT interaction energies (the use of δ_{int}^{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

$$\tilde{E}_{\rm dl} = E_{\rm int}^{\rm SAPT} - E_{\rm dispx}.$$
(B.5)

For Ar₂ at R > 3.5 Å, it would lead to identical conclusions as the definition used, based on CCSD(T), since the differences between SAPT and CCSD(T) interaction energies are less than 4% of E_{dispx} (see Table B.1). However, for smaller R, as it has been discussed above, while the differences between SAPT and CCSD(T) interaction energies remain reasonably small as a fraction of either energy (6% at R = 1.5 Å), they are large as a fraction of E_{dispx} (52% at R = 1.5 Å). 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 CCSD(T) is the only choice.



Figure B.1: The ratio of the interaction energies from DFT to the corresponding CCSD(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 CCSD(T) interaction energies for the Ar–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 density-functional 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 $E_{\rm disp}^{(2)}$ and $E_{\rm disp,as}^{(2)}$. 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

$$D3BJ(DFT) = -\sum_{a \in A, b \in B} \sum_{n=6,8} s_n \frac{C_n^{ab}}{R_{ab}^n + \left[f_{damp}(a_1, a_2, R_0^{ab}) \right]^n},$$
(B.6)

where C_n^{ab} is the effective isotropic vdW dispersion constant for atom pair ab and R_{ab} 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

$$f_{\rm damp}(a_1, a_2, R_0^{ab}) = a_1 R_0^{ab} + a_2,$$
 (B.7)

where a_i , i = 1, 2 are adjustable parameters and $R_0^{ab} = \sqrt{C_8^{ab}/C_6^{ab}}$. The parameters s_n and a_i are different for each DFT method and are fitted to minimize the error of DFT+D on a set of wave function benchmarks. Table B.5 gives values of D3BJ × R^6 corresponding to various DFT methods for Ar₂. 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 $R \ge 4$ Å. To understand it, we show in Table B.6 the components of D3BJ(revPBE) at R = 6 Å. Clearly, the damping coming from f_{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 Å⁶ kcal/mol).

B.7 Argon-proton

The argon-proton interaction energies obtained using various DFT methods and CCSD(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 CCSD(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- ω PBEh [71] and ω B97 [72]. Almost



Figure B.4: The ratios $E_{\text{extra}}/E_{\text{dispx}}$, $\Delta E_{\text{x}}/E_{\text{dispx}}$, $\Delta E_{\text{c}}/E_{\text{dispx}}$, and $\Delta E_{\text{xc}}/E_{\text{dispx}}$ for the argon dimer using LRC- ω PBEh (Ref. [71]).

everywhere, $E_{\text{int}}^{\text{DFT}}$ is below $E_{\text{int}}^{\text{CCSD(T)}}$. The errors at the vdW minimum, R = 1.4Å, are between 0.04% and 3.6%, whereas at R = 2.5 Å 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- ω PBEh and PBE0 give a ratio that is fairly constant with R, which is a desired



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

behavior.

B.8 Argon–Lithium Cation $(Ar - Li^+)$

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- ω PBEh functional behaves very similarly to PBE0 and these two functionals give smaller errors at large R than the other functionals except for ω B97. All functionals considered switch the sign of the error at very short separations.

B.9 E_{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_{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_{extra} from RSH functionals behaves. We have computed this quantity for two RSH functionals: LRC- ω PBEh [71] and ω 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 ΔE_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 LRC- ω 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 $\omega B97$ is different from all other functionals in that it flattens after reaching 1 at R of about 3.5 Å, 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 $\Delta E_{\text{c}}/E_{\text{dispx}}$, and the very large contribution of the non-xc terms in this region do not allow one to conclude that ω B97 genuinely reproduces dispersion interactions for $1.5 \leq R \leq 3.5$ Å. The components behave more smoothly in the case of LRC- ω 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_{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 Å, E_{extra} is about $0.4E_{\text{dispx}}$ and ΔE_{c} is close to zero. Since we assume that E_{extra} is the dispersion energy, the only remaining component of SCAN which may give this type contribution is $\Delta E_{\rm x}$. However, $\Delta E_{\rm x}$ is *positive* and equal to about $-E_{\rm dispx}$. Thus, it cannot represent dispersion [of course, one may also say that ΔE_x consists of two components: $E_{\text{disp}x}$ and $-2E_{\text{dispx}}$, but this is hardly a convincing explanation]. Thus, the only source of E_{extra} is the non-xc part of $E_{\text{int}}^{\text{DFT}}$, but since non-xc components cannot describe correlation effects, we conclude that E_{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

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

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, $\Delta E_{\rm c}$ appears to be related to $E_{\rm extra}$. As discussed above, $\Delta E_{\rm non-xc}$ should contribute only to $E_{\rm dl}$. Furthermore, all the terms included in $\Delta E_{\rm non-xc}$ are also a part of $E_{\rm int}^{\rm HF}$. The latter quantity includes in addition the exchange energy. As seen in Fig. 2.4, $E_{\rm int}^{\rm HF}$ is a reasonably good approximation of $E_{\rm dl}$. Thus, we can evaluate DFT methods by checking how close is $\Delta E_{\rm non-xc}$ 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 Å. The SCAN and PBE curves show significant attractive interactions, which is, of course, physically not allowed: the attractive interactions in Ar_2 come almost exclusively from the dispersion component and ΔE_{non-xc} has no physical mechanisms to describe dispersion interactions. If $\Delta E_{\rm non-xc}$ 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 ΔE_{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 $E_{\rm int}^{\rm HF}$ 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 $E_{\rm int}^{\rm HF}$ curve is very close to the $E_{\rm dl}$ 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, $\Delta E_{\rm c}$ is virtually the same in the KS and HF cases. The same is true for $E_{\rm extra}$. On the other hand, the KS vs. HF differences are very large for $\Delta E_{\rm x}$, 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 $\Delta E_{\rm x}$. The differences in $\Delta E_{\rm x}$ partly cancel with the differences in the non-xc contribution and the total interaction energies $E_{\rm int}^{\rm DFT}$ @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 Å and the attractive interaction comes from the xc term. In the case of SCAN@HF, the value at R = 3.76 Å is about 0.4 kcal/mol below $E_{\rm dl}$, the energy that it should recover. Thus, this 0.4 kcal/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 $\Delta E_{\rm xc}$ contribution less negative with HF densities.

The B3LYP results are also similar to the SCAN results for $\Delta E_{\rm c}$ and $E_{\rm extra}$ in terms of @KS vs. @HF closeness. However, the $\Delta E_{\rm x}$ @KS vs. @HF values are in this case also quite close to each other for all R smaller than 4.1 Å. 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 Ar–Li⁺ are listed in Table B.3. The ratios of DFT interaction energies $E_{\text{int}}^{\text{DFT}}$ and E_{dispx} to $E_{\text{int}}^{\text{CCSD}(\text{T})}$ 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_{extra} , to E_{dispx} for the argon dimer. These are plotted in Fig. 2.4. Tables B.10 and B.11 give the exchange, ΔE_{x} , and correlation, ΔE_{c} , contributions to the interaction energy. Figure 2.5 shows the ratio of these contributions to E_{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_{extra} to E_{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 $R = \sim 2.2$ Å, $E_{\text{extra}}/E_{\text{dispx}}$ is reasonably flat for smaller R, getting up to 1.017 at 1.5 Å, 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 Ar₂ CCSD(T) interaction energies from Ref. [84]. The separation R = 1.5 Å is not included in that work, but at 1.8 Å the values relative to our benchmarks and to Ref. [84] benchmarks are 1.09 and 1.02, respectively. At 2.0 Å, 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 Å have the value of $E_{\text{extra}}/E_{\text{dispx}}$ at 1.5 Å 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 Å, goes up to 1.11 at 3.0 Å, and then down to 1.06 at the shortest R of 1.8 Å, cf. Table B.14. For the water dimer, the crossing is at about 3.3 Å, whereas the value at the shortest distance of 2.5 Å 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 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 Ar_2 .



Figure B.7: Ratios of SCAN Ar₂ interaction energy components to E_{dispx} computed with KS and HF densities.



Figure B.8: Ratios of PBE Ar_2 interaction energy components to E_{dispx} computed with KS and HF densities.



Figure B.9: Ratios of B3LYP Ar_2 interaction energy components to E_{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.

	$E_{\rm dl}$	53.8566	32.7728	24.7116	33.7097	8.6685	2.1578	0.7519	0.4435	0.3014	0.2199	0.1306	0.0244	0.0052	0.0008	0.0004	0.0002	0.0001	0.0000
1	CSD(T)	196.2324 5	200.5711 2	104.2369 1	25.2058 3	4.9867	0.5032	-0.1804	-0.2630	-0.2777	-0.2736	-0.2499	-0.1450	-0.0773	-0.0237	-0.0087	-0.0038	-0.0018	-0.0010
	$APT + \delta_{mt}^{HF}$ (466.4067	174.7374	90.5825	22.1845	4.3242	0.3399	-0.2416	-0.3013	-0.3052	-0.2950	-0.2647	-0.1508	-0.0796	-0.0244	-0.0091	-0.0039	-0.0019	-0.0010
I	δ ^{HF} S.	680.1441	340.1033	229.7032	12.7766	0.2387	-0.0904	-0.0366	-0.0211	-0.0139	-0.0098	-0.0054	-0.0008	-0.001	0.0000	0.0000	0.0000	0.0000	0.0000
	SAPT	4213.7375 4	665.3660 8	139.1208	9.4079	4.0855	0.4303	-0.2051	-0.2802	-0.2913	-0.2852	-0.2592	-0.1500	-0.0795	-0.0243	-0.0091	-0.0039	-0.0019	-0.0010
	E_{dispx}	-57.6242	-32.2018 -	-20.4747 -	-8.5039	-3.6817	-1.6545	-0.9323	-0.7065	-0.5790	-0.4935	-0.3804	-0.1694	-0.0825	-0.0245	-0.0091	-0.0039	-0.0019	-0.0010
d B.5.	HF	540.4592	224.4164	119.9453	32.2303	8.2048	2.0086	0.6850	0.3979	0.2666	0.1919	0.1106	0.0173	0.0026	0.0001	0.0000	0.0000	0.0000	0.0000
3.4 an	dIDF	533.4967	227.3893	124.3718	35.1326	9.3151	2.2827	0.7509	0.4251	0.2792	0.1975	0.1101	0.0086	-0.0077	-0.0031	-0.0004	0.0000	0.0000	0.0000
Figs.]	LDA	452.1223	177.4198	89.6312	19.2374	2.4653	-0.5362	-0.6814	-0.5972	-0.5198	-0.4556	-0.3560	-0.1351	-0.0456	-0.0045	-0.0004	0.0000	0.0000	0.0000
lsed for]	revPBE-PW92	498.3600	210.3462	114.8459	33.0069	9.3293	2.5458	0.8844	0.4897	0.3021	0.1932	0.0739	-0.0479	-0.0395	-0.0075	-0.0009	-0.0001	0.0000	0.0000
are u	PW91	472.7001	191.8303	100.6966	25.3765	5.5607	0.8086	-0.0788	-0.2352	-0.2910	-0.3129	-0.3188	-0.2276	-0.1200	-0.0149	-0.0008	0.0000	0.0000	0.0000
7 which	rPW86-PBE	481.8373	198.3228	105.0372	26.8461	6.0476	1.1219	0.2422	0.0898	0.0323	0.0055	-0.0153	-0.0139	-0.0042	0.0000	0.001	0.0000	0.0000	0.0000
$d \omega B9$	PBE	472.7002	192.3081	101.2833	25.8645	5.8764	1.0299	0.1199	-0.0410	-0.0998	-0.1246	-0.1375	-0.0902	-0.0406	-0.0053	-0.0005	0.0000	0.0000	0.0000
Eh an	PBE0	483.0912	195.6572	102.5283	25.8516	5.8149	1.0582	0.1790	0.0217	-0.0379	-0.0649	-0.0831	-0.0581	-0.0253	-0.0030	-0.0003	0.0000	0.0000	0.0000
$-\omega PB$	SSdL	481.0277	196.9044	103.8193	26.6660	6.4528	1.4720	0.4026	0.1700	0.0670	0.0115	-0.0419	-0.0630	-0.0335	-0.0047	-0.0005	0.0000	0.0000	0.0000
LRC	SCAN	486.5683	197.5729	103.5956	25.6255	5.2306	0.6411	-0.0703	-0.1596	-0.1794	-0.1799	-0.1621	-0.0790	-0.0296	-0.0032	-0.0003	0.0000	0.0000	0.0000
pt for	B3LYP	491.9259	201.8033	106.7940	27.7102	6.6374	1.5035	0.5104	0.3152	0.2310	0.1849	0.1361	0.0685	0.0356	0.0070	0.0013	0.0002	0.0000	0.0000
exce	$\omega B97$	496.5423	201.6153	105.5903	25.3491	4.6360	0.3544	-0.1023	-0.1051	-0.0812	-0.0580	-0.0235	0.0181	0.0114	0.0013	0.0001	0.0000	0.0000	0.0000
	LRC-~PBEh	486.7159	196.8503	103.2249	26.2455	6.1253	1.2889	0.3493	0.1654	0.0883	0.0482	0.0103	-0.0115	-0.0044	-0.0002	0.0000	0.0000	0.0000	0.0000
	В	1.50	1.80	2.00	2.40	2.80	3.20	3.50	3.65	3.76	3.85	4.00	4.50	5.00	6.00	7.00	8.00	9.00	10.00

Table B.1: The interaction energies (kcal/mol) of the argon dimer in the complete basis set limit. The midbond functions (3s3p2d2flg) were added to aug-cc-pVQZ basis sets. These data are plotted in Fig. 2.1
--

> -> -		^{zd1}	2745	1966	215	046	425	355	614	1334	027	010	005	002	1000	001	000
0		P	108.	54.	9.2	1.5	0.3	0.2	0.1	0.0	0.0	-0.0	-0.0	-0.0	-0.(-0.0	0.0
	e B.14.	CCSD(T)	91.6568	43.6466	5.6797	0.2695	-0.2128	-0.2228	-0.2181	-0.1521	-0.0802	-0.0417	-0.0129	-0.0049	-0.0021	-0.0010	-0.0005
	truct Tabl	$_{ m SAPT+\delta_{int}^{ m HF}}$	82.0502	40.1484	5.3605	0.2071	-0.2397	-0.2456	-0.2375	-0.1609	-0.0834	-0.0432	-0.0135	-0.0051	-0.0022	-0.0011	-0.0006
	to cons	$\delta_{ m int}^{ m HF}$	83.1233	17.1363	-0.1958	-0.0795	-0.0162	-0.0108	-0.0072	-0.0014	-0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
· · ·	are used	SAPT	-1.0731	23.0121	5.5563	0.2867	-0.2235	-0.2349	-0.2303	-0.1595	-0.0832	-0.0431	-0.0135	-0.0051	-0.0022	-0.0011	-0.0006
	se data a	E_{dispx}	-16.6176	-10.5500	-3.5418	-1.2350	-0.5553	-0.4583	-0.3795	-0.1854	-0.0829	-0.0407	-0.0124	-0.0047	-0.0020	-0.0010	-0.0005
	ts. Thes	LDA	78.8848	35.4210	2.7518	-0.7566	-0.6194	-0.5391	-0.4614	-0.2231	-0.0799	-0.0273	-0.0033	-0.0006	-0.0002	-0.0001	0.0000
	basis se	PW91	89.7418	43.3852	6.0592	0.3339	-0.3137	-0.3451	-0.3547	-0.2928	-0.1690	-0.0773	-0.0080	-0.0007	-0.0002	-0.0001	0.0000
	g-cc-pVQZ	rPW86-PBE	93.1504	45.2845	6.4918	0.6355	0.0077	-0.0267	-0.0434	-0.0411	-0.0173	-0.0059	-0.0007	-0.0003	-0.0002	-0.0001	0.0000
	and aug	PBE	90.4809	43.9975	6.3835	0.5451	-0.1209	-0.1556	-0.1694	-0.1361	-0.0673	-0.0275	-0.0038	-0.0007	-0.0002	-0.0001	0.0000
	STVq-	PBE0	90.7823	43.8005	6.2555	0.5869	-0.0521	-0.0879	-0.1045	-0.0894	-0.0430	-0.0170	-0.0024	-0.0005	-0.0002	-0.0001	0.0000
	o aug-co	TPSS	91.8335	44.7715	0.9870	0.9501	0.0766	0.0036	-0.0425	-0.0885	-0.0545	-0.0240	-0.0034	-0.0006	-0.0002	-0.0001	0.0000
	added to	SCAN	90.7037	43.1437	5.3933	0.1338	-0.2573	-0.2518	-0.2336	-0.1340	-0.0534	-0.0199	-0.0026	-0.0005	-0.0002	-0.0001	0.0000
		B3LYP	93.6139	45.6150	6.8568	0.9094	0.1978	0.1454	0.1120	0.0586	0.0341	0.0176	0.0033	0.0004	0.0000	-0.0001	0.0000
		R	1.80	2.00	2.50	3.00	3.40	3.50	3.60	4.00	4.50	5.00	6.00	7.00	8.00	9.00	10.00

2f1g) were	
s (3s3p2d	blo D 11
functions	at much To
midbond	100 to 000
it. The	011 040 0
CBS lim	hore dat
in the (T T
Ar-HF	77 hadia
/mol) of	JVr oo n
es (kcal,	יוס ליחס
n energi	7T17
nteractio	10 0110 04
The in	00000
Table B.2	

$_{\mathrm{to}}$	
led	
adó	
re a	
We:	
6	
2f1	
2d	\sim
s3p	ř
Ö	9
SUG	La.h
tic	÷
Inc	JIL
l fi	st
onc	COT
db	ç
mi	ç
he	11SC
H	Ч
iit.	ת ה
lin	lat.
SS	e c
G	he
he	E
n t	27
i.	$\sum_{i=1}^{n}$
no	5-1-
ul/I	0-0
kce	511
y	n d
Srg	Z
en(F
uc	-1-
cti	j j
era	-0 []
inte	α V
+	set
Ë.	<u>.</u>
Ar	has
÷	
B	
e	
abl	
Ĥ	

Table B.4: Water dimer interaction energies (kcal/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.

		10010	<u>D.11.</u>								
R	B3LYP	SCAN	TPSS	PBE0	PBE	rPW86-PBE	LDA	E_{dispx}	SAPT	CCSD(T)	E_{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

		_	_	_	_	_	_	_	_	_	_	_	_	_	_	_	_	_	_	_
p who move		$E_{\rm disp}^{(2)} + E_{\rm exch-disp}^{(2)}$	-734.4276	-904.0558	-1157.5271	-1295.6572	-1342.3525	-1331.9884	-1317.4727	-1304.0924	-1291.7738	-1269.3001	-1231.4309	-1195.6194	-1133.7492	-1053.3497	-1008.6366	-981.6035	-963.6885	-951.3900
exch-dis		$E_{ m disp}^{(2)}$	-959.9901	-1148.5780	-1381.7046	-1455.9841	-1435.9632	-1387.7360	-1359.2328	-1337.4758	-1319.3539	-1289.0590	-1242.4250	-1201.5335	-1135.2930	-1053.4248	-1008.6378	-981.6035	-963.6885	-951.3900
dstp		$E_{ m disp,as}^{(2)}$	-8451.2051	-5629.2311	-3150.3087	-2184.6563	-1728.4102	-1530.7961	-1458.2640	-1413.0482	-1380.1979	-1332.3692	-1267.8402	-1217.4230	-1144.6500	-1060.5440	-1015.1621	-987.6799	-969.6851	-957.2193
disp' arro disp'		D3(no-switching)	-3634.7170	-3113.3689	-2434.2444	-2024.7537	-1758.9786	-1616.5231	-1558.0986	-1519.6245	-1490.5676	-1446.4270	-1382.9793	-1329.8096	-1246.3939	-1137.7340	-1072.2155	-1029.6915	-1000.5372	-979.6832
		D3BJ(revPBE)	-46.8925	-87.4027	-249.4446	-560.9712	-988.5546	-1289.4380	-1407.9254	-1477.8739	-1524.3842	-1581.8012	-1630.5843	-1637.4600	-1586.9128	-1430.1856	-1302.2883	-1210.7043	-1147.1860	-1098.1417
or	gs. 2.2 and B.2.	D3BJ(rPW86-PBE)	-18.1226	-33.8899	-98.4007	-231.8400	-449.0563	-647.3145	-746.0287	-814.5178	-866.8932	-945.1687	-1047.5751	-1116.1303	-1177.7570	-1165.8135	-1116.2472	-1072.5261	-1037.1362	-1010.2904
	otted in Fig	D3BJ(PBE)	-18.2506	-34.0441	-97.8515	-225.8133	-423.0281	-591.9335	-672.5505	-727.3139	-768.6803	-829.8660	-909.7547	-964.7075	-1020.9776	-1034.3594	-1013.6292	-991.9221	-973.7742	-960.0896
and milder	data are pl	D3BJ(TPSS)	-23.3947	-43.7550	-127.0349	-298.6532	-574.0162	-818.0945	-935.8670	-1015.6294	-1075.3146	-1161.8175	-1268.0802	-1331.2276	-1368.4610	-1304.5869	-1218.8651	-1149.8400	-1100.4982	-1060.4911
	These	D3BJ(B3LYP)	-35.1336	-65.5546	-188.1684	-429.8938	-781.5818	-1051.7995	-1167.0738	-1239.1004	-1289.5193	-1356.5933	-1426.1650	-1454.8252	-1442.1934	-1334.4495	-1233.6303	-1159.7099	-1103.8330	-1066.7662
		R	1.80	2.00	2.40	2.80	3.20	3.50	3.65	3.76	3.85	4.00	4.25	4.50	5.00	6.00	7.00	8.00	9.00	10.00

Table B.5:	The dispersion correction multiplied by R^6 (Å ⁶ kcal/mol) 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 $E_{\text{disp,as}}$, SAPT(DFT) term $E_{\text{disp}}^{(2)}$, and the sum $E_{\text{disp}}^{(2)} + E_{\text{exch-disp}}^{(2)}$ is also listed.

Table B.6: The antidamping effect for D3BJ(revPBE) at R = 6 Å 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 (Å ⁶ kcal/mol)
$-C_{6}/R^{6}$	-890.7797
$-C_8/R^8$	-246.9544
$-C_6/R^6 - C_8/R^8$	-1137.7341
$-C_6/(R^6 + f_{\rm damp}^6)$	-856.5795
$-C_8/(R^8 + f_{\rm damp}^8)$	-243.6297
$-C_6/(R^6 + f_{\rm damp}^6) - C_8/(R^8 + f_{\rm damp}^8)$	-1100.2092
$-s_6C_6/(R^6+f_{\rm damp}^6)$	- 856.5795
$-s_8C_8/(R^8+f_{\rm damp}^8)$	-573.7480
$-s_6C_6/(R^6+f_{\rm damp}^6)-s_8C_8/(R^8+f_{\rm damp}^8)$	-1430.3275

							I									,
	CCSD(T)	753.6490	164.1810	-13.9070	-63.1327	-64.6791	-58.4391	-50.8143	-36.0868	-24.7522	-9.7319	-4.2767	-1.1977	-0.4669	-0.2201	-0.1173
	LDA	756.1457	169.3147	-10.4262	-61.6991	-64.7061	-58.9960	-51.7665	-37.4657	-26.1692	-10.5874	-4.6800	-1.3040	-0.5069	-0.2365	-0.1279
	rPW86-PBE	749.6861	163.3107	-14.1683	-63.7009	-65.6752	-59.6350	-52.1800	-37.6591	-26.2886	-10.6243	-4.6873	-1.3037	-0.5067	-0.2359	-0.1277
	PW91	749.6538	163.9257	-13.8808	-64.0381	-66.2582	-60.1685	-52.5891	-37.7467	-26.1475	-10.4343	-4.6071	-1.2880	-0.5011	-0.2334	-0.1264
g. B.1.	PBE	751.0239	164.2504	-14.0371	-64.2865	-66.4736	-60.3636	-52.7661	-37.8933	-26.2731	-10.5126	-4.6424	-1.2957	-0.5038	-0.2348	-0.1271
otted in Fig	PBE0	749.5913	162.2994	-15.4582	-64.7903	-66.1564	-59.7609	-51.9723	-36.9509	-25.3876	-10.0187	-4.4117	-1.2350	-0.4812	-0.2250	-0.1215
int plo	TPSS	748.7106	161.9528	-15.7076	-65.2748	-66.9928	-60.7499	-53.0595	-38.0252	-26.2502	-10.3455	-4.5424	-1.2686	-0.4937	-0.2302	-0.1252
te $E_{\rm int}^{\rm DFT}/E$	B3LYP	749.6319	163.8900	-13.1992	-62.6308	-64.6312	-58.6179	-51.1907	-36.7378	-25.4931	-10.2421	-4.5303	-1.2659	-0.4926	-0.2300	-0.1241
to calcula	$\omega B97$	749.6323	162.1159	-15.4186	-64.0915	-64.7473	-58.1892	-50.4516	-35.9485	-24.9344	-10.0070	-4.3991	-1.2260	-0.4770	-0.2246	-0.1197
are used	LRC-wPBEh	749.9664	162.5272	-15.4599	-64.9474	-66.3243	-59.8886	-52.0515	-36.9421	-25.3294	-9.9716	-4.3956	-1.2320	-0.4796	-0.2258	-0.1203
	R	0.60	0.80	1.00	1.20	1.40	1.50	1.60	1.80	2.00	2.50	3.00	4.00	5.00	6.00	7.00

ese data	
Th	
The midbond functions were not used.	
CBS limit.	
the (
) in	
mol	ŕ
(kcal)	
1 energy	Ē
nteraction	
Ar-proton i	
Table B.7:	

	in Fig. 2.3.									
	LRC- <i>w</i> PBEh	$\omega B97$	B3LYP	TPSS	PBE0	PBE	PW91	rPW86-PBE	LDA	$E_{ m dispx}$
	0.8909	1.0539	0.8886	0.9115	0.8759	0.8780	0.8258	0.9257	0.5750	-0.1825
	1.3819	0.8702	1.4554	1.3744	1.4538	1.5167	1.7308	1.3538	2.4443	0.4759
	1.0700	1.0181	1.1113	1.1088	1.0926	1.1439	1.1983	1.1167	1.2469	0.0460
	1.0586	1.0358	1.1069	1.1171	1.0827	1.1536	1.2106	1.1321	1.1948	0.0215
	1.0549	1.0322	1.1035	1.1228	1.0787	1.1623	1.2194	1.1425	1.1764	0.0136
	1.0503	1.0247	1.0948	1.1188	1.0711	1.1570	1.2051	1.1398	1.1606	0.0105
	1.0457	1.0210	1.0806	1.1039	1.0583	1.1379	1.1615	1.1265	1.1362	0.0075
	1.0413	1.0210	1.0664	1.0765	1.0429	1.1049	1.1020	1.1017	1.1061	0.0048
	1.0378	1.0172	1.0612	1.0677	1.0381	1.0911	1.0867	1.0907	1.0954	0.0033
	1.0351	1.0169	1.0585	1.0626	1.0358	1.0850	1.0777	1.0866	1.0895	0.0024
	1.0323	1.0289	1.0581	1.0585	1.0342	1.0816	1.0736	1.0893	1.0865	0.0018
	1.0277	1.0329	1.0566	1.0516	1.0309	1.0762	1.0628	1.0896	1.0840	0.0014
0	1.0267	1.0319	1.0569	1.0502	1.0306	1.0748	1.0592	1.0892	1.0846	0.0011

Table B.8: The ratio $E_{\text{int}}^{\text{DFT}}/E_{\text{int}}^{\text{CCSD(T)}}$ and $E_{\text{dispx}}/E_{\text{int}}^{\text{CCSD(T)}}$ for $\operatorname{Ar-Li^+}$. All energies were computed in the CBS limit wit	1.1 Liv 0.2	Table B.8: The (3s3) (3s3) (3s3)	ratio $E_{\text{int}}^{\text{DFT}}/E_{\text{int}}^{\text{CCSD}(T)}$ and $E_{\text{dispx}}/E_{\text{int}}^{\text{CCSD}(T)}$ for Ar–Li ⁺ . All energies were computed in the CBS limit wit p2d2f1g) midbond functions added to aug-cc-pVTZ and aug-cc-pVQZ basis sets. These data are plotted in a set of the computer of t
		(3s3)	p2d2f1g) midbond functions added to aug-cc-pVTZ and aug-cc-pVQZ basis sets. These data are plottee

_

125
ΗF	0.2325	0.2595	0.2328	0.1740	0.1260	0.0902	0.0717	0.0646	0.0601	0.0568	0.0524	0.0419	0.0312	0.0290	0.0439	0.0449	0.0285	0.0320
dIDF	0.3533	0.1672	0.0166	-0.1673	-0.1756	-0.0755	0.0011	0.0261	0.0383	0.0453	0.0538	0.0931	0.1569	0.1564	0.0860	0.0559	0.0304	0.0309
LDA	1.7655	1.7189	1.7134	1.7018	1.6848	1.6283	1.5374	1.4731	1.4181	1.3688	1.2790	0.9416	0.6155	0.2168	0.0903	0.0533	0.0313	0.0306
revPBE-PW92	0.9631	0.6964	0.4818	0.0826	-0.1795	-0.2346	-0.1421	-0.0654	-0.0013	0.0541	0.1489	0.4268	0.5416	0.3372	0.1400	0.0676	0.0356	0.0262
PW91	1.4084	1.2714	1.1729	0.9799	0.8441	0.8154	0.8910	0.9607	1.0231	1.0797	1.1812	1.4875	1.5183	0.6401	0.1273	0.0503	0.0280	0.0307
rPW86-PBE	1.2498	1.0698	0.9609	0.8071	0.7119	0.6261	0.5467	0.5006	0.4647	0.4345	0.3835	0.2262	0.1146	0.0308	0.0309	0.0385	0.0275	0.0301
PBE	1.4084	1.2566	1.1443	0.9225	0.7584	0.6817	0.6779	0.6858	0.6928	0.6982	0.7046	0.6764	0.5559	0.2466	0.1033	0.0568	0.0308	0.0309
PBE0	1.2280	1.1526	1.0834	0.9241	0.7750	0.6646	0.6145	0.5971	0.5859	0.5770	0.5616	0.4872	0.3699	0.1527	0.0741	0.0497	0.0296	0.0309
TPSS	1.2639	1.1139	1.0204	0.8283	0.6018	0.4145	0.3747	0.3871	0.4048	0.4223	0.4533	0.5160	0.4689	0.2220	0.0951	0.0540	0.0304	0.0304
SCAN	1.1677	1.0931	1.0313	0.9506	0.9337	0.9167	0.8819	0.8537	0.8302	0.8102	0.7694	0.6107	0.4217	0.1614	0.0767	0.0508	0.0300	0.0314
B3LYP	1.0747	0.9617	0.8751	0.7055	0.5517	0.3954	0.2590	0.1817	0.1215	0.0709	-0.0144	-0.2602	-0.3686	-0.2532	-0.0943	-0.0100	0.0094	0.0250
$\omega B97$	0.9946	0.9676	0.9339	0.9831	1.0952	1.0900	0.9162	0.7765	0.6607	0.5631	0.4049	0.0375	-0.0745	-0.0204	0.0331	0.0436	0.0270	0.0331
LRC- ω PBEh	1.1651	1.1155	1.0494	0.8777	0.6908	0.5251	0.4319	0.3936	0.3679	0.3480	0.3163	0.2119	0.1161	0.0387	0.0447	0.0463	0.0293	0.0332
R	1.50	1.80	2.00	2.40	2.80	3.20	3.50	3.65	3.76	3.85	4.00	4.50	5.00	6.00	7.00	8.00	9.00	10.00

2.4.
Fig.
se data are plotted in l
The
argon dimer.
$_{\mathrm{the}}$
, for
$_{\rm a}/E_{ m disp}$
E_{extr}
The ratio
Table B.9:

	LDA	-216.9670	-138.3774	-93.1199	-36.9260	-12.5151	-3.4213	-0.9678	-0.3989	-0.1426	-0.0038	0.1298	0.1748	0.0919	0.0149	0.0020	0.0003	0.0000	0.0000
	revPBE-PW92	-170.9996	-109.3425	-73.0283	-28.9208	-10.6443	-3.9001	-1.8513	-1.2689	-0.9557	-0.7531	-0.4973	-0.0856	0.0214	0.0186	0.0033	0.0004	0.0000	0.0000
	PW91	-177.8487	-112.6483	-74.7006	-28.6328	-9.7497	-3.1892	-1.4304	-0.9731	-0.7342	-0.5808	-0.3849	-0.0366	0.0829	0.0498	0.0044	0.0002	0.0000	0.0000
	RPW86PBE	-168.2746	-107.3402	-72.0307	-28.3178	-9.5767	-2.7544	-0.9411	-0.5150	-0.3173	-0.2053	-0.0871	0.0205	0.0149	0.0015	-0.0002	-0.0001	0.0000	0.0000
	PBE	-176.4667	-111.4299	-73.7076	-28.1514	-9.5234	-2.9802	-1.1870	-0.7260	-0.4939	-0.3519	-0.1853	0.0278	0.0471	0.0139	0.0021	0.0003	0.0000	0.0000
	PBE0	-135.8978	-85.1712	-55.9407	-21.0343	-6.9537	-2.1262	-0.8479	-0.5267	-0.3665	-0.2690	-0.1548	-0.0055	0.0153	0.0051	0.0007	0.0001	0.0000	0.0000
2.5.	TPSS	-170.8250	-109.3381	-73.1282	-27.8849	-9.0326	-2.8408	-1.2772	-0.8560	-0.6295	-0.4828	-0.2979	-0.0185	0.0323	0.0126	0.0019	0.0002	0.0000	0.0000
sed in Fig.	SCAN	-157.7725	-106.4426	-72.0564	-28.2954	-9.2601	-2.3440	-0.5728	-0.1820	-0.0215	0.0680	0.1497	0.1455	0.0755	0.0121	0.0015	0.0002	0.0000	0.0000
ata are us	B3LYP	-145.2499	-92.9395	-61.6607	-23.4273	-7.5138	-1.9377	-0.5353	-0.2292	-0.0975	-0.0293	0.0313	0.0345	-0.0010	-0.0076	-0.0022	-0.0005	-0.0001	0.0000
. These d	$\omega B97$	-184.4228	-107.8890	-69.6170	-24.2702	-6.0499	-0.3713	0.5468	0.5677	0.5022	0.4256	0.2896	0.0250	-0.0147	-0.0034	-0.0003	0.0000	0.0000	0.0000
limit	LRC- <i>w</i> PBEh	-151.0601	-91.5284	-59.5784	-22.0224	-7.0991	-2.1094	-0.8241	-0.5074	-0.3519	-0.2586	-0.1509	-0.0161	0.0017	0.0004	0.0000	0.0000	0.0000	0.0000
	R	1.50	1.80	2.00	2.40	2.80	3.20	3.50	3.65	3.76	3.85	4.00	4.50	5.00	6.00	7.00	8.00	9.00	10.00

CBS	
the (
in	
dimer	
argon	
the	
of 1	
energy	
raction .	
inte	
he	
int	
ol)	
l/m	
kca.	
×	2
ΔE	o. 9
ntributions	e used in Fi
V CC	a. a.r
energy	se data
Exchange	limit. The
10:	
B .]	
Table	

	LDA	-11.2185	-8.7268	-6.3879	-3.0285	-1.2911	-0.4983	-0.2273	-0.1496	-0.1088	-0.0831	-0.0521	-0.0085	-0.0001	0.0005	0.0001	0.0000	0.0000	0.0000	
	revPBE-PW92	-11.0460	-8.8287	-6.5762	-3.2894	-1.5512	-0.7102	-0.3879	-0.2841	-0.2250	-0.1852	-0.1328	-0.0388	-0.0077	0.0010	0.0003	0.0000	0.0000	0.0000	
	PW91	-29.0067	-20.8005	-15.1253	-7.1897	-3.0431	-1.1346	-0.4965	-0.3189	-0.2270	-0.1696	-0.1005	-0.0007	0.0192	0.0076	0.0006	0.0000	0.0000	0.0000	
	RPW86PBE	-29.7096	-21.1848	-15.3229	-7.2223	-3.0303	-1.1025	-0.4639	-0.2908	-0.2036	-0.1508	-0.0899	-0.0131	-0.0008	0.0001	0.0000	0.0000	0.0000	0.0000	
	PBE	-29.7612	-21.2802	-15.4067	-7.2208	-2.9991	-1.0939	-0.4678	-0.2958	-0.2077	-0.1534	-0.0894	-0.0050	0.0068	0.0021	0.0003	0.0000	0.0000	0.0000	
	PBE0	-29.9518	-21.2217	-15.2819	-7.0908	-2.8946	-1.0258	-0.4269	-0.2663	-0.1854	-0.1362	-0.0790	-0.0061	0.0038	0.0012	0.0002	0.0000	0.0000	0.0000	
2.5	TPSS	-28.7636	-20.2098	-14.4567	-6.7075	-2.7712	-1.0079	-0.4416	-0.2868	-0.2068	-0.1569	-0.0967	-0.0113	0.0043	0.0018	0.0003	0.0000	0.0000	0.0000	
ed in Fig.	SCAN	-36.4957	-23.4462	-16.1467	-7.3736	-3.1985	-1.2950	-0.6257	-0.4289	-0.3242	-0.2567	-0.1732	-0.0451	-0.0108	-0.0004	0.0000	0.0000	0.0000	0.0000	
ta are use	B3LYP	-18.7508	-14.4641	-11.1538	-6.1406	-3.1481	-1.5024	-0.8187	-0.5935	-0.4651	-0.3790	-0.2668	-0.0762	-0.0205	-0.0021	-0.0004	-0.0001	0.0000	0.0000	
These da	$\omega B97$	-32.3097	-21.6633	-16.2481	-9.9606	-5.6812	-2.7075	-1.2885	-0.8155	-0.5573	-0.3952	-0.2072	-0.0060	0.0051	0.0007	0.0000	0.0000	0.0000	0.0000	
limit.	LRC- ω PBEh	-30.4473	-21.3282	-15.3282	-7.1043	-2.9008	-1.0351	-0.4388	-0.2786	-0.1976	-0.1482	-0.0904	-0.0143	-0.0013	0.0000	0.0000	0.0000	0.0000	0.0000	
	R	1.50	1.80	2.00	2.40	2.80	3.20	3.50	3.65	3.76	3.85	4.00	4.50	5.00	6.00	7.00	8.00	9.00	10.00	

$\tilde{\mathbf{v}}$	
CB	
the	
in	
imer	
n d	
argoi	
the	
of	
energy	
action	
inter	
$_{\mathrm{the}}$	
in	
ol	
/m	
(kcal	
$\Delta E_{\rm c}$	с С
tions	ц Ц
ibu	 - 7
ntri	0011
00	r.o
energy	data a
uc	000
atio	Ē
rrel	.±
Coj	lim
1:	
3.1	
еΕ	
ıbl	
Ĥ	

Table B.12: Exchange energy contributions ΔE_x (kcal/mol) in the interaction energy of Ar–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 Ar₂ 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 $\Delta E_{\rm c}$ (kcal/mol) in the interaction energy of Ar–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 Ar₂ 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 Ar–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.

		COAN					DUI01	
	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 ΔE_x (kcal/mol) to the interaction energy of the water dimer in the CBS limit. The basis sets utilized are augcc-pVTZ and aug-cc-pVQZ with midbond functions (3s3p2d2f). These data are not discussed in chapter 2 but are included for compatibility with Ar₂ 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 $\Delta E_{\rm c}$ (kcal/mol)in the interaction energy of the water dimer in the CBS limit. The basis sets utilized are augcc-pVTZ and aug-cc-pVQZ with midbond functions (3s3p2d2f). These data are not discussed in chapter 2 but are included for compatibility with Ar₂ 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 basissets 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.

	\ I	/				1	0
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 CCSD(T) results that are listed in Table 3.2 are also given. The ratios of DADE and disp(vdW-DF2) to $E_{\rm dispx}$ 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 (kcal/mol) at various separations of monomers (angstrom) for the benzene-methane dimer.

			(01		.) 101 0.	ne sonnene .		ie anneit	
R	E_{disp}	$E_{\text{exch-disp}}$	E_{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.

monomore (angettern) for the sendence water anner.												
R	$E_{\rm disp}$	$E_{\rm exch-disp}$	E_{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 (kcal/mol) at various separations of monomers (angstrom) for the diamino-dinitroethylene (FOX-7) dimer.

					101 01				
R	E_{disp}	$E_{\text{exch-disp}}$	E_{dispx}	$\operatorname{CCSD}(T)$	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 (kcal/mol) at various separations of monomers (angstrom) for the ethanol dimer.

			(0	/				
R	E_{disp}	$E_{\text{exch-disp}}$	E_{dispx}	$\operatorname{CCSD}(T)$	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 (kcal/mol) at various separations of monomers (angstrom) for the ethylenedinitramine (EDNA) dimer.

		1110110111	oro (an	80010m)	101 011	e eengieneen	111010011		(i) annon
R	E_{disp}	$E_{\text{exch-disp}}$	E_{dispx}	$\operatorname{CCSD}(T)$	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.

			- ··· (···	0					
R	E_{disp}	$E_{\text{exch-disp}}$	E_{dispx}	$\operatorname{CCSD}(T)$	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 (kcal/mol) at various separations of monomers (angstrom) for the methylformate dimer.

monomens (angstrom) for the methynormatic uniter.											
R	$E_{\rm disp}$	$E_{\text{exch-disp}}$	E_{dispx}	$\operatorname{CCSD}(T)$	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 (kcal/mol) at various separations of monomers (angstrom) for the nitrobenzene dimer.

	momonions (angettern) for the meresenzene anner.											
R	E_{disp}	$E_{\text{exch-disp}}$	E_{dispx}	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 (kcal/mol) at various separations of monomers (angstrom) for the nitromethane dimer.

				0					
R	E_{disp}	$E_{\text{exch-disp}}$	E_{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 (kcal/mol) at various separations of monomers (angstrom) for the water dimer.

		mono	lifer (angouor	m) 101	the water a			
R	E_{disp}	$E_{\text{exch-disp}}$	E_{dispx}	$\operatorname{CCSD}(T)$	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.

			()	0			
R	E_{disp}	$E_{\text{exch-disp}}$	E_{dispx}	$\operatorname{CCSD}(T)$	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
9.0000 10.0000	-0.0019 -0.0010	0.0000	-0.0019 -0.0010	-0.0018 -0.0010	-0.0016 -0.0008	-0.0011 -0.0005	0.0000 0.0000	-0.0034 -0.0016 -0.0008	-0.0011 -0.0005

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

R	E_{disp}	$E_{\text{exch-disp}}$	Edispx	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

some anno	1.	
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.13: APEs and MedAPEs relative to CCSD(T) values for the benzenemethane dimer.

 Table C.14: APEs and MedAPEs relative to CCSD(T) values for the benzene-water dimer.

\bar{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 CCSD(T) values for the diaminodinitroethylene (FOX-7) dimer.

11010001191011		
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

R	dlDF+DADE	dIDF + 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.16: APEs and MedAPEs relative to CCSD(T) values for the ethanol dimer. $\frac{R}{R} \frac{dIDE + DADE}{dIDE + dIDE + disp(vdWDE2)}$

 Table C.17: APEs and MedAPEs relative to CCSD(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 CCSD(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

IIICI.		
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.19: APEs and MedAPEs relative to CCSD(T) values for the methylformate dimer.

 Table C.20: APEs and MedAPEs relative to CCSD(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 CCSD(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

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.22: APEs and MedAPEs relative to CCSD(T) values for the water dimer.

Table C.23: APEs and MedAPEs relative to CCSD(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

\mathbf{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

Table C.24: APEs and MedAPEs relative to CCSD(T) values for the Ar-HF dimer.

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_{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_{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.

ns		ing							ns		ing										at		[jui					
paratio		KDM10[No-switch	-16.3847 -4 9811	-0.8620	-0.2339	-0.0824	-0.0345	-0.0162	paratio		KDM110[No-switch	-57.4421	-13.4503	-4.2445	-1.6387	-0.7296	-0.361	5011.U-	c140.0-	-0.0180	dimer		KDM10[No-switch	-46.8788 -93.4579	-1 9183	-0.4017	-0.1318 -0.0548	010010-
lomer se		lisp(vdW-DF1) 2	-5.3392 -3.0833	-1.0294	-0.3364	-0.1086	-0.0394	-0.0171	omer se		disp(vdW-DF1) 2	-7.6366	-4.5823	-2.6582	-1.5285	-0.8799	-0.5052	1001.0-	e/ en n-	-0.0242	FOX-7)		disp(vdW-DF1) 3	-7.0876	-1.8486	-0.5701	-0.1788 -0.0664	-0.000-
IOUS MOL		M8[No-switching] <	-9.5350 -3.4903	-0.7330	-0.2157	-0.0788	-0.0336	-0.0159	uom suo.		M8[No-switching]	-26.1473	-8.0898	-3.0306	-1.3040	-0.6226	-0.3226	0.0401	1050.0-	-0.0176	nylene (l		M8[No-switching]	-20.0337 -11.6962	-1 4909	-0.3640	-0.1261 -0.0536	neen
the at var		[48] [PW86-PBE] XD	-1.5732 -1 1371	-0.5009	-0.1910	-0.0754	-0.0330	-0.0158	er at vari		M8[PW86-PBE] XI	-1.4903	-1.2693	-0.9708	-0.6720	-0.4284	-0.2611	0.090.0-	-0.0389	-0.0174	dinitroet]		M8[PW86-PBE] XI	-1.7689	-0.7408	-0.2988	-0.1192	0700.0-
ne-meun		D3MBJ[PBE] XDN	-2.2004 -1 3404	-0.4537	-0.1575	-0.0620	-0.0274	-0.0134	zene-wat		D3MBJ[PBE] XD	-2.6948	-1.9134	-1.1994	-0.6934	-0.3913	-0.2238	-0.0803	-0.0327	-0.0149	diamino-		D3MBJ[PBE] XD	-2.4131 -9.0669	-0.8338	-0.3000	-0.1164 -0.0516	ATCA -
ue penze		[JM10[PW86-PBE]	-1.9841 -1.4074	-0.5848	-0.2080	-0.0789	-0.0339	-0.0161	the ben		DM10[PW86-PBE]	-1.8872	-1.6076	-1.2180	-0.8222	-0.5041	-0.2947	6701.0-	-0.0403	-0.0178	for the		[DM10[PW86-PBE]	-2.1430 -1 8870	-0.8612 -0.8612	-0.3283	-0.1248 -0.0538	0.0000.0-
Ods Ior t) D3BJ[PBE] X	-2.1391 -1 3666	-0.4822	-0.1669	-0.0649	-0.0285	-0.0138	thods for		9) D3BJ[PBE] >	-2.4821	-1.8700	-1.2326	-0.7331	-0.4173	-0.2384	-0.0540	-0.0341	-0.0154	nethods		9) D3BJ[PBE] >	-2.4131 -2.0669	-0.8338	-0.3000	-0.1164 -0.0516	ATPAN-
meth		0 disp(VV09	-2.8191 -1 8584	-0.6531	-0.2208	-0.0828	-0.0349	-0.0163	is met		0 disp(VV0	-2.7249	-2.1553	-1.4358	-0.8536	-0.4830	-0.2712	-0060-0 10-00-0	-0.0330	-0.0135	u sno		0) disp(VV0	-3.9041	-1.9464	-0.4112	-0.1542	T100/0-
arious) disp(MBD	-2.1436 -1.3683	-0.4389	-0.1464	-0.0573	-0.0255	-0.0125	variou		2) disp(MBI	-2.4318	-1.9143	-1.2357	-0.6964	-0.3787	-0.2108	-0.0741	-0.0303	-0.0138	n vari	om).	2) disp(MBI	-2.6593	1796-0-	-0.3371	-0.1306	1100/0-
ITOM V		disp(vdW-DF2	-3.7809 -2.0061	-0.5968	-0.1520	-0.0417	-0.0154	-0.0069	l) from		() disp(vdW-DF	-5.3623	-3.1561	-1.7751	-0.9630	-0.5055	-0.2576	-0.0053	-0.0239	-0.0110	ol) fror	(angstr	i) disp(vdW-DF	-4.7574 -3.7708	-0.11.02	-0.2629	-0.0732	707N'N-
1/11101		disp(VV10)	-2.3490 -1.4317	-0.4961	-0.1732	-0.0661	-0.0290	-0.0142	ol/mo]		g] disp(VV10	-3.1240	-2.0428	-1.2394	-0.7214	-0.4144	-0.2386	-0.0500	-0.0349	-0.0162	cal/m	tions	g] disp(VV10	-3.4051	-2.1332	-0.3195	-0.1238	#00010-
les (kca		D3[No-switching]	-6.9535 -9.6680	-0.5949	-0.1812	-0.0677	-0.0292	-0.0140	jies (kc		D3[No-switchin	-18.1232	-5.9130	-2.3209	-1.0361	-0.5090	-0.2695	-0.0590	-0.0303	-0.0157	gies (k	separa	D3[No-switchin	-14.8842 -8 0846	-1.3012	-0.3406	-0.1223	00000-
energi		DADE I	-5.8932 -9.8173	-0.6549	-0.1872	-0.0646	-0.0256	-0.0115	energ	1	F] DADE	7 -9.2485	5 -4.7651	3 -2.2675	3 -1.0548	2 -0.5113	0.2638	0.0006	-0.0300	5 -0.0127	l ener	nomer	F] DADE	4 -6.5088 5 -4.8760	10781	0.2955	4 -0.1033 2 -0.0424	10-10-10
UOIS.	rom).	D3BJ[HF	-5.2977	-0.5726	-0.1776	-0.0668	-0.0289	-0.0139	rsion	rom).	D3BJH	40 -10.196	57 -4.724	2 -2.095	626.0- 6	10-0.491	53 -0.262	1920-0-020-0-020-0-020-0-020-0-020-020-02	-0.034	8 -0.015	ersion	s mor	D3BJ[H	22 -6.954 35 -5.3134	21 -1198 1911 - 12	85 -0.331	24 -0.120 72 -0.052	12 -000
Uisper	angsti	dispx D _{as}	5936 -5.6088 5631 -2.4594	6226 -0.5815	1834 -0.1729	0661 -0.0627	0279 -0.0264	0132 -0.0125	Dispe	angsti	Edispx Das	0.9100 -11.27	1.4188 -4.756	9942 -2.108	0.9302 -0.994	0.4564 -0.501	0.2376 -0.268	10/04 -0.05	1.0290 -0.030	0.0131 -0.015	Dispe	rarious	Edispx D _{as}	-8.9068 -9.76 6.3741 -6.89	13799 -134	0.3980 -0.36	0.1501 -0.13	0000- 010000-
	\smile	exch-disp E	1.3290 -5. 1.3844 -5.	0.0282 -0.1	0.0017 -0.	0.0001 -0.	0.0000 -0.	0.0000 -0.	.2:	\smile	Sexch-disp I	3.0565 -9	0.8814 -4	0.2328 -1	0.0580 -0	0.0139 -0	0.0032 -0	0.0002	1- 0000.0	0.0000 -0).3:		$E_{exch-disp}$	1.7913 -	0.0582 -	0.0026 -	0.0001	
		$E_{disp} E_{i}$	-6.9226 -2 9475 1	-0.6508	-0.1851	-0.0662	-0.0279	-0.0132	le D		E_{disp} 1	-12.9665	-5.3002	-2.2270	-0.9882	-0.4703	-0.2408	-0.000	-0.0290	-0.0131	ole L		$E_{\rm disp}$	-10.6981	-1 4311	-0.4006	-0.1502	0100/0-
Lat		В	3.2800	4.8000	5.8000	6.8000	7.8000	8.8000	Tab		R	2.5000	3.0000	3.5000	4.0000	4.5000	5.0000	0.0000	00007	8.0000	Tat		В	6.3790	7.5790	8.5790	9.5790	TU-UL-DU

1: Dispersion energies (kcal/mol) from various methods for the benzene-methane at various monomer separation	
Dispersic	(a matter of
Table D.1:	

able D.4	: Dis	persic	on en	lergies	(kcal	/mol	from v	rarious	meth	ods fo	r the e	thano	l dime	sr at ve	arious me	onomer s	eparations
	(ang	stron	n).														
2 E _{disp} E _{exch-di}	sp Edispx	D _{as} D3E	3J[HF] D/	ADE D3[No-2	switching] di	isp(VV10) di	sp(vdW-DF2)	disp(MBD) di	I (60VV)qsi	D3BJ[PBE] X	DM10[PW86-P	BE D3MBJ	PBE XDM	S[PW86-PBE]	XDM8[No-switchin]	g] disp(vdW-DF1)	XDM10[No-switching]
560 -8.8101 1.5662	-7.2439 -	7.1825 -6.	.3730 -7.4	4522 -8.	9176	-3.1356	-4.9447	-2.8046	-3.6244	-2.4455	-2.2652	-2.43	06	-1.8135	-12.7011	-7.0948	-22.4405
580 -5.1426 0.7116	-4.4316 -	4.3805 -4.	.0315 -4.4	8290 -4.	8825	-2.3361	-3.5174	-2.2146	-2.8884	-1.9267	-1.9080	-1.86	43	-1.5371	-6.7307	-5.1562	-10.4028
580 -1.0289 0.0454	-0.9835 -	0.9902 -0.	.9303 -1.(0934 -0.	9778	-0.8007	-1.0126	-0.7495	-1.0480	-0.7244	-0.8539	-0.67	47	-0.7207	-1.2356	-1.7136	-1.5083
580 -0.2766 0.0025	0.2741 -	0.2815 -0.	.2703 -0.1	2988 -0.	2763	-0.2721	-0.2537	-0.2443	-0.3484	-0.2480	-0.3065	-0.23,	30	-0.2774	-0.3310	-0.5486	-0.3647
580 -0.0953 0.0001	-0.0952 -	0.0977 -0.	.0962 -0.0	0995 -0.	09.75	-0.1009	-0.0666	-0.0922	-0.1270	-0.0927	-0.1119	-0.08	83	-0.1062	-0.1129	-0.1729	-0.1188
580 -0.0390 0.0006	- 0.0390 -	0.0397 -0.	1.0- 8050.	0381 -0.	0403	-0.0424	-0.0226	-0.0397	-0.0525	-0.0391	-0.0459	-0.03	77	-0.0446	-0.0457	-0.0596	-0.0470
580 -0.0181 0.0000	-0.0181 -	0.0182 -0.	.0185 -0.0	0166 -0.	0187	-0.0200	-0.0096	-0.0189	-0.0241	-0.0183	-0.0211	-0.01	78	-0.0207	-0.0209	-0.0244	-0.0213
able D.5	: Dis	persic	on er	lergies	(kcal	$/\mathrm{mol})$	from v	/arious	meth	tods fo	\mathbf{r} the ϵ	sthyler	nedinit	ramin	e (EDN/	A) dimer	at various
	mor	nomer	seps.	ratior	ıs (anξ	gstron	1).										
$R = E_{disp} = E_{exch-}$	-disp Edisps	D _{as} 1	D3BJ[HF]	DADE D3	[No-switching]	disp(VV10)	disp(vdW-DF2	(MBD)	disp(VV09)	D3BJ[PBE]	XDM10[PW86.	N-PBE D3MB	J[PBE] XD1	VI8[PW86-PBE]	XDM8[No-switchin	ng] disp(vdW-DF1)	XDM10[No-switching]
4980 -23.9854 4.09	38 -19.8946	-24.4346	-17.7913	-17.7126	-26.1640	-9.5904	-14.4684	-6.9914	-13.1721	-6.5807	-5.6962	-6.7	7360	-4.6114	-33.6874	-20.0113	-62.1068
7980 -16.3291 2.30	52 -14.0239	-16.7138	-12.7443	-12.9756	-16.5486	-7.7606	-11.2365	-6.0289	-10.9922	-5.5520	-5.0237	-5.5	5686	-4.0813	-20.7969	-15.8015	-34.3110
7980 -4.9909 0.34:	23 -4.6486	-5.1082	-4.1598	-4.4335	-4.5360	-3.5553	-4.4677	-3.0559	-5.1282	-2.7880	-2.9428	-2.(3643	-2.4427	-5.3280	-6.8558	-6.9332
7980 -1.7678 0.050	54 -1.7124	-1.7566	-1.4854	-1.5959	-1.5446	-1.5350	-1.6030	-1.3426	-2.1534	-1.2371	-1.4176	i.1-	1655	-1.2342	-1.7293	-2.8483	-1.9921
7980 -0.6965 0.00	30 -0.6875	-0.6688	-0.5856	-0.6214	-0.5996	-0.6568	-0.5279	-0.5851	-0.8973	-0.5345	-0.6170	-0.5	5045	-0.5655	-0.6545	-1.1298	-0.7110
7980 -0.2944 0.00.	11 -0.2933	-0.2761	-0.2486	-0.2553	-0.2527	-0.2877	-0.1698	-0.2638	-0.3847	-0.2369	-0.2678	-0.5	2252	-0.2543	-0.2713	-0.4282	-0.2851
7980 -0.1340 0.00	01 -0.1339	-0.1232	-0.1131	-0.1105	-0.1146	-0.1326	-0.0600	-0.1248	-0.1736	-0.1102	-0.1217	i.0-	1056	-0.1180	-0.1215	-0.1631	-0.1253
7980 -0.0657 0.00	90 -0.0657	-0.0592	-0.0552	-0.0509	-0.0558	-0.0650	-0.0242	-0.0625	-0.0835	-0.0543	-0.0589	-0.()525	-0.0578	-0.0586	-0.0670	-0.0597

Table D.6: Dispersion energies (kcal/mol) from various methods for the imidazole dimer at various monomer separations trom رمسم

	XDM10[No-switching]	-145.8190	-28.4491	-1.3500	-0.2659	-0.0869	-0.0360	-0.0171
	disp(vdW-DF1)	-4.4786	-3.2577	-1.1350	-0.3769	-0.1240	-0.0458	-0.0204
	XDM8[No-switching]	-38.6554	-11.2234	-1.0155	-0.2395	-0.0828	-0.0351	-0.0169
	XDM8[PW86-PBE]	-1.2934	-1.0544	-0.4872	-0.1960	-0.0782	-0.0343	-0.0167
	D3MBJ[PBE]	-1.7328	-1.3228	-0.4921	-0.1735	-0.0675	-0.0300	-0.0149
	XDM10[PW86-PBE]	-1.5910	-1.2829	-0.5675	-0.2160	-0.0821	-0.0353	-0.0170
	D3BJ[PBE]	-1.7104	-1.3315	-0.5188	-0.1840	-0.0708	-0.0312	-0.0153
	disp(VV09)	-2.0297	-1.7189	-0.7213	-0.2417	-0.0883	-0.0372	-0.0175
	disp(MBD)	-1.7134	-1.3656	-0.5680	-0.2013	-0.0786	-0.0351	-0.0172
	disp(vdW-DF2)	-2.9359	-2.1125	-0.6812	-0.1878	-0.0538	-0.0203	-0.0098
	disp(VV10)	-2.1117	-1.5951	-0.5773	-0.1995	-0.0772	-0.0343	-0.0171
	D3[No-switching]	-25.2617	-7.9541	-0.8266	-0.2081	-0.0743	-0.0321	-0.0156
	DADE	-5.5920	-3.5851	-0.7904	-0.1979	-0.0656	-0.0261	-0.0120
. (111	D3BJ[HF]	-4.8306	-3.3393	-0.7502	-0.2018	-0.0727	-0.0313	-0.0152
SULU.	Das	-9.5702	-4.9855	-0.8556	-0.2222	-0.0779	-0.0330	-0.0159
(aug	E_{dispx}	-8.6006	-4.6927	-0.9120	-0.2416	-0.0850	-0.0365	-0.0178
	$E_{exch-disp}$	2.5149	1.1944	0.0781	0.0041	0.0002	0.0000	0.0000
	E_{disp}	-11.1155	-5.8871	-0.9901	-0.2457	-0.0852	-0.0365	-0.0178
	R	4.9250	5.2470	6.2470	7.2470	8.2470	9.2470	10.2470

Table D	.7:	Dispe	rsion	ener)	gies (k	scal/mc	ol) fron	n varic	m suc	ethods	for th	e methy	lformate	dimer a	various	monomer
		separat	ions	(angs)	trom).											
$R = E_{disp} = E_{exc}$	xch-disp	Edispx D _{as}	D3BJ[HF]	DADE D.	3[No-switching]	(1 disp(VV10)	disp(vdW-DF2)	disp(MBD)	disp(VV09)	D3BJ[PBE] X	DM10[PW86-PF	3E] D3MBJ[PBE]	XDM8[PW86-PBE	XDM8[No-switchin	g] disp(vdW-DF1)	XDM10[No-switching]
4.2430 -5.5211 0.9	0.9202	-4.6009 -4.2766	-3.7549	-4.2640	-5.4713	-1.9976	-2.9155	-1.7097	-2.2193	-1.5509	-1.4450	-1.5437	-1.1826	-7.0379	-4.3965	-12.2873
4.4340 -3.8547 0.0	0.5398	-3.3149 -3.0627	-2.8050	-3.1936	-3.5996	-1.6406	-2.3321	-1.4665	-1.9139	-1.3238	-1.2719	-1.2954	-1.0452	-4.5393	-3.5670	-7.1329
5.4340 -0.7280 0.0	0.0293	-0.6987 -0.6471	-0.6300	-0.6894	-0.6618	-0.5438	-0.6490	-0.5086	-0.6829	-0.4945	-0.5541	-0.4627	-0.4735	-0.7711	-1.1520	-0.9245
6.4340 -0.1976 0.0	0.0015	-0.1961 -0.1834	-0.1840	-0.1884	-0.1880	-0.1830	-0.1594	-0.1676	-0.2242	-0.1700	-0.1964	-0.1600	-0.1797	-0.2086	-0.3581	-0.2272
7.4340 -0.0702 0.0	0001	-0.0701 -0.0651	-0.0669	-0.0638	-0.0678	-0.0695	-0.0440	-0.0644	-0.0822	-0.0647	-0.0727	-0.0617	-0.0695	-0.0731	-0.1125	-0.0764
8.4340 -0.0298 0.0	0000	-0.0298 -0.0272	-0.0284	-0.0251	-0.0287	-0.0303	-0.0161	-0.0283	-0.0343	-0.0279	-0.0305	-0.0269	-0.0298	-0.0304	-0.0402	-0.0311
Table D.	ŝ	Disper	sion.	energ	ies (kc	al/mol) from	variou	s metl	hods fc	or the r	uitroben:	zene dime	er at vari	ous mond	omer sepa-
		rations	(ang	strom	1).											
$R = E_{disp} = E_{ex}$	exch-disp	E_{dispx} D _{as}	D3BJH	F] DADE	D3[No-switch	ning] disp(VV10	 disp(vdW-DF 	2) disp(MBD)	(VV09) disp(VV09)) D3BJ[PBE]	XDM10[PW86-1	PBE D3MBJ[PB	3 XDM8[PW86-PB]	ZDM8[No-switchi	<pre>ug] disp(vdW-DF1)</pre>	XDM10[No-switching]
2.9000 -31.1856 6.	6.3583	-24.8273 -29.541 15.6597 17.9104	6 -22.741	1 -26.5027	-27.6407	-12.4214	-19.3432	-9.7119	-19.6198	-10.0426	-8.1202	-11.0262	-6.4175 5 695 6	-31.8972	-25.5940	-50.0757
3.2000 -16.0090 2. 4.2000 -3.0405 0	1039	010711- 770001- 30207- 770201-	010°71- 00	11/2017-0-000000000000000000000000000000000	0017/01-	-3.4900	-10/074	011171-	-5 9566 AL	-0.9640	7386.8-	-0.0191	-2.050	1070.9T-	-4010'9-	-4 8711
5.2000 -1.1270 0.	0.0107	-1.1163 -1.2355	3 -1.1305	1671.1- 6	-1.1598	-1.2089	-1.0211	-1.0097	-1.7459	-1.0559	-1.2000	-0.9918	-1.0914	-1.2448	-1.9648	-1.3603
6.2000 -0.4084 0.	0.0006	-0.4078 -0.4570	0 -0.4325	2 -0.4066	-0.4403	-0.4740	-0.2833	-0.4021	-0.6459	-0.4186	-0.4650	-0.3965	-0.4415	-0.4643	-0.6459	-0.4880
7.2000 -0.1739 0.	0.0000	-0.1739 -0.1945	9 -0.1884	4 -0.1612	-0.1915	-0.2098	-0.1038	-0.1791	-0.2776	-0.1853	-0.2012	-0.1773	-0.1951	-0.1995	-0.2356	-0.2056
8.2000 -0.0827 0.	0.0000	-0.0827 -0.0924	4 -0.0906	5 -0.0721	-0.0921	-0.1022	-0.0469	-0.0872	-0.1299	-0.0900	-0.0959	-0.0867	-0.0941	-0.0951	-0.1018	-0.0969
4 : :	(Ļ			:	ŕ	•			• •		:	;			
Table D.	<u>.</u>	Disper	sion.	energ.	ies (kc	al/mol) from	variou	s meth	nods fo	w the n	itrometl	nane dim	er at vari	ous mond	omer sepa-

seps		No-switchin	(4.5945)	.1.4245	1.6170	0.3763	0.1193	0.0462	0.0205
omer) XDM10		-	ĩ	ĩ	ĩ	Ť	Ŧ
us mon		disp(vdW-DF1)	-10.4078	-7.1687	-2.1440	-0.6267	-0.1823	-0.0623	-0.0260
at variou		XDM8[No-switching]	-14.5276	-7.5704	-1.3382	-0.3432	-0.1136	-0.0449	-0.0202
ane dimer		XDM8[PW86-PBE]	-1.8679	-1.6167	-0.7840	-0.2906	-0.1073	-0.0439	-0.0199
ometh		D3MBJ[PBE]	-2.8484	-2.2151	-0.7921	-0.2610	-0.0956	-0.0397	-0.0184
or the nitr		XDM10[PW86-PBE]	-2.3298	-2.0109	-0.9343	-0.3206	-0.1128	-0.0451	-0.0203
ods to		D3BJ[PBE]	-2.6591	-2.1510	-0.8359	-0.2779	-0.1007	-0.0414	-0.0190
i meth		disp(VV09)	-5.3602	-4.2056	-1.4333	-0.4450	-0.1532	-0.0605	-0.0269
arious		disp(MBD)	-2.6499	-2.2466	-0.8886	-0.2882	-0.1044	-0.0433	-0.0200
trom v		disp(vdW-DF2)	-7.4249	-4.9847	-1.2792	-0.2831	-0.0717	-0.0256	-0.0114
- (lom)		disp(VV10)	-4.5359	-3.2710	-1.0393	-0.3268	-0.1166	-0.0481	-0.0223
es (kcal		D3[No-switching]	-12.1014	-6.3821	-1.1815	-0.3143	-0.1066	-0.0428	-0.0194
nergi	trom	DADE	-8.6551	-5.4106	-1.1759	-0.3192	-0.1049	-0.0394	-0.0169
on e	angsi	D3BJ[HF]	-8.6011	-5.1963	-1.1167	-0.3066	-0.1050	-0.0423	-0.0192
spersi	ons (D_{as}	-12.4325	-6.8637	-1.3039	-0.3364	-0.1107	-0.0434	-0.0194
Die	rati	E_{dispx}	-10.6671	-6.2476	-1.2823	-0.3333	-0.1102	-0.0437	-0.0197
.9. -		$E_{exch-disp}$	2.4216	1.0156	0.0553	0.0026	0.0001	0.0000	0.0000
ole I		E_{disp}	-13.0887	-7.2632	-1.3376	-0.3359	-0.1103	-0.0437	-0.0197
Ta		R	2.8130	3.1310	4.1310	5.1310	6.1310	7.1310	8.1310

XDM10[No-switching] 24.5945 -11.2945 -11.2945 -0.1763 -0.3763 -0.1193 -0.1462 -0.0462

	1		
1	10	5	
1	$4\dot{a}$	5	

tions	witching	712	31	02 51	38	88 20	60	21	/3 47	31	14	ions		witching	40	40 28	29	78	10 22	35	36	17	ions		witching]	29	8	36	120	8	21
eparat	X DM10[No	-417.2 -64.29	-14.97	-1.78	-0.18	20.0-	-0.02	-0.01	0.0-	0.0-	0.00.0-	eparat	I	XDM10[No-s	-2.15	40'T-	-0.25	-0.16	-0.08	0.00	-0.00	0.0-0-	eparat		XDM10[No-s	-0.53 -0.53	-0.20	-0.08	-0.01	-00.0-	-0.00
nomer s	disn(vdW-DF1)	-2.3594	-1.6383 -1.1383	-0.7960	-0.2450	-0.1321	-0.0376	-0.0211	-0.0079 -0.0079	-0.0052	-0.0026	nomer s		disp(vdW-DF1)	-1.5941	-1.0883 -0.7845	-0.4261	-0.3120	-0.1647 -0.0437	-0.0126	-0.0051	-0.0028 -0.0013	nomer s		disp(vdW-DF1)	-1.2402 -0.6486	-0.3444	-0.1800	-0.0912	-0.0088	-0.0035 -0.0015
rious mo	TDMf8[No-switchind]	-19.4749	-6.2368 -2.4472	-1.1086	-0.1503	-0.0698	-0.0197	-0.0116	-0.0046	-0.0030	-0.0014	ous mo		DM8 No-switching	-1.4612	2697-0-	-0.2117	-0.1445	-0.0719 -0.0919	-0.0082	-0.0035	-0.0017 -0.0009	rious mo		[DM8[No-switching]	-1.1713 -0.4145	-0.1704	-0.0786	-0.0396 -0.0123	-0.0047	-0.0020 -0.0010
ier at vai	V [JHG-38/Md/8/M	-0.3367 -0.3263	-0.2589 -0.2589	-0.2132	-0.0893	-0.0530	-0.0182	-0.0110	-0.0045	-0.0030	-0.0014	ter at var		DM8[PW86-PBE] X	-0.2752	-0.2011	-0.1310	-0.1014	-0.0591	-0.0080	-0.0035	-0.0009	ner at val		DM8[PW86-PBE] X	-0.2247 -0.1662	-0.1047	-0.0605	-0.0342	-0.0046	-0.0020 -0.0010
vater din	D 3MR ([D RF] Y	-0.5390	-0.3933 -0.3152	-0.2434 -0.1467	-0.0825	-0.0456	-0.0151	-0.0092	-0.0038	-0.0025	-0.0012	rgon din	J	D3MBJ[PBE] X	-0.5708	-0.4066	-0.1559	-0.1132	-0.0614	-0.0081	-0.0036	-0.0009	r-HF din		D3MBJ[PBE] XI	-0.3247 -0.1916	-0.1033	-0.0553	-0.0305	-0.0041	-0.0019 -0.0009
for the w	ZDM10[PW/86_PBF]	-0.4197	-0.3738 -0.3213	-0.2613 -0.1712	-0.1046	-0.0600	-0.0193	-0.0115	-0.0046	-0.0030	-0.0014	for the a		KDM10[PW86-PBE]	-0.3503	-0.3040	-0.1587	-0.1197	-0.0665 -0.0218	-0.0082	-0.0036	-0.0009	or the A		(DM10[PW86-PBE]	-0.2816	-0.1254	-0.0689	-0.0375 -0.0123	-0.0047	-0.0020 -0.0010
ethods	, D3R1[PRE]	-0.5455	-0.4097 -0.3333	-0.2601	-0.0890	-0.0488	-0.0159	-0.0096	-0.0039	-0.0026	-0.0013	ethods		D3BJ[PBE]	-0.3940	-0.3220	-0.1544	-0.1162	-0.0653 -0.0222	-0.0086	-0.0038	-0.0018 -0.0010	thods f		D3BJ[PBE] >	-0.2828 -0.1859	-0.1068	-0.0586	-0.0111	-0.0043	-0.0019 -0.0009
ous mo	(DUA/Mash (C	0.4483	-0.2321 -0.2859	-0.2566	-0.0932	-0.0506	-0.0152	-0.0086	-0.0029	-0.0017	-0.0005	ous me		(VV09) (0	-0.6206	-0.4957	-0.2218	-0.1641	-0.0908	-0.0110	-0.0046	-0.0022 -0.0011	ous me		() disp(VV09)	-0.4053	-0.1578	-0.0860	-0.0470	-0.0057	-0.0025 -0.0012
m vari	 disn(MRI 	-0.4958 -0.4799	-0.4357	-0.2895	8060.0-	-0.0476	-0.0150	-0.0091	-0.0038	-0.0025	-0.0012	m vari		2) disp(MBI	-0.2398	6881.0-	-0.1214	-0.0932	-0.0538	-0.0075	-0.0034	-0.0017	n varie		2) disp(MBD	-0.1692	-0.0981	-0.0536	-0.0296	-0.0041	-0.0018 -0.0009
ol) fro	disn/wdW_DF	-2.0923 -1.4609	-1.0167 -0.7062	-0.4874 -0.2520	-0.1229	-0.0570	-0.0136	-0.0077	-0.0031	-0.0022	-0.0010	ol) froi		disp(vdW-DF	-1.0385	-0.454/0	-0.2296	-0.1554	-0.0680	-0.0059	-0.0024	-0.0011	ol) fror		disp(vdW-DF	-0.7749	-0.1785	-0.0781	-0.0334	-0.0033	-0.0012 -0.0005
scal/mo	disn/WW10)	-1.2018 -0.9148	-0.6700 -0.4756	-0.3300	-0.0916	-0.0491	-0.0158	-0.0095	-0.0039	-0.0026	-0.0013	cal/me		g] disp(VV10)	-0.6772	-0.4707	-0.1818	-0.1320	-0.0702	-0.0087	-0.0039	-0.0019	cal/mc		disp(VV10)	-0.5149 -0.2686	-0.1370	-0.0704	-0.0375	-0.0047	-0.0021 -0.0010
gies (l	D3[No-switching	-48.9340 -12.4934	-4.2245 -1.7329	-0.8152	-0.2204	-0.0575	-0.0169	-0.0100	-0.0040	-0.0027	-0.0013	gies (k		D3[No-switching	-1.6382	-0.8794	-0.2347	-0.1601	-0.0798	-0.0091	-0.0039	-0.0019 -0.0010	gies (k		03[No-switching	-1.0230	-0.1550	-0.0727	-0.0372 -0.0118	-0.0045	-0.0020 -0.0010
n ener). 1 DADE	-4.1889	-1.7297 -1.0493	-0.6221	-0.1174	-0.0582	-0.0172	-0.0100	-0.0038	-0.0025	0.0011	1 enei		DADE	-1.4119	-0.53390	-0.2349	-0.1601	-0.0799	-0.0084	-0.0034	-0.0016	n ener		DADE L	-1.0066	-0.1744	-0.0821	-0.0422 -0.0129	-0.0046	-0.0019 -0.0009
ersion	ULUIII	2 -3.5761	5 -1.7335 2 -1.0824	5 -0.6365 0 -0.5507	8 -0.1149	9 -0.0559 2 -0.0905	0.0166	2 -0.009	1 -0.0040	0.0027	1 -0.0013	ersioi	trom	D3BJ[HF	2 -1.2706	1 -0.7473 0 -0.4786	7 -0.2189	5 -0.1514	5 -0.0767	-0.0090	7 -0.0039	7 -0.0019	ersior	trom	D3BJ[HF]	-0.8209 -0.3328	-0.1461	-0.0699	-0.0362	-0.0045	-0.0020 -0.0010
Disp	allgs	641 -8.642 641 -8.642 720 -4.427	1053 -2.292 205 -1.221	395 -0.6730 970 -0.9719	295 -0.121	0617 -0.0590 0319 -0.0310	100.0- 610	0104 -0.010	0.054 -0.004 0041 -0.004	027 -0.002	013 -0.001	Disp	(angs	box Das	5756 -1.070	4457 -0.700 870 -0.532	531 -0.251	702 -0.172	1821 -0.084 1941 -0.094		038 -0.003	019 -0.001	Disp	(angs	px D _{as}	519 -1.2050 359 -0.4669	878 -0.1940	335 -0.0880	108 -0.0434 121 -0.0129	45 -0.0047	020 -0.0020 09 -0.0010
10:	E.	1567 -8.5 4370 -4.4	6097 -2.4 2487 -1.3	7.0- 1000 7.0- 1000	0041 -0.1	0.00 -0.0	0000 -0.0	0000 -0.0	0000 -0.0	0000 -0.0	0000 -0.0	11:	_	da-disp Edu	2370 -1.6	0878 -0.5 0369 -0.5	0066 -0.2	0027 -0.1	0005 -0.0	0000 -0.0	0000 -0.6	0000 -0.0	12:		1-disp Edis	601 -1.2i 271 -0.46	044 -0.15	30.0- 700	100 - 0.04 10.0- 0.00	000 -0.00	000 -0.00
e D.	1. 1.	1.7208 3. (.9090 1.	5.0150 0. .5692 0.	1.8386 0.	11336 0.	0.0625 0.	0.178 0.0	0.0104 0.	1.0064 v. 1.0041 0.	0.0027 0.	0.0013 0.	e D.		$E_{disp} = E_{ex}$	1.9126 0.	L.0335 U. 16232 D.	0.2597 0.	9.1729 0.	0.0826 0.	0.0089 0.0	0.0038 0.	0.0019 0.0	e D.		Vdisp Eexd	4120 0.1 4023 0.0	1922 0.0	.0842 0.0	.0409 0.0 0121 0.0	.0045 0.0	.0020 0.0
Tabl	а	2.3100 -1 2.6100 -5	2.9100 ÷ 3.2100 ÷1	3.5100 -C	4.5100 -0	5.0100 -C	0.0100 -0	6.5100 -C	1- 01011/1	8.0050 -0	9.0050 -0	Tabl		R	3.2000 -	3.5000 -1	4.2500 -(4.5000	5.0000 -1	2.0000 -1	8.0000 +	9.0000 -	Tabl		R 1	3.0000 -0	4.0000 -0	4.5000 -0	5.0000 -0.	7.0000 -0	8.0000 -0 -0 -0 -0 -0 -0 -0 -0 -0 -0 -0 -0

								I	l xi		-									I			20		
	KDM10[No-switching	2.9292	1.9434	1.3846	1.2756	1.2460	1.2360	1.2267	at variou		KDM10[No-switching	5.7964	3.0439	2.1284	1.7616	1.5986	1.5196	1.4455	1.4024	1.3742	ie (FOX-7	,	XDM10[No-switching	5.2633 3.6801	0000 1
	disp(vdW-DF1) 2	0.9545	1.2030	1.6534	1.8344	1.6430	1.4133	1.2934	me-water		disp(vdW-DF1) 2	0.7706	1.0370	1.3330	1.6432	1.9280	2.1263	2.1684	1.9418	1.8444	troethyler	2	disp(vdW-DF1) 2	0.7958 0.8961	10101
	KDM8[No-switching]	1.7046	1.3618	1.1774	1.1764	1.1921	1.2042	1.2068	the benze		(DM8[No-switching]	2.6385	1.8308	1.5197	1.4019	1.3641	1.3577	1.3611	1.3549	1.3457	mino-dini		XDM8 [No-switching]	2.2493 1.8350	1 0000
	XDM8[PW86-PBE] 3	0.2813	0.4436	0.8045	1.0413	1.1401	1.1818	1.1961	values for		XDM8[PW86-PBE]	0.1504	0.2872	0.4868	0.7224	0.9386	1.0989	1.2636	1.3149	1.3275	s for the dia		XDM8[PW86-PBE]	0.1986 0.2455	
	D3MBJ[PBE]	0.3934	0.5230	0.7287	0.8590	0.9373	0.9826	1.0116	$E_{ m dispx}$	I	D3MBJ[PBE]	0.2719	0.4330	0.6014	0.7454	0.8574	0.9421	1.0504	1.1049	1.1338	_{xx} values		D3MBJ[PBE]	0.2709 0.3242	0.000
	XDM10[PW86-PBE]	0.3547	0.5491	0.9393	1.1342	1.1934	1.2134	1.2159	ods to the		XDM10[PW86-PBE]	0.1904	0.3638	0.6108	0.8839	1.1046	1.2403	1.3462	1.3622	1.3560	to the $E_{ m dist}$		XDM10[PW86-PBE]	0.2406 0.2962	0.0000
	D3BJ[PBE]	0.3824	0.5332	0.7745	0.9101	0.9822	1.0200	1.0420	s meth		D3BJ[PBE]	0.2505	0.4232	0.6181	0.7881	0.9144	1.0035	1.1071	1.1520	1.1726	ethods	m).	D3BJ[PBE]	0.2709 0.3242	0.00.00
	disp(VV09)	0.5040	0.7251	1.0489	1.2042	1.2521	1.2519	1.2371	variou		disp(VV09)	0.2750	0.4877	0.7200	0.9177	1.0582	1.1415	1.1856	1.1312	1.0309	ious m	ngstro	disp(VV09)	0.4383 0.5304	0.00
rom).	disp(MBD)	0.3832	0.5338	0.7050	0.7981	0.8670	0.9157	0.9482	r from	rom).	disp(MBD)	0.2454	0.4332	0.6196	0.7487	0.8298	0.8874	0.9694	1.0224	1.0539	om var	ions (a	disp(MBD)	0.2986 0.3639	0.000
ıs (angst	disp(vdW-DF2)	0.6759	0.8178	0.9585	0.8288	0.6308	0.5525	0.5232	n energy	ns (angst	disp(vdW-DF2)	0.5411	0.7142	0.8901	1.0353	1.1076	1.0841	0.8944	0.8064	0.8381	energy fr	separat	disp(vdW-DF2)	0.5341 0.5930	0 101 0
aratior	disp(VV10)	0.4200	0.5586	0.7968	0.9446	1.0004	1.0400	1.0727	spersio	aratior	disp(VV10)	0.3152	0.4623	0.6215	0.7755	0.9081	1.0042	1.1200	1.1787	1.2345	ersion e	onomer	disp(VV10)	0.3823 0.4385	0.000
mer set	3 [No-switching]	1.2431	1.0409	0.9554	0.9880	1.0249	1.0478	1.0625	io of di	mer set	3[No-switching]	1.8288	1.3381	1.1638	1.1138	1.1153	1.1344	1.1727	1.1913	1.1994	of disp	rious m	D3[No-switching]	1.6711 1.4095	0.0.0
monc	DADE D	1.0536	1.0992	1.0518	1.0207	0.9768	0.9170	0.8710	Rat	monc	DADE D:	0.9332	1.0784	1.1371	1.1339	1.1204	1.1187	1.0985	1.0327	0.9710	Ratic	at va	DADE I	0.7308 0.7650	0 1 0
	D3BJ[HF]	0.9471	0.9241	0.9197	0.9683	1.0105	1.0353	1.0501	D.14:		D3BJ[HF]	1.0289	1.0692	1.0509	1.0531	1.0762	1.1060	1.1542	1.1768	1.1860).15:		D3BJ[HF	0.7808	0.0000
	D_{as}	00 1.0027	00 0.9595	00 0.9341	00 0.9426	00 0.9487	00 0.9477	00 0.9448	uble 1		Das	00 1.1376	00 1.0765	00 1.0572	00 1.0696	00 1.0979	00 1.1290	00 1.1757	00 1.1964	00 1.2047	uble I		C Das	790 1.0960 790 1.0705	00000 000
	F	3.28	3.80	4.80	5.80	6.80	7.80	8.80	\mathbf{L}^{a}		E	2.50	3.00	3.50	4.00	4.50	5.00	6.00	7.00	8.00	$\mathbf{T}_{\mathbf{a}}$		ľ	6.37	1

at various	
enzene-methane	
le b	
th th	
values for	
E_{dispx}	
$_{\mathrm{the}}$	
$_{\rm to}$	
spc	
various methe	
from	
energy	for a new of
persion	onotion o
dis	
of	500
Ratio	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
Table D.13:	

150	

 $\mathbf{T}_{\mathbf{a}}$

	XDM10[No-switching	5.2633	3.6801	1.3973	1.0092	0.8782	0.8125
	disp(vdW-DF1)	0.7958	0.8961	1.3465	1.4324	1.1910	0.9832
	XDM8[No-switching]	2.2493	1.8350	1.0860	0.9145	0.8398	0.7939
	XDM8[PW86-PBE]	0.1986	0.2455	0.5396	0.7509	0.7941	0.7789
	D3MBJ[PBE]	0.2709	0.3242	0.6073	0.7537	0.7752	0.7649
	XDM10[PW86-PBE]	0.2406	0.2962	0.6273	0.8249	0.8314	0.7974
m).	D3BJ[PBE]	0.2709	0.3242	0.6073	0.7537	0.7752	0.7649
ngstro	disp(VV09)	0.4383	0.5304	0.9079	1.0331	1.0270	0.9948
ions (a	disp(MBD)	0.2986	0.3639	0.7022	0.8470	0.8698	0.8550
separat	disp(vdW-DF2)	0.5341	0.5930	0.7814	0.6605	0.4876	0.4183
nomer	disp(VV10)	0.3823	0.4385	0.6885	0.8027	0.8251	0.8206
rious mc	D3[No-switching]	1.6711	1.4095	0.9478	0.8558	0.8145	0.7857
at va	DADE I	0.7308	0.7650	0.7853	0.7426	0.6883	0.6275
	D3BJ[HF]	0.7808	0.8336	0.8732	0.8339	0.8020	0.7753
	D_{as}	1.0960	1.0705	0.9798	0.9259	0.8823	0.8478
	ж	6.3790	6.5790	7.5790	8.5790	9.5790	10.5790

Table	D.16	: Rat	io of di	spersio	n energy	from	variou	s meth	ods to th	e E_{dispx}	values for	the ethan	ol dimer a	at various
		mont	omer sep	aratior	ıs (angst	rom).								
R D _{as}	D3BJ[HF] DADE E	D3[No-switching]	disp(VV10)	disp(vdW-DF2)	disp(MBD)	disp(VV09)	D3BJ[PBE] 3	XDM10[PW86-PBE]	D3MBJ[PBE]	XDM8[PW86-PBE]	XDM8[No-switching]	disp(vdW-DF1) XI	M10[No-switching]
3.2560 0.991	5 0.8798	1.0288	1.2311	0.4329	0.6826	0.3872	0.5003	0.3376	0.3127	0.3355	0.2503	1.7533	0.9794	3.0979
3.5580 0.988	5 0.9097	1.0897	1.1017	0.5272	0.7937	0.4997	0.6518	0.4348	0.4305	0.4207	0.3468	1.5188	1.1635	2.3474
4.5580 1.006	8 0.9459	1.1117	0.9942	0.8141	1.0296	0.7620	1.0656	0.7365	0.8682	0.6860	0.7328	1.2563	1.7424	1.5336
5.5580 1.027	0.986.0 0	1.0899	1.0079	0.9926	0.9257	0.8913	1.2712	0.9047	1.1182	0.8499	1.0119	1.2075	2.0014	1.3304
6.5580 1.026	6 1.0101	1.0449	1.0239	1.0603	0.6993	0.9684	1.3341	0.9740	1.1757	0.9278	1.1153	1.1856	1.8157	1.2474
7.5580 1.019	2 1.0217	0.9761	1.0322	1.0861	0.5791	1.0173	1.3454	1.0029	1.1778	0.9656	1.1436	1.1716	1.5288	1.2059
8.5580 1.007	7 1.0227	0.9153	1.0320	1.1038	0.5317	1.0441	1.3295	1.0120	1.1637	0.9822	1.1432	1.1557	1.3460	1.1761
Table	D.17:	Rati	io of dis _l	persion	energy	from v	arious	method	ls to the J	$E_{ m dispx}$ va	lues for the	ethylened	linitramine	(EDNA)
		dime	r at vari	ous mc	nomer s	eparati	ions (a	ngstror	n).	•				
R D _a	, D3BJ[Hi	F 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) X1	M10[No-switching]
4.4980 1.22	82 0.8943	0.8903	1.3151	0.4821	0.7273	0.3514	0.6621	0.3308	0.2863	0.3386	0.2318	1.6933	1.0059	3.1218
4.7980 1.19	18 0.9088	0.9253	1.1800	0.5534	0.8012	0.4299	0.7838	0.3959	0.3582	0.3971	0.2910	1.4830	1.1268	2.4466
5.7980 1.09	89 0.8949	0.9537	0.9758	0.7648	0.9611	0.6574	1.1032	0.5997	0.6331	0.5731	0.5255	1.1462	1.4748	1.4914
6.7980 1.02	58 0.8674	0.9319	0.9020	0.8964	0.9361	0.7840	1.2575	0.7224	0.8279	0.6806	0.7207	1.0099	1.6633	1.1634
7.7980 0.97	28 0.8517	0.9039	0.8722	0.9553	0.7679	0.8510	1.3052	0.7774	0.8975	0.7338	0.8226	0.9520	1.6434	1.0341
8.7980 0.94	15 0.8476	0.8705	0.8615	0.9810	0.5789	0.8994	1.3116	0.8078	0.9130	0.7677	0.8669	0.9249	1.4600	0.9722
9.7980 0.91	98 0.8450	0.8251	0.8555	0.9903	0.4481	0.9321	1.2968	0.8228	0.9091	0.7885	0.8813	0.9075	1.2177	0.9355
10.7980 0.90	13 0.8398	0.7754	0.8487	0.9888	0.3681	0.9518	1.2709	0.8270	0.8967	0.7987	0.8797	0.8919	1.0204	0.9089
Tahle	D 18.	, Rat	io of dis	nersior	Anerow	from	varions	methc	ds to the	Н.:.	ralites for t	ha imidazı	dimer	at warions
Table		T	IN OF AT	hana	I CITCLEY		an ot to v			xdsib				CINCITIDA OF
		mont	omer sep	aratior	ıs (angst	rom).								
R D_a	D3BJ[H	F] 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) X1	DM10[No-switching]
4.9250 1.11	27 0.5617	0.6502	2.9372	0.2455	0.3414	0.1992	0.2360	0.1989	0.1850	0.2015	0.1504	4.4945	0.5207	16.9545
5.2470 1.00 6.2470 0.93	24 U./110 31 0.8296	0.7040	0.9064 0.9064	0.6330	0.7470	0162-0	0.7908	0.263/	0.2734	0.2519	0.2247	2.3917	0.0942	0.0024
7 2470 0.91	38 0.8353	0.8190	0.8612	0.8258	0 7775	0.8331	1 0003	0 7615	0.8941	0.7180	0.8112	0 9914	1 5601	1 1006
8.2470 0.91	53 0.8551	0.7715	0.8745	0.9078	0.6334	0.9250	1.0392	0.8328	0.9662	0.7941	0.9196	0.9738	1.4589	1.0219
9.2470 0.90	47 0.8582	0.7152	0.8787	0.9388	0.5551	0.9629	1.0184	0.8543	0.9661	0.8228	0.9409	0.9603	1.2540	0.9856
10.2470 0.89	26 0.8535	0.6714	0.8784	0.9612	0.5487	0.9682	0.9857	0.8609	0.9548	0.8352	0.9400	0.9482	1.1451	0.9630

 $\frac{R}{3.2560}$ 3.5580
4.5580
5.5580
6.5580
8.5580
8.5580

B	I	D3BJ[HF]	DADE L	Al No-switchin of	disn(VV10)	disn(vdW-DF2)	disn(MBD)	disn(VV09)	D3B.I[PBE]	XDM10[PW86-PBE]	D3MBJ[PBE]	XDM8[PW86-PBE]	XDM8[No-switching]	disn(vdW-DF1) X	DM10[No-switchin]
1 9 4 9 0	1 00.05	0.9161	0 0968	1 1800	0.42.49	0.6227	0.2716	(m · ·) dom	0.2271	0.2141	0.2255	0.9570	1 5007	0.0556	0.6706
4.2430	0676.0	1010.0	076.0	7691.1	74047	1000.0	01/2/10	0.4524	1/00-0	1416.0	0.0000	0/ 07:0	1670-1	000610	2.0700
4.4340 (0.9239	0.8462	0.9634	1.0859	0.4949	0.7035	0.4424	0.5774	0.3994	0.3837	0.3908	0.3153	1.3693	1.0760	2.1518
5.4340 (0.9261	0.9017	0.9867	0.9472	0.7783	0.9288	0.7279	0.9774	0.7077	0.7930	0.6623	0.6777	1.1037	1.6488	1.3232
6.4340 (0.9354	0.9384	0.9608	0.9585	0.9333	0.8129	0.8547	1.1432	0.8669	1.0018	0.8159	0.9164	1.0636	1.8259	1.1583
7.4340 (0.9286	0.9543	0.9104	0.9671	0.9921	0.6281	0.9192	1.1733	0.9227	1.0374	0.8799	0.9910	1.0424	1.6052	1.0895
8 4340 6	0131	0.0533	0.8411	0.0632	1 0158	0 5419	0.9508	1 1507	0.0368	1 0951	0.9025	0 0004	1 0195	1 3488	1 0.453
DEPE-0	TOTO	000000	TTEO'O	70000	ODINT	711.010	00000	100111	000000	T070'T	07000	10000	DO TO'T	DOLO'T	DOLOT
Tabl	e D	.20:	Rati	io of dis	persion	energy	from va	arious	methoc	Is to the E	J _{dispx} valı	here = 1	i nitrobenzo	ene dimer	at various
			mone	omer set	oaratior	ns (angs	trom).								
R	Das I	D3BJ[HF]	DADE I	03[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) X	DM10[No-switching]
2.9000	1.1899	0.9160	1.0675	1.1133	0.5003	0.7791	0.3912	0.7903	0.4045	0.3271	0.4441	0.2585	1.2848	1.0309	2.0170
3.2000	1.1378	0.9146	1.1208	1.0357	0.6026	0.8733	0.4969	0.9717	0.5095	0.4535	0.5315	0.3601	1.1896	1.1829	1.6981
4.2000	1.0860	0.9460	1.1043	0.9888	0.9105	1.0394	0.7614	1.3994	0.7891	0.8750	0.7486	0.7358	1.0936	1.6012	1.2968
5.2000	1.1066	1.0131	1.0508	1.0390	1.0830	0.9147	0.9045	1.5640	0.9459	1.0750	0.8885	0.9777	1.1151	1.7601	1.2186
6.2000	1.1205	1.0597	0.9971	1.0797	1.1625	0.6947	0.9860	1.5838	1.0264	1.1402	0.9723	1.0826	1.1385	1.5838	1.1968
7.2000	1.1208	1.0833	0.9267	1.1012	1.2064	0.5971	1.0301	1.5963	1.0658	1.1569	1.0194	1.1220	1.1471	1.3548	1.1820
8.2000	1.1173	1.0958	0.8721	1.1138	1.2359	0.5670	1.0543	1.5709	1.0879	1.1597	1.0487	1.1376	1.1499	1.2312	1.1720
Tabl	e D	.21:	Rati	io of disj	persion	energy	from va	trious 1	nethod	Is to the E	dispx valu	ies for the	nitrometh	ane dimer	at various
			mon(omer sep	oaratior	ns (angs	trom).								
В	D _{as} I	D3BJ[HF]	DADE I	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) X	DM10[No-switching]
2.8130	1.1655	0.8063	0.8114	1.1345	0.4252	0.6961	0.2484	0.5025	0.2493	0.2184	0.2670	0.1751	1.3619	0.9757	2.3056
3.1310	1.0986	0.8317	0.8660	1.0215	0.5236	0.7979	0.3596	0.6732	0.3443	0.3219	0.3546	0.2588	1.2117	1.1474	1.8286
4.1310	1.0168	0.8708	0.9171	0.9214	0.8105	0.9976	0.6930	1.1178	0.6519	0.7286	0.6177	0.6114	1.0436	1.6720	1.2610
5.1310	0.0033	0.9200	0.9577	0.9431	0.9804	0.8495	0.8646	1.3352	0.8338	0.9618	0.7832	0.8720	1.0298	1.8802	1.1290
6.1310	1.0043	0.9528	0.9522	0.9672	1.0584	0.6507	0.9474	1.3899	0.9136	1.0240	0.8671	0.9735	1.0311	1.6541	1.0824
7.1310 (0.9940	0.9683	0.9023	0.9789	1.1018	0.5860	0.9911	1.3839	0.9473	1.0327	0.9085	1.0039	1.0274	1.4256	1.0563
8.1310 (0.9847	0.9766	0.8567	0.9855	1.1303	0.5802	1.0145	1.3638	0.9639	1.0302	0.9323	1.0127	1.0234	1.3198	1.0409

Table D.19:	Ratio of dispersion energy from various methods to the E_{dispx} values for the methylformate dimer at various
	monomer separations (angstrom).

Table]). 22:	Ratic) of disp	ersion .	energy f	rom vai	rious m	lethods	to the $E_{\rm dis}$	_{spx} value	s for the w	ater dimer	at variou	s monomer
		separ:	ations (angstro	om).									
R D _{as}	D3BJ[HF]	DADE D3	[No-switching]	disp(VV10)	disp(vdW-DF2)	disp(MBD)	disp(VV09)	D3BJ[PBE] >	(DM10[PW86-PBE]	D3MBJ[PBE]	XDM8[PW86-PBE]	XDM8[No-switching]	disp(vdW-DF1)	XDM10[No-switching]
2.3100 1.0091 2.6100 0.0000	0.4176	0.4891	5.7139 2.7037	0.1403	0.2443	0.0579	-0.0523 0.0023	0.0637	0.0490	0.0629 0.1053	0.0393	9.6265 4 3540	0.3927 0.5976	48.7233 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	0.8413	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	1770.1	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 9.01 EE	1.0915
0770-T 0600-6	66/6.0	0.8094	8196.0	1196.0	7.716.0	0.9470	0.3007	2076.0	1.1014	10460	1.089U	1.0954	cc10.2	8701-1
Ē		Ĥ	·		ر			-	۲ -	-		:	•	
Table	J.23:	Ratic	ot disp	ersion (energy r	rom var	nous m	lethods	to the $E_{\rm dis}$	_{spx} value	s for the a	rgon dimer	at variou	s monomer
) provite	on water	(
		separs	automs (allgsur	.(111									
R D _{as}	D3BJ[HF	DADE D.	3[No-switching]	disp(VV10)	disp(vdW-DF2)	disp(MBD)	disp(VV09)	D3BJ[PBE] 3	KDM10[PW86-PBE]	D3MBJ[PBE]	XDM8[PW86-PBE]	XDM8[No-switching]	disp(vdW-DF1)	XDM10[No-switching]
3.2000 0.638	7 0.7583	0.8426	0.9777	0.4042	0.6198	0.1431	0.3704	0.2351	0.2090	0.3407	0.1643	0.8720	0.9514	1.2855
3.5000 0.810	4 0.7902	0.8877	0.9298	0.4977	0.7264	0.2328	0.5241	0.3405	0.3215	0.4299	0.2525	0.8345	1.1507	1.1356
3.7600 0.906	0.8154	0/06/0	0.0970	1676.0	0.608.0	0.3200	0.0547	0.4385	0.4320	0.0008	0.3420	0.8247	1.5305	1.0028
4.2000 U.994	4 0.5045 7 0.9906	1026.0	0.0411	0.7766	0.907.5	0.4793	0.6703	2689 U	1/20/0	2010.U	0.5060	0.6304	1.0550	0.080 0
5 0000 1 00004	0.0995	0.770.0	11200	00110	P 2020	0.6551	1 1059	0.7055	0.0005	22V2 0	00212.0	0.075.4	0.0051	0.0746
01001 00000 9 01010	0.0860	0.0806	1.0106	0.0255	0.9915	1182.0	1 9938	0.0510 0	0.0005	0.8599	0.4427	0.0007	1000.7	0.06/2
2 0000 0 080	3 1 0062	0.9386	1 0297	0.9810	0.6621	0.8442	1 2303	0.9668	0.9254	0 9041	0.8938	0.9196	1 4151	0.9513
8.0000 0.957	1 1.0084	0.8834	1.0214	1.0082	0.6364	0.8788	1.2089	0.9840	0.9253	0.9301	0.9059	0.9179	1.338	0.9372
9.0000 0.929	3 1.0052	0.8427	1.0155	1.0222	0.6001	0.8992	1.1851	0.9883	0.9183	0.9409	0.9059	0.9119	1.5019	0.9242
10.000 0.907	3 1.0025	0.8151	1.0097	1.0315	0.5078	0.9132	1.1662	0.9895	0.9115	0.9507	0.9033	0.9065	1.2914	0.9147
Table]	0.24:	Ratio	of disp	ersion (energy fi	com var	ious m	ethods 1	to the $E_{\rm dist}$	_{ax} values	s for the A	r-HF dimer	at variou	s monomer
		senar	ations (anestro	m).				•					
<i>B</i> D	D3BJ[HF]	$\sim \sim \mathbf{r} \sim$ DADE D3	[No-switching]	disn(VV10)	disn(vdW-DF2)	disn(MBD)	disn(VV09)	D3BJ[PBE] X	(DM10[PW86-PBE]	D3MBJ[PBE]	XDM8[PW86-PBE]	XDM[8[No-switchine]	disn(vdW-DF1)	$XDM10[No-switchin \sigma]$
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	0.9000	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 2.0000 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
7.0000 1.0517	0.9925	0100.1	0.3120 1.0036	1.0539	0.7242	0.9040	1.2766	0.9660	1.0431	0.9214	u.soou 1.0156	1.0375	2.1000	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	1.0555
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

		IF] DADE I	alle.											
1	mage and mage of the second se		D3[No-switching]	disp(VV10) (disp(vdW-DF2)	disp(MBD)	disp(VV09)	D3BJ[PBE] >	(DM10[PW86-PBE]	D3MBJ[PBE]	XDM8[PW86-PBE]	XDM8[No-switching]	disp(vdW-DF1) >	XDM10[No-switching]
.2800 0.2	711 5.2907	7 5.3561	24.3121	58.0047	32.4069	61.6774	49.6012	61.7589	64.5290	60.6623	71.8741	70.4619	4.5482	192.9180
8000 4.0.	454 7.5891	1 9.9176	4.0942	44.1421	18.2196	46.6166	27.4950	46.6799	45.0884	47.7026	55.6359	36.1769	20.2970	94.3403
8000 6.5!	939 8.031£	5 5.1802	4.4550	20.3167	4.1500	29.4982	4.8939	22.5511	6.0663	27.1319	19.5459	17.7371	65.3404	38.4576
8000 5.7.	391 3.1671	1 2.0727	1.2035	5.5382	17.1224	20.1894	20.4180	8.9940	13.4195	14.0989	4.1262	17.6366	83.4420	27.5561
8000 5.11	286 1.0471	1 2.3210	2.4864	0.0354	36.9154	13.2970	25.2105	1.7820	19.3443	6.2723	14.0147	19.2126	64.2957	24.5999
8000 5.23	347 3.5278	8.3012	4.7753	4.0019	44.7457	8.4261	25.1877	1.9984	21.3418	1.7352	18.1758	20.4218	41.3302	23.5950
8000 5.5.	173 5.0127	7 12.8951	6.2479	7.2723	47.6847	5.1842	23.7140	4.2046	21.5924	1.1621	19.6131	20.6849	29.3373	22.6653
APE 4.6	472 4.8094	4 6.5777	6.7964	19.9016	28.7493	26.4127	25.2172	21.1384	27.3402	22.6808	28.9980	28.9045	44.0844	60.5903
able	D.26	: APEs	s at varic	ous mor	tomer se	paratic	ns (an	estrom) relative	to the <i>j</i>	$E_{ m diam}$ value	s and MAF	Es for th	e benzene-
		water	5			4	/)	~					
R D)as D3BJ[1	HF 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) 2	XDM10[No-switching]
5000 13.7	7638 2.895	31 6.6756	82.8778	68.4763	45.8896	75.4614	72.5038	74.9534	80.9568	72.8070	84.9621	163.8479	22.9408	479.6373
0000 7.6	1464 6.915	92 7.8360	33.8147	53.7712	28.5760	56.6793	51.2251	57.6817	63.6182	56.6995	71.2755	83.0774	3.6999	204.3873
5000 5.7	7178 5.085	50 13.7052	16.3828	37.8490	10.9875	38.0377	28.0025	38.1893	38.9209	39.8564	51.3195	51.9704	33.2962	112.8398
000 6.9	1562 5.308	85 13.3929	11.3814	22.4476	3.5251	25.1295	8.2338	21.1916	11.6061	25.4551	27.7581	40.1886	64.3242	76.1617
000 9.7	7926 7.625	39 12.0373	11.5340	9.1918	10.7563	17.0214	5.8223	8.5588	10.4616	14.2578	6.1445	36.4061	92.7966	59.8579
000 IZ:	9040 I0.60.	11.8/12	13.43/5	0.4240	8.4130	07.07.11	14.1450	0.3487	24.0251	2.191.6	9.8870	30.77.28	112.6340	0206.10
10 10 10 4	0/23 10.4L 3266 17.670	0.0 2.0605	2002.11	12.0041	10.2502	0.000/0 00000	15.3049 12.1949	15 1080	34.0249 36.9160	1240.6 10.4096	20:3013	30.1003 25.4000	0/ 1845 0/ 1845	44.0051 0 0279
000 000 000	1750 18.60	0207 0 72 00 08 00 08 00 08 00 08 00 08 00 08 00 08 00 08 00 08 00 08 00 08 00 08 00 08 00 08 00 08 00 08 00 08	10 0389	93 4500	16 1001	5 3860	3 0019	17 96.98	35 5067	13 3828	0207-TC	34 5680	24.1040 8/ /300	0167-0 1
APE 12.7	7183 10.014	45 9.0601	25.0846	27.2757	17.1397	26.0302	23.8570	27.1216	37.3362	27.0872	37.9936	57.4919	69.4616	123.0067
able	D.27	: APE	ls at vari	ious mo	nomer se	sparati	ons (ar	lgstron	ι) relative	to the .	$E_{\rm dispx}$ value	s and MAI	PEs for th	e diamino
		dinitı	roethyle	ne (FO)	X-7) dim	ter.					4			
R I	D _{as} D3BJ	[HF] 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) 2	XDM10[No-switching]
3790 9.0	5038 21.91	198 26.9227	67.1108	61.7697	46.5866	70.1435	56.1671	72.9076	75.9402	72.9076	80.1396	124.9260	20.4244	426.3264
5790 7.(0499 16.63	379 23.5032	40.9542	56.1472	40.7005	63.6127	46.9571	67.5838	70.3809	67.5838	75.4528	83.4957	10.3884	268.0077
5790 2.(9223 12.67	798 21.4713	5.2204	31.1516	21.8582	29.7792	9.2109	39.2661	37.2721	39.2661	46.0448	8.5983	34.6494	39.7274
5790 7.4	4063 16.61	138 25.7442	14.4202	19.7313	33.9472	15.3027	3.3076	24.6326	17.5124	24.6326	24.9126	8.5537	43.2441	0.9185
5790 11.	.7671 19.79	992 31.1661	18.5490	17.4894	51.2446	13.0152	2.7017	22.4831	16.8626	22.4831	20.5860	16.0181	19.1036	12.1813
5790 15.	22200 22.46	577 37.2529	21.4314	17.9390	58.1684	14.5031	0.5226	23.5089	20.2615	23.5089	22.1127	20.6074	1.6774	18.7481
APE o.	8449 15.35	030 27.0708	21.94/0	34.0380	42.0843	34.392/	2118.61	41.7304	39.7049	41.7304	44.8/48	43.0999	21.0812	127.0310

			dinitı	roethylen	te (FO)	ζ-7) dim∈	er.								
R	D_{as}	D3BJ[HF]	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]
.3790	9.6038	21.9198	26.9227	67.1108	61.7697	46.5866	70.1435	56.1671	72.9076	75.9402	72.9076	80.1396	124.9260	20.4244	426.3264
.5790	7.0499	16.6379	23.5032	40.9542	56.1472	40.7005	63.6127	46.9571	67.5838	70.3809	67.5838	75.4528	83.4957	10.3884	268.0077
.5790	2.0223	12.6798	21.4713	5.2204	31.1516	21.8582	29.7792	9.2109	39.2661	37.2721	39.2661	46.0448	8.5983	34.6494	39.7274
.5790	7.4063	16.6138	25.7442	14.4202	19.7313	33.9472	15.3027	3.3076	24.6326	17.5124	24.6326	24.9126	8.5537	43.2441	0.9185
.5790	11.7671	19.7992	31.1661	18.5490	17.4894	51.2446	13.0152	2.7017	22.4831	16.8626	22.4831	20.5860	16.0181	19.1036	12.1813
0.5790	15.2200	22.4677	37.2529	21.4314	17.9390	58.1684	14.5031	0.5226	23.5089	20.2615	23.5089	22.1127	20.6074	1.6774	18.7481
IAPE	8.8449	18.3530	27.6768	27.9476	34.0380	42.0843	34.3927	19.8112	41.7304	39.7049	41.7304	44.8748	43.6999	21.5812	127.6516

thanol	D-switching	.7853	.7406	3567	0431	7421	5902	6146	5532	ylene-		o-switching	.1793	1100.	3364	1148	7836	1539	2600	5105	dazole		o-switching]	5.4515	.2407	0228	0629	1912	1397	39/3
· the e	NDM10[N	209	134	53.	ŝ	24.	20.	17.	-02	he eth		NDM10[N	212	144	49. 16.	e,	2.7	6.4	9.1	55.	he imi		NDM10[N	1595	506	48.	10.	2.1	1.4	0.0
PEs for	disp(vdW-DF1	2.0583	16.3499	74.2375	100.1407	81.5654	52.8809	34.5991	51.6903	Es for t		disp(vdW-DF1	0.5864	12.0705 47.4819	41.4012	64.3406	45.9954	21.7721	2.0397	32.6532	Es for t		disp(vdW-DF1	47.9266	30.5788	24.4491	56.0069	45.8921	25.3952	14.0151
es and MA	XDM8[No-switching]	75.3347	51.8798	25.6298	20.7528	18.5640	17.1620	15.5715	32.1278	and MAP		XDM8[No-switching]	69.3292	1067.2401	0.9888	4.7987	7.5104	9.2493	10.8087	20.6996	and MAP		XDM8[No-switching]	349.4500	139.1673	11.3521	0.8624	2.6217	3.9687	99/T°C
E _{dispx} valu	XDM8[PW86-PBE]	74.9652	65.3153	26.7231	1.1890	11.5309	14.3621	14.3247	29.7729	d _{ispx} values		XDM8[PW86-PBE]	76.8210	10.89/3	27.9265	17.7436	13.3138	11.8679	12.0286	34.7565	dispx values	-	XDM8[PW86-PBE]	84.9612	77.5310	46.5758	18.8848	8.0416	5.9065	0.0027
to the	D3MBJ[PBE]	66.4464	57.9323	31.4021	15.0104	7.2182	3.4440	1.7827	26.1766	to the E		D3MBJ[PBE]	66.1418	00.2922	31.9381	26.6202	23.2312	21.1513	20.1334	36.5242	to the E		D3MBJ[PBE]	79.8531	71.8109	46.0438	28.1974	20.5868	17.7189	10.4648
n) relative	XDM10[PW86-PBE]	68.7301	56.9456	13.1805	11.8199	17.5687	17.7759	16.3659	28.9124	() relative t		XDM10[PW86-PBE]	71.3683	04.1779 96 6044	30.0344 17.2134	10.2538	8.6992	9.0897	10.3324	28.4786	1) relative t		XDM10[PW86-PBE]	81.5009	72.6612	37.7787	10.5876	3.3767	3.3886	4.0220
ngstroi	D3BJ[PBE]	66.2399	56.5241	26.3495	9.5274	2.5976	0.2889	1.1989	23.2466	gstrom		D3BJ[PBE]	66.9224	00.4108 40.0951	27.7584	22.2555	19.2218	17.7161	17.2967	33.9508	Igstrom		D3BJ[PBE]	80.1125	71.6260	43.1182	23.8521	16.7184	14.5727	13.9113
ions (a	disp(VV09)	49.9658	34.8219	6.5589	27.1221	33.4071	34.5445	32.9530	31.3390	ons (an		disp(VV09)	33.7907	21.0155	25.7528	30.5156	31.1584	29.6774	27.0861	26.2396	ons (ar	,	disp(VV09)	76.4001	63.3707	20.9152	0.0300	3.9239	1.8445	1.4340
eparati	disp(MBD)	61.2830	50.0268	23.7971	10.8716	3.1593	1.7258	4.4093	22.1818	paratic		disp(MBD)	64.8576	1010.76	21.5954	14.8959	10.0627	6.7872	4.8231	26.7869	paratic		disp(MBD)	80.0787	70.8990	37.7163	16.6857	7.5024	3.7134	3.1807
nomer se	disp(vdW-DF2)	31.7403	20.6290	2.9570	7.4286	30.0734	42.0916	46.8260	25.9637	nomer sel) dimer.	disp(vdW-DF2)	27.2747	19.870U	0.0912 6.3900	23.2100	42.1123	55.1911	63.1905	30.1420	nomer se		disp(vdW-DF2)	65.8639	54.9826	25.3028	22.2513	36.6582	44.4948	40.1524
ous me	disp(VV10)	56.7134	47.2846	18.5864	0.7398	6.0261	8.6117	10.3848	21.1924	tom su	EDNA	disp(VV10)	51.7938	44.0019	10.3625	4.4690	1.8968	0.9665	1.1199	17.3488	out suc		disp(VV10)	75.4470	66.0097	36.7030	17.4241	9.2247	6.1215	3.8/89
s at vari.	[No-switching]	23.1055	10.1740	0.5795	0.7923	2.3857	3.2242	3.1995	6.2087	at vario	amine (I	03[No-switching]	31.5132	6700.81	9.8012	12.7804	13.8490	14.4506	15.1350	14.7444	at varic		03[No-switching]	193.7196	69.4995	9.3615	13.8816	12.5513	12.1308	12.1000
APEs dimer.	DADE D3	2.8756	8.9676	11.1730	8.9947	4.4878	2.3885	8.4748	6.7660	APEs	dinitra	DADE D	10.9677	1.4141 4.6970	6.8052	9.6147	12.9456	17.4878	22.4639	11.5484	APEs	dimer.	DADE D	34.9815	23.6031	13.3382	18.1046	22.8472	28.4813	27.8012
.28:	D3BJ[HF]	12.0226	9.0274	5.4053	1.4002	1.0079	2.1714	2.2736	4.7584	.29:		D3BJ[HF]	10.5722	10 61 44	13.2579	14.8276	15.2381	15.4994	16.0169	13.1313	.30:		D3BJ[HF]	43.8342	28.8410	17.7440	16.4680	14.4889	14.1773	14.0017
le D	D _{as} I	0.8475	1.1536	0.6818	2.6975	2.6567	1.9221	0.7720	1.5330	le D		Das	22.8202	0.0070	2.5805	2.7222	5.8546	8.0205	9.8664	10.1167	le D.		D_{as}	11.2735	6.2403	6.1891	8.0174	8.3654	9.5347	IU. / 301
Tab	R	3.2560	3.5580	4.5580	5.5580	6.5580	7.5580	8.5580	MAPE	Tab		R	4.4980	4.7080 5.7080	0.7980	7.7980	8.7980	9.7980	10.7980	MAPE	Tab		R	4.9250	5.2470	6.2470	7.2470	8.2470	9.2470	10.24/0

r the methyl-	71) XDM10[No-switching]	167.0621 115.1780	32.3162	15.8340	8.9527	4.5297	57.3121	the nitroben-		[71] XDM10[No-switching]	101.6959	00 6703 00 6703	21.8575	19.6769	18.2008	17.2004	39.7320	Is for the ni-	71) XDM10[No-swittching]	130.5644	82.8630	26.1022	12.9037	8.2428	5.6294	4.0901
APEs fc] disp(vdW-D]	4.4417 7.6042	64.8826	82.5944	60.5151	34.8823	42.4867	PEs for] disp(vdW-D	3.0880	10.2001 60 1185	76.0136	58.3801	35.4843	23.1249	39.2140	I MAPI	disn(vdW-D)	2.4309	14.7436	67.2028	88.0219	65.4071	42.5570	1002'10
ues and M/	XDM8[No-switching]	52.9676 36.9348	10.3674	6.3594	4.2389	1.9541	18.8037	es and MAI		[] XDM8[No-switching	28.4764	0 2558	11.5125	13.8523	14.7059	14.9897	15.9786	values and	XDM8[No-switching	36.1907	21.1731	4.3614	2.9830	3.1126	2.7375	7-0034
$E_{\rm dispx}$ val	XDM8[PW86-PBE	74.2967 68.4682	32.2318	8.3597	0.9003	0.0574	30.7190	Z _{dispx} valu		XDM8[PW86-PBF	74.1515	2464.36	2.2313	8.2611	12.2020	13.7641	28.7185	he $E_{\rm dispx}$	XDM8[PW86-PBF	82.4892	74.1230	38.8599	12.8020	2.6547	0.3868	1.2001
e to the	D3MBJ[PBE]	66.4486 60.9210	33.7725	18.4110	12.0144	9.7481	33.5526	to the E		D3MBJ[PBE]	55.5885 46.9500	95, 1270	11.1509	2.7699	1.9351	4.8707	21.1864	tive to t	D3MBJ[PBE]	73.2970	64.5449	38.2317	21.6790	13.2932	9.1475 6.7675	0.1000
m) relativ	XDM10[PW86-PBE	68.5936 61.6321	20.6976	0.1760	3.7366	2.5099	26.2243	n) relative		XDM10[PW86-PBE	67.2932 54 5465	19 5011	7.5022	14.0198	15.6876	15.9731	26.8034	rom) relat	XDM10[PW86-PBF	78.1590	67.8137	27.1373	3.8169	2.3976	3.2699	1010.6
angstrc	D3BJ[PBE]	66.2909 60.0648	29.2253	13.3102	7.7266	6.3158	30.4889	ngstror		D3BJ[PBE]	59.5502	91 0031	5.4126	2.6435	6.5792	8.7860	21.8733	(angst	D3BJ[PBE]	75.0717	65.5715	34.8091	16.6220	8.6353	5.2705	0710.6
tions (a	(VV09) disp	51.7632 42.2626	2.2561	14.3158	17.3269	15.0730	23.8329	ions (a) disp(VV09	20.9749 9 9909	20.0400	56.4044	58.3797	59.6251	57.0854	42.1771	rations	disn(VV09	49.7501	32.6840	11.7787	33.5176	38.9896	38.3937	00.0113
separa	disp(MBD)	62.8392 55.7618	27.2140	14.5280	8.0763	4.9178	28.8895	eparat) disp(MBD	60.8822 50.21.00	02.15.00 9.2 8611	9.5485	1.4001	3.0126	5.4326	22.0641	r sepaı	disn(MBD)	75.1577	64.0402	30.7007	13.5425	5.2576	0.8854	1.4401
lonomer	disp(vdW-DF2)	36.6324 29.6493	7.1176	18.7051	37.1934	45.8819	29.1966	onomer se) disp(vdW-DF2	22.0890 19.6667	3 0/36	8.5269	30.5316	40.2915	43.3033	23.0504	monome) disn(vdW-DF2	30.3942	20.2139	0.2406	15.0503	34.9274	41.3979	41.3100
rious n er.	ζ] disp(VV10)	56.5829 50.5077	22.1650	6.6744	0.7876	1.5847	23.0504	ious mc		ng] disp(VV16	49.9688	8 0596	8.2992	16.2453	20.6390	23.5896	23.9190	arious	<u>ulliter.</u>	57.4776	47.6438	18.9513	1.9638	5.8396	10.1801	10.0200
ीs at va ate dim	D3[No-switching	18.9182 8.5898	5.2761	4.1502	3.2875	3.6812	7.3172	s at var	dimer.	D3[No-switchin	11.3318	1000.0	3.8958	7.9745	10.1151	11.3828	7.0558	Es at v	<u>eullalle</u> D3[No-switchin	13.4461	2.1524	7.8625	5.6909	3.2757	2.1071	1.4042
APE	DADE	7.3216 3.6607	1.3302	3.9230	8.9603	15.8876	6.8472	APE	zene	DADE	6.7480	10.4964	5.0848	0.2928	7.3306	12.7919	7.8218	[dV]	1 DADE	18.8616	13.3979	8.2950	4.2314	4.7771	9.7689	14.0000
0.31:	D3BJ[HF]	18.3882 15.3808	9.8280	6.1616	4.5666	4.6733	9.8331).32:		D3BJ[HF	3 8.4027	5 4098	3 1.3071	5.9749	5 8.3257	9.5827	2 6.7915).33:	D3BJIHF	1 19.3679	16.8272	12.9179	8.0048	4.7176	3.1740	21007
Table I	R D _{as}	4.2430 7.0487 4.4340 7.6084	5.4340 7.3917	6.4340 6.4647	7.4340 7.1398	8.4340 8.6880	MAPE 7.3902	Table I		R D _{as}	2.9000 18.988	4 2000 8 5072	5.2000 10.6555	6.2000 12.0526	7.2000 12.0785	8.2000 11.7319	MAPE 12.5552	Table I	R D	2.8130 16.5496	3.1310 9.8614	4.1310 1.6819	5.1310 0.9255	6.1310 0.4257	7.1310 0.6001	0.101U 1.0041

Jer		on	II
· the wat	 CDM10[No-switch] 4772,3304 4772,3304 5337,7699 5325,2653 140,7301 66,7145 39,6015 27,7419 57,7419 57,7417 57,7417 57,7417 57,7419 57,7417 57,7417 57,7419 57,7417 57,7419 57,7417 57,7417	the arg $\frac{135635}{2855485}$ $\frac{2855485}{135625}$ $\frac{135625}{6.2764}$ 0.02764 0.02764 0.2396 3.5696 3.5644 7.5644	the Ar-F $\frac{14.85}{1000000000000000000000000000000000000$
IAPEs for	disp(edN-DF1) X 60.7288 47.2402 147.2402 113.7890 7.6351 49.735 114.0302 111.0442 111.0442 111.0442 111.0442 111.0442 111.0442 111.0442 111.05406 91.7241 91.7241 91.7241 91.7642 1101.5402 91.0603	(APEs for disp(4(W-DF1)) 4.8622 15.0720 15.0720 35.3572 83.3572 83.3572 83.3572 83.3572 83.3572 83.3572 83.3572 83.3572 83.3535 81.1443 41.5120 33.3835 50.1917 29.1368 42.1533 42.1533 44.5120 33.3835 50.1317 44.5120 33.3835 50.1317 44.5120 33.3835 50.1317 44.5120 50.1317 50.1572 50.	APEs for disp(edW-DF1) > y 0.9374 0.9374 0.9374 0.9374 0.9374 0.9374 0.15.207 11.6.203 0.1.6.223 0.1.6.233 0.
ues and M	XDM8[No-switching] 862.6544 862.6544 159.35465 159.354856 159.354856 49.9182 24.68266 10.0418 13.0909 10.0418 13.0909 10.0418 10.0418 11.1701 10.9645 10.19645 10.19645	ues and M XDMS[Ne-switching] 16.5541 17.5529 16.541 17.5329 16.5417 15.1111 12.4633 9.0331 8.0422 8.8109 9.3539 9.3539 9.3539	tes and M <u>xpns[No-switching]</u> <u>6.4882</u> 0.8908 0.29185 1.0.8055 2.9185 1.5616 3.7568 3.8617 3.5496 5.3616 3.5496
$E_{ m dispx}$ val	XDM8.[PW86-PBE] 96.0686 95.0686 95.7028 87.5531 80.3551 71.1743 51.9099 31.9464 14.0718 31.2917 5.1908 7.7076 9.0731 9.076 9.0776 9.0776 9.076 9.0776 9.0776 9.0776 9.0776 9.0776 9.0776 9.0776 9.0776 9.07776 9.07777 9.07776 9.0777 9.0777 9.0777 9.07777 9.07776 9.0777 9.07777 9.07777 9.07777 9.07777 9.07777 9.07777 9.07777 9.07776 9.07777 9.07777 9.07777 9.07777 9.07777 9.07777 9.07777 9.07777 9.07777 9.07777 9.07777 9.07777 9.07777 9.07777 9.07777 9.07777 9.07777 9.07777 9.07776 9.07777 9.07777 9.07776 9.07777 9.07777 9.07776 9.0776 9.0776 9.07777 9.07776 9.07776 9.07776 9.07776 9.0777777777777777777777777777777777777	$E_{ m dispx}$ vall $E_{ m dispx}$ vall $\frac{1}{74.7531}$	Edispx valu Rougewee-PBE 64.2799 64.2799 64.2799 16.1121 3.4375 1.609 2.8433 3.3396 2.8433
ve to the	D3.MBJ.[PBE] D3.MBJ.[PBE] 93.7062 93.7062 83.4652 83.4652 83.4652 83.4652 83.6658 83.6.0718 50.7018 50.5058 50.7018 50.7018 50.7018 50.7018 50.7018 50.2005 11.7866 11.7866 9.5994 11.7866 9.5594 7.5571 5.8737 7.8573 5.3008 5.3008 37.8519 37.8519	e to the $\frac{1}{5,0056}$ = $\frac{10,0056}{57,0056}$ = $\frac{55,3340}{57,0056}$ = $\frac{55,3340}{57,0056}$ = $\frac{5,33426}{5,3022}$ = $\frac{14,7776}{5,9079}$ = $\frac{14,7776}{5,9079}$ = $\frac{14,9277}{5,9079}$ = $\frac{14,927}{5,9079}$ = $\frac{14,927}{5,907$	$\stackrel{\text{e to the}}{\overset{1}{_{12}}} \stackrel{\text{panelpel}}{\overset{1}{_{2}}} \stackrel{\text{panelpel}}{\overset{1}} \stackrel{\text{panelpel}}{$
m) relativ	DM10[PW86-PBE] 95.0997 95.0997 95.0997 94.4585 75.0673 42.4559 42.3355 19.2335 19.2335 19.2335 19.2336 19.2336 8.5776 19.2336 8.5776 11.2104 11.7319 11.7319 12.1084 8.5776 8.5776 11.2104 11.2104 11.2104 11.2108 8.5776 8.57776 8.57776 8.57776 8.5776 8.5776 8.5776 8.577777776 8.5777777777777777777777777777777777777	n) relativ $\frac{20001000}{12000}$ relativ $\frac{79,0951}{75,06}$ 56.7,443 56.7,443 56.7,443 56.7,443 56.7,443 56.7,443 57.743 7.7438 7.454 7.4734 8.8514 8.8514 8.8514 8.8514	n) relativ $\frac{DM10[PW86-PBE]}{77.5029}$ 55.5443 33.2379 17.4813 8.0435 1.74813 8.0435 1.74813 4.3101 4.3263 4.147 2.2863
angstro	D3BJ[PEE] X 93.6307 93.6307 82.9654 74.7632 64.8221 64.8221 64.8221 64.8221 64.8221 64.8221 64.8221 10.9148 7.8043 7.8043 7.8043 7.8043 7.8043 7.8043 7.8043 7.8043 7.8043 7.8322 2.8522 2.8522 2.8577 34.9415	angstror 56.5518 65.5518 56.1502 31.7268 31.7278 31.7278 31.7278 31.7278 31.7278 31.7278 31.7278 31.7278 31.7278 31.727780 31.72788 31.727888 31.727888 31.72788 31.72788 31.72788 31.72788 31.727888 31.727888 31.727888 31.727888 31.727888 31.7278888 31.727888 31.727888 31.7278888 31.7278888 31.7278888 31.7278888 31.7278888 31.72788888 31.72788888 31.7278888888888 31.72788888888888888888888888888888888888	angstroi <u>77.4127</u> 77.4127 60.0425 40.0426 43.428 29.8431 2.9442 3.3890 1.1791 0.5342 2.9542 3.3890 0.5342 2.955
tions	disp(VV09) 105.2345 99.7651 99.3724 78.3503 65.2962 86.0957 18.0338 14.5076 14.5076 14.5076 14.5076 14.5076 14.5076 14.5076 14.5078 14.5776 13.328 85.584 14.5776 13.3746 63.3274 85.584 14.5775 85.584 14.5775 85.584 14.5775 85.584 14.5775 85.584 14.5775 85.584 14.5775 85.584 14.5775 85.584 14.5775 85.584 14.5775 85.584 14.5775 85.584 14.5775 85.584 14.5775 85.584 14.5775 85.584 14.5775 85.584 14.5775 85.584 14.5775 85.584 14.5775 14.5775 85.584 14.5775 14.5755 14.57755 14.57755 14.57755 14.57755 14.57755 14.577555 14.5775555555555555555555555555555555555	ions (disp(VV09 0.2.9600 0.2.98000 0.2.98000 0.2.98000 0.2.98000 0.2.98000 0.2.98000 0.2.98000 0.2.98000 0.2.98000 0.2.980000000000000000000000000000000000	ions (ions (67.621 41.0402 15.825 15.825 15.825 15.815 15.1165 25.8723 25.8723 25.8723 25.6125 25.6125 25.6125 25.6125 25.6125 25.6125 27.6111 26.6155 27.6111 27.6112 27.6111 27.6112 27.6111 27.6112 27.6111 27.6112 27.
separa	disp(MBD) 94.2105 94.2105 81.8841 72.2291 40.2514 42.2514 42.2514 42.2514 42.2514 42.2514 42.2514 15.5584 15.5584 15.5584 15.558 8.1557 8.1558 8.1558 8.1553 8.15555 8.155555 8.15555555555555555555	Separat 56001 56002 56002 56009 56009 56009 56009 52,0469 545,2069 34,52069 34,52069 34,52069 21,8880 15,5805 12,1212 10,0771 8,6821 39,1304	$\begin{array}{c} \text{Separat}\\ \text{alge}(\text{ABD})\\ & \frac{\text{disp}(\text{ABD})}{80.8314}\\ & \frac{80.8314}{63.629}\\ & \frac{47.775}{25.3622}\\ & \frac{25.3622}{25.3622}\\ & \frac{25.2322}{25.3624}\\ & \frac{10.1018}{6.1018}\\ & \frac{29.3256}{29.3256}\\ & \frac{29.3256}{20.3256}\\ & $
onomer	Jisp (vdW-D F2) 75.5684 75.5684 77.5584 77.5684 77.5684 77.5684 77.5684 77.561 75.133 75.135 76.5173 96.5173 46.5173 46.5173 7.6006 113.84 5.1135 7.6006 113.84 23.8479 23.8479 23.4402 23.5156 23.4402 23.5355 26.4402 23.5556 26.5166 23.5576 19.3767 16.6388 8.7846 29.401	1001001 (100000000000000000000000000000	$\begin{array}{c} \textbf{DD} \textbf{DD} \textbf{DD} \textbf{DD} \textbf{D} \textbf{D} \textbf{D}$
rious me	disp(VV10) 85.9670 79.5447 79.5447 73.53787 73.5458 65.3787 65.3787 11.2914 20.4456 11.2914 11.2914 20.4456 11.2914 8.5198 8.5198 6.3645 4.9964 2.38066 2.38066 2.38066 2.38066 2.38066 2.38066 2.38066 2.38066 2.38066 2.38066 2.38066 2.38066 2.38066 2.38066 2.38066 2.38066 2.38067 2.39067 2.39067 2.39067 2.39067 2.39067 2.39067 2.39067 2.39067 2.39067 2.39067 2.39067 2.39067 2.38067 2.3907 2.	ious mo ^{59,5837} ^{59,5837} ^{59,5837} ^{59,289012} ^{22,4472} ^{1,45206} ^{6,4491} ^{0,4591} ^{1,4891} ^{0,2196} ^{2,2169} ^{2,2169} ^{2,21692}	ious mc disp(VV10) disp(VV10) disp(VV10) disp(15,25,44,25,54,42,55,44,25,54,42,55,44,25,56,56,44,25,56,56,44,25,56,56,44,25,56,56,44,25,56,56,44,25,56,56,56,56,56,56,56,56,56,56,56,56,56
s at var	[No-switching] 471.3856 75.3890 75.3890 75.3897 75.3897 31.2329 3.5713 6.8725 5.1823 3.5713 6.8725 5.1823 3.5713 5.1823 3.7766 5.1823 3.7766 1.1237 3.7766 3.37766 3.37766 3.37766 3.37766 3.37766 3.37766 3.37766 3.37766 3.37766 3.37766 3.37766 3.37766 3.37766 3.37766 3.37766 3.37766 3.377766 3.377766 3.377766 3.377766 3.377766 3.377766 3.377766 3.377766 3.377766 3.377766 3.377766 3.377766 3.377766 3.3777766 3.377766 3.377766 3.377766 3.377766 3.3777666 3.3777666 3.3777666 3.3777666 3.3777666 3.3777666 3.377766666 3.3777666666 3.37776666666666	$ at vari \\ 2380 \\ 7070 \\ 7070 \\ 8.818 \\ 7.070 \\ 8.848 \\ 7.205 \\ 5.882 \\ 7.205 \\ 2.882 \\ 2.1430 \\ 1.542 \\ 2.1430 \\ 1.542 \\ 0.9722 \\ 3.7887 \\ 0.9722 \\ 1.548 \\ 0.9722 \\ 1.548 \\ 0.9722 \\ 1.548 \\ 0.9722 \\ 1.548 \\ 0.9722 $	S at Var S at Var <u>18.2803</u> <u>18.2803</u> <u>18.4589</u> 13.0135 <u>8.9801</u> 1.2814 <u>1.5691</u> <u>1.5691</u> <u>1.5619</u> <u>0.3561</u> <u>1.5619</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3561</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.3664</u> <u>0.366465555555555555555555555555555555555</u>
APE	QUILIEL QUILIEL 51.0874 51.0874 51.0874 15.339 9.3756 5.6800 9.3756 5.6800 9.3756 5.6800 9.3756 5.6800 13.4809 14.4809	$\substack{\text{APEs}\\ \frac{1}{15,367}\\ 1,273\\ 5,9160\\ 5,9160\\ 5,9160\\ 1,2713\\ 1,1273\\ 5,9160\\ 1,2713\\ 1,1273\\ 5,9160\\ 1,2713\\ 1,1273\\ 1,12$	APE, AppE, <u>11,768</u> 11,768 11,768 11,768 11,768 1,755
.34:	D3BJ HF 58.2436 42.4069 42.4069 18.0222 18.0225 18.0225 18.0225 18.0225 18.0225 18.0225 18.0225 18.0225 11.2525 5.6473 5.6473 11.2525 5.8124 4.7875 3.8145 5.8124 4.7875 5.8124 4.7875 14.2077 14.2077	1.35: 1.35: 24.1094 2.8.4645 2.8.4645 2.8.4645 13.3215 11.0427 6.6510 1.3064 0.6238 0.6338000	.36: .36: .36: .3124 .34.284 .34.284 .34.284 .12.21855 .12.21855 .12.218555 .12.2185555555555555555555555555555
le D	$\begin{array}{c} D_{\rm sm} & 1\\ 0.9114 & 0.9114 \\ 0.9016 & 0.9846 \\ 7.5174 & 8.89119 \\ 8.81119 & 8.81119 \\ 8.81119 & 8.81119 \\ 5.02415 & 0.1798 \\ 1.36427 & 3.6427 \\ 5.0245 & 6.0245 \\ 6.02645 & 6.02412 \\ 7.00219 & 7.9129 \\ 7.7021 & 4.8617 \end{array}$	$\lim_{\substack{D_{ab} \\ 13776}} \frac{D_{ab}}{13776} \\ 13717 \\ 0.5599 \\ 1.3717 \\ 0.5599 \\ 1.3717 \\ 0.5599 \\ 1.9483 \\ 1.9483 \\ 1.9483 \\ 0.5599 \\ 1.9483 \\ 0.5596 \\ 1.9483$	$\lim_{m \to \infty} \frac{1}{2.762} \sum_{m=1}^{2m} \frac{1}{3.701}$
Tab	$\begin{array}{c} R\\ 2.3100\\ 2.56100\\ 3.5100\\ 3.5100\\ 3.5100\\ 5.50100\\ 5.50100\\ 6.0100\\ 6.0100\\ 5.50100\\ 6.0100\\ 5.5000\\ 8.0050\\ $	$\frac{\text{Tab}}{\frac{R}{3.2000}}$	$\frac{\mathbf{Tab}}{\frac{R}{3.000}}$

zene-	switching]	836 53	81	46	17	20 20	48	zene-		switching]	035	690 07	22 SS	22	36	57	23 23	87	-onin		switching	826	578	49	98 86	81	253
ne ben	XDM10[No-	136.6	32.45	26.35	24.41	23.50	47.88	le ben		XDM10[No-	343.0	153.7	90.05 65.83	55.12	49.94	44.17	40.25	37.76	ne dian		XDM10[No-	338.1	215.8	34.04	0.20 12.25	18.74	103.2
Es for th	disp(vdW-DF1)	22.8730	58.1760	81.7573	64.0475	41.3302	43.1614	Es for th		disp(vdW-DF1)	41.1054	13.5449	19.3021 54.6796	87.0984	109.8083	116.2717	94.1845 84 4300	68.9439	Es for th		disp(vdW-DF1)	33.7486	23.0871	29.1735	42.3144 19.0243	1.6774	24.8376
and MAI	DM8[No-switching]	37.7366 18.41.73	12.6354	16.5562	19.0325	20.4218 00.6840	20.7835	and MAI		DM8[No-switching]	101.6529	52.6324 36.0949	30.0842 31.9606	32.3745	33.9685	35.7509	35.4900 34.5680	43.8313	and MAI		DM8[No-switching]	87.2641	57.4928	4.1818	9.1472 16.0740	20.6074	32.4612
_{disp} values	DM8[PW86-PBE] X	77.2737 61.4916	23.0321	3.1699	13.8425	18.1758	30.9327	lisp values		DM8[PW86-PBE] X	88.5068	76.0523	30.4083 31.9982	8.9184	8.4267	26.0314	31.4890 32.7456	40.0641	d _{isn} values	4	DM8[PW86-PBE] X	83.4651	78.9313	48.2391	20.6389 20.6389	22.1127	46.4645
o the E	3MBJ[PBE] XI	68.2143 5.4 5020	30.2894	14.8879	6.4139	1.7352	25.3180	o the E_{ϵ}		3MBJ[PBE] XI	79.2170	63.9001	46.1435 29.8303	16.7919	7.0436	4.7679	10.4926 13.3828	30.1744	o the E		3MBJ[PBE] X	77.4439	72.1775	41.7360	25.1218 22.5347	23.5089	43.7538
) relative t	M10[PW86-PBE] D	71.3387	10.1366	12.3778	19.1640	21.3418	21.3924) relative t		DM10[PW86-PBE] D	85.4457	69.6683	45.3058	7.1968	22.3769	34.2734	36.2159 35.5967	39.2082) relative t		DM10[PW86-PBE] [79.9688	74.5782	39.8231	18.0477 16.9179	20.2615	41.5995
ngstrom	D3BJ[PBE] XI	69.1004 53.6337	25.9070	9.8298	1.9303	1.9984	4.2040 23.8006	ligstrom)		D3BJ[PBE] XI	80.8575	64.7191	44.6507 25.8171	11.2614	0.9848	10.4204	15.1989 17.2628	30.1303	ngstrom)	D3BJ[PBE] XI	77.4439	72.1775	41.7360	25.1218 22.5347	23.5089	43.7538
ons (a	disp(VV09)	59.2768 36.0507	0.3487	19.3121	25.0213	25.1877	27.1159	ons (ar		disp(VV09)	78.9853	59.3362 ar rass	30.0288 13.6198	2.6947	12.6287	18.2553	13.1243 3.0912	26.3627	ons (a		disp(VV09)	63.5065	54.4737	12.9031	2.6371 2.6334	0.5226	22.7794
parati	disp(MBD)	69.0345 53.5787	32.5532	20.9224	13.4280	8.4261	29.0182	paratic		disp(MBD)	81.2457	63.8833	44.5149 29.5239	19.4738	12.4419	3.3088	2.2383 5.3860	29.1130	parati	er.	disp(MBD)	75.1427	68.7691	32.6350	13.0731 13.0731	14.5031	36.6626
nomer se	disp(vdW-DF2)	45.3834	8.3033	17.8836	37.0107	44.7457	41.0041 32.8424	10mer se		disp(vdW-DF2)	58.6447	40.4535	20.2925	7.4829	6.9729	10.7935	19.3593 16 1901	20.3045	nomer se	X-7) dime	disp(vdW-DF2)	55.5302	49.1038	25.0361	51.2770 51.2770	58.1684	45.5819
om sno	Γ . disp(VV10)	66.0670 51.4268	23.7695	6.4058	0.1158	4.0019	22.7227	tom su		disp(VV10)	75.9072	61.4588	44.3460 26.9994	11.8757	0.9099	11.7117	17.8663 23.4500	30.5028	om suc	e (FO)	disp(VV10)	68.1711	62.3615	33.9516	20.2523 17.5443	17.9390	36.7033
s at varic	<u>ne dime</u> 3[No-switching]	0.4467	8.5951	2.1108	2.3316	4.7753 6.9470	0.2479 4.8555	at vario	dimer.	3[No-switching]	39.7694	11.5619	4.2167 4.8442	8.2376	11.9300	16.9590	19.1298 19.9382	15.1763	s at varie	oethvlen	03[No-switching]	39.1296	20.9798	9.0749	14.9750 18.6032	21.4314	20.6991
APE_s	$\frac{\text{metha}}{\text{DADE} D}$	14.8701 A AT 7A	0.6226	1.1353	2.4685	8.3012	6.3872	APEs	water	DADE D	28.6743	10.0966	0.7375	8.7260	10.3846	9.5635	3.2695 2.9028	9.1304	APEs	dinitro	DADE L	39.1589	34.3434	24.6649	26.2261 31.2120	37.2529	32.1430
.37:	D3BJ[HF]	23.4730 1 0.6400	12.0166	4.0565	0.8944	3.5278	9.8031	.38: .38:		D3BJ[HF]	21.3611	10.8610	1006.6	4.4430	9.1314	15.1144	17.6792 18.6041	11.5519	39:		D3BJ[HF]	34.9936	28.4511	16.2309	17.1550	22.4677	23.1918
ole D	D_{as}	18.9790	10.6413	6.6048	5.2719	5.2347	9.8298	le D		D_{as}	13.0529	10.2547	0.6787	6.5476	11.4036	17.2654	19.6366 20.4750	11.6275	le D		Das	8.7484	8.1200	6.0068	11.8258) 15.2200	9.6547
Tat	R	3.2800	4.8000	5.8000	6.8000	7.8000	MAPE	Tab		R	2.5000	3.0000	3.5000	4.5000	5.0000	6.0000	8 0000	MAPE	Tab		R	6.3790	6.5790	7.5790	9.5790	10.5790	MAPE

ğ
ē
th
or
SF
Ĕ
ΑF
X
F
an
ŝ
lué
۲a.
đ
dib
Щ
he
o t
ţ
Ne
ati
el
Ш
LIC
S
gu
ns
tic
ra.
pa
se]
θĽ
Ш
DO I
JO
n
ns
ric
vaj
Ľť,
s S
Ĕ
ΑF
۲
4
ç
Ω
le
٩e
Ĥ

lon	ching									ine-		ching	5								sole		ching]							
the etha	XDM10[No-swit	154.7137	102.2861	46.5898	31.8406	24.6112	20.5902	17.6146	56.8923	e ethyle		XDM10[No-swit	158.9360	110.1219	38.9159	12.6906	2.0785	0.1400	9.1097	42.6904	e imidaz		XDM10[No-swit	1211.8529	383.2440	36.3466	8.2262	1.4397	3.6973	235.2512
PEs for 1	disp(vdW-DF1)	19.4697	0.2637	66.5493	98.3317	81.3749	52.8809	34.5991	50.4956	Es for th		disp(vdW-DF1)	16.5690	3.2311	37.3662	61.1218	62.2170 45 4400	40.4439 91.6812	2.0397	31.2095	Es for th		disp(vdW-DF1)	59.7083	44.6633	14.6324	53.4037	45.5497 25.3952	14.5131	36.8379
es and MAI	XDM8[No-switching]	44.1649	30.8813	20.0864	19.6614	18.4396	17.1620	15.5715	23.7096	and MAP		XDM8[No-switching]	40.4495	27.3610	6.7548	2.1760	6.0289 7 9560	0.0000	10.8087	13.8440	and MAPI		XDM8[No-switching]	247.7612	90.6440	2.5686	2.5167	2.8503	5.1788	50.7840
$E_{ m disp}$ value	XDM8[PW86-PBE]	79.4158	70.1107	29.9565	0.2744	11.4139	14.3621	14.3247	31.4083	J _{disp} values	4	XDM8[PW86-PBE]	80.7743	75.0058	51.0574	30.1852	18.8065	11.0227	12.0286	36.6786	Z _{disp} values	1	XDM8[PW86-PBE]	88.3637	82.0896	50.7900	20.2384	8.2575 5.9065	6.0027	37.3783
to the	D3MBJ[PBE]	72.4113	63.7484	34.4289	15.7785	7.3156	3.4440	1.7827	28.4156	to the E		D3MBJ[PBE]	71.9165	65.8978	46.6161	34.0710	27.5684 99 E 190	1016-16	20.1334	38.8664	to the H		D3MBJ[PBE]	84.4114	77.5301	50.2999	29.3956	20.7732	16.4848	42.3734
m) relative	XDM10[PW86-PBE]	74.2891	62.8982	17.0114	10.8093	17.4453	17.7759	16.3659	30.9421	a) relative		XDM10[PW86-PBE]	76.2515	69.2350	41.0362	19.8078	0.0403	9.040.0 0 1576	0.3324	30.7843	n) relative		XDM10[PW86-PBE]	85.6864	78.2078	42.6868	12.0796	3.6035 3.3886	4.5225	32.8822
ngstrc	D3BJ[PBE]	72.2415	62.5349	29.5993	10.3451	2.6998	0.2889	1.1989	25.5583	lgstron		D3BJ[PBE]	72.5639	65.9996	44.1385	30.0223	23.2600	17 7775	17.2967	36.3228	ngstroi)	D3BJ[PBE]	84.6121	77.3826	47.6051	25.1228	16.9139 14.5727	13.9113	40.0179
ions (ĉ	disp(VV09)	58.8606	43.8332	1.8570	25.9731	33.2671	34.5445	32.9530	33.0412	ons (ar		disp(VV09)	45.0830	32.6835	2.7514	21.8119	28.8291	00.0000	27.0861	27.3117	ons (a	,	disp(VV09)	81.7396	70.8022	27.1535	1.6392	3.6800 1.8445	1.4345	96 8001
eparat	disp(MBD)	68.1659	56.9359	27.1595	11.6772	3.2609	1.7258	4.4093	24.7621	paratic		disp(MBD)	70.8513	63.0790	38.7715	24.0525	10.9056	6 9567	4.8231	29.3535	parati	4	disp(MBD)	84.5859	76.8032	42.6293	18.0760	7.7195	3.1807	33.8154
onomer s	disp(vdW-DF2)	43.8751	31.6026	1.5859	8.2653	30.1468	42.0916	46.8260	29.1990	10mer se	dimer.	disp(vdW-DF2)	39.6783	31.1872	10.4828	9.3236	24.2023 40.2026	42.3200 55 9945	63.1905 63.1905	34.4522	nomer se		disp(vdW-DF2)	73.5872	64.1160	31.1949	23.5487	36.8069 44.4948	45.1324	45 5544
ous mo	disp(VV10)	64.4086	54.5729	22.1788	1.6369	5.9149	8.6117	10.3848	23.9584	iom su	EDNA	disp(VV10)	60.0156	52.4740	28.7653	13.1716	5.7034 9.9624	10404	1.1199	20.5692	om suc		disp(VV10)	81.0022	72.9058	41.6959	18.8021	9.4378 6.1215	3.8789	33 40.63
s at vari	3[No-switching]	1.2206	5.0583	4.9664	0.1186	2.2783	3.2242	3.1995	2.8666	at vario	Imine (I	[No-switching]	9.0832	1.3443	9.1150	12.6279	13.9075	14 5144	15.1350	11.2373	at varie		3[No-switching]	127.2651	35.1107	16.5112	15.3186	12.7565 12.1308	12.1550	33 0354
APEs dimer.	DADE D	15.4129	6.0979	6.2675	8.0096	4.3781	2.3885	8.4748	7.2899	APEs	dinitra	DADE D3	26.1525	20.5367	11.1683	9.7258	10.7827	17 5402	22.4639	16.4562	APE_{S}	dimer.	DADE D	49.6920	39.1028	20.1742	19.4712	23.0283 28.4813	32.8612	30 4016
.40:	D3BJ[HF]	27.6627	21.6050	9.5792	2.2914	0.9020	2.1714	2.2736	9.4979	.41:		D3BJ[HF]	25.8244	21.9532	16.6517	15.9763	15.9281	15 5695	16.0169	17.9335	.42:		D3BJ[HF]	56.5418	43.2780	24.2324	17.8619	14.0896 14.1773	14.6517	96.400A
ole D	D_{as}	18.4741	14.8198	3.7608	1.7693	2.5490	1.9221	0.7720	5 6.2953	le D		D_{ac}	1.8727) 2.3562) 2.3512	0.6342) 3.9792) 6.9064	10070 0	9 9.8664	3 4.4194	ole D		D_{as}	13.9023) 15.3142	0 13.5890	0 9.5524	0 8.5805 0 9.5347	0 10.7361	3 11.6013
Tał	R	3.2560	3.5580	4.5580	5.5580	6.5580	7.5580	8.5580	MAPE	Tat		В	4.4980	4.7980	5.7980	6.7980	0.7080	0 7080	10.7980	MAPE	Tał		В	4.9250	5.2470	6.2470	7.2470	8.2470 9.2470	10.2470	MAPF

ethan
the
ls for
IAPE
and N
values a
$E_{\rm disp}$
o the
relative t
(angstrom)
APEs at various monomer separations (
le D.40:
Lab

27.5356 33.0054 24.9531 10.470 25.1935 6.307 11.4540 25.195 6.307 3.0126 59.6251 6.5792 5.4326 57.0854 8.7864 25.0055 45.4587 24.8648 25.0055 45.4587 24.8648 27.0854 8.7087 24.8648 27.0957 70.5858 69.0684 42.0967 70.5858 69.0684 42.0967 70.5858 69.0684 42.0967 70.5858 69.0684 42.0967 70.5858 69.0684 42.0967 70.5858 69.0684 71.574 37.5043 5.3435 38.8696 8.7181	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$
	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
$\frac{0.4392}{7.3300} \frac{7.8159}{0.0.1151} \frac{7.8159}{11.3888} \frac{12.7919}{11.3888} \frac{12.7919}{11.3888} \frac{12.7919}{11.010} \frac{12.7914}{10.010} \frac{12.1014}{10.010} \frac{12.1014}{10.000} 12.1014$	

fer	ing]																on	(jug)										IF	ing	5							
the wat	XDM10[No-switch	3460.0918	988.1210 306.6103	001000 196.5194	112.2823	55.9011	35.3173	26.1068	21.0583	17.5951	15.9797	14.4868	13.8425	0.15.20	2001.6	336.7099	the arg	XDM10[No-switch 12.6216	3.9169	0.0976	2.5920	2.9538	3.6104	4.8757	6.2790	7.5762 8 5303	5.1041	the Ar-F	XDM10[No-switch	20.6068	8.1823	5.2493	5.3793 5.3793	6.3976	6.5050	5.5447	7.5125
APEs for	disp(vdW-DF1)	71.3055	00.0708 45 6698	27.4600	5.0845	39.6073	83.3680	111.2906	118.2224	111.0442	103.2497	95.0006 61 7041	91.7241	90.1009 01 0062	101 5462	78.0557	APEs for	disp(vdW-DF1) 16.6496	5.2982	25.8795	64.0903	80.4416	81 0447	41.5052	33.3818	50.1917 20.1368	47.9102	APEs for	disp(vdW-DF1)	12.1687	31.7597	79.2028	1 22 7205	116.7784	94.6182	77.3079	78.8394
les and M	(DM8[No-switching]	603.3879	229.3803	55.9516	32.2019	16.5955	12.4807	11.6434	11.3911	10.9143	11.1791	10.9643	11.4576	0764.11 7.6180	0.5432	72.0590	es and M	(DM8[No-switching] 23.6004	23.6418	22.3275	18.4815	16.4483	0.0831	8.0466	8.2151	8.8109 9.3539	14.6327	ss and M_{I}	(DM8[No-switching]	17.0459	15.7968	11.3148 2 7094	0.7034 3.1816	1.6717	3.7485	3.8607	7.4303
$E_{\rm disp}$ valu	OM8[PW86-PBE] >	97.1275	94.4774 00.0701	30.0701 83.5022	74.5807	55.0291	33.1625	15.1717	3.8943	2.1187	5.9088	7.7076	10.0676	6 2081	8.8070	37.3435	$E_{ m disp}$ valu	DM8[PW86-PBE] 3 85.6084	76.8975	67.7275	49.5670	41.3355	15, 1757	10.6232	9.4084	9.4078 9.6748	36.7211	$E_{ m disp}$ value	OM8[PW86-PBE])	84.0845	66.2465	45.5097	26.2001 16.3304	3.4601	1.5586	2.8422 3.0366	27.9204
ve to the	D3MBJ[PBE] XI	95.4013	92.0272 86.0545	79.9115	70.9719	53.8002	38.2166	27.0181	19.7922	15.3215	0.7004	9.5994	1/00.7	0.0101 7 8553	5.3908	39.2174	e to the	D3MBJ[PBE] X 70.1547	60.6574	52.8335	39.9785	34.5009 af 6456	20.0400	9.5908	6.9897	5.9079 4 9277	29.6374	e to the	D3MBJ[PBE] XI	77.0070	61.0849	46.2522	95 5864	14.0049	7.8617	5.0302	30.4877
m) relativ	[DM10[PW86-PBE]	96.4195	93.1034 87.6012	79.5238	68.8414	46.1112	21.7025	4.0342	4.9191	8.5776	10.6461	11.2104	10.1084	4001771 8 9494	10.1360	35.9318	n) relativ	(DM10[PW86-PBE] 81.6852	70.5849	59.2591	38.8762	30.7527 10.5046	0 7950	7.4628	7.4740	8.1734 8.8514	31.1291	m) relativ	DM10[PW86-PBE]	80.0536	57.9919	34.7739	10.1004 8 2926	1.2161	4.3087	4.5252	23.7159
(angstro) D3BJ[PBE] X	95.3461	91.8237 86.4109	20:41.02 78.7630	68.9792	50.1806	33.3976	21.8876	14.9246	10.9148	7.8043	5.9716 1.2420	4.3432	2.0022 5.5429	2020-0	36.3825	(angstroi	() D3BJ[PBE] > 79.4006	68.8437	58.6996	40.5464	32.8022 00.8078	8 1 705	3.3241	1.6049	1.1695 1.0479	28.7733	(angstroi) D3BJ[PBE] X	79.9735	62.2424	44.4304	20.4277 20.6347	8.856	3.4011	1.1801	27.9678
tions	disp(VV09	103.8247	99.8222 09.3034	92.3004 81.7815	69.3972	48.0021	30.2190	19.0830	14.4460	14.5078	17.1766	22.4153	23.00.62	51 2746	63 3293	49.7422	ions	disp(VV0 67.5492	52.0383	38.3360	14.5885	5.1019	99.3118	23.0290	20.8873	18.5086 16.6156	26.2667	tions	disp(VV09	71.2921	44.2948	0.0071	2.02/1	25.9427	27.6583	26.0852	28.2533
separa	disp(MBD)	95.7698 01.0701	91.8791 95.5475	20.0410 76.6305	65.4828	45.9971	31.9991	23.8261	18.8459	15.5587	12.4775	0.2732	8.1383 6.0160	0.2100	5 2301	37.6235	eparat	disp(MBD) 87.4597	78.7008	69.8003	53.2617	46.0700	91 0300	15.5846	12.1223	10.0771 8.6821	39.8673	separat	disp(MBD)	83.0047	65.6295	48.9766	20.5902 27.5800	16.1709	9.6014	6.1016	33.0636
onomer	disp(vdW-DF2)	82.1484	66.9780	54.9937	41.8789	20.3805	8.0255	8.7833	16.6560	23.8479	26.4402	26.5156	23.9320	19.5707	8 7846	32.4972	onomer s	disp(vdW-DF2) 45.6995	33.5309	23.8032	11.5718	10.1076	17 8079 17 8079	33.7950	36.3582	39.9944 40.2234	29.0549	onomer s	disp(vdW-DF2)	45.1223	22.7032	7.1041	18 4730	14.7139	27.5857	36.7551	25.1927
ious m	disp(VV10)	89.7464	54.0192 77 7781	69.6924	60.6518	45.0579	31.4081	21.4639	14.9248	11.2914	8.5198	6.3645	4.9954	5.0600	1 8902	33.5165	om sno	disp(VV10) 64.5912	54.4564	45.4580	29.9845	23.6689	6 5013	1.9038	0.8183	2.2169 3.1500	22.5224	m suo	disp(VV10)	63.5307	45.4375	28.7179	8 2005	0.9319	5.3901	7.2107	20.4869
s at vari	33[No-switching]	317.4974	40 1167 AD	10.4340	2.7875	9.8258	9.7305	7.9245	6.2565	5.1823	3.7796	3.0024	2:000	2 00.48	1.8174	33.5599	at varie	D3[No-switching] 14.3462	14.9147	13.7084	9.6206	7.3707	0.4000	2.2636	2.1417	1.5468 0.9722	6.4841	s at vari	03[No-switching]	27.5454	24.9134	19.3579	0.9267 0.2267	2.8256	0.3569	1.2803	11.2012
APE	DADE D	64.2608	03.4000 49.6317	33.1301	25.8141	17.9687	12.1567	6.8962	3.6454	3.1877	3.9143	5.8524 7 rrs7	1.3331	0.3030	13.0580	19.7495	APEs dimer.	DADE 1 26.1767	18.7674	14.5183	9.5415	7.3980	0.2002 1.0081	6.1486	11.6616	15.7264 18.4869	12.0706	APE	DADE D	28.7084	16.6266	9.2752	2.0240 3.0653	6.1506	1.9712	3.1596 e en c7	8.7086
.46:	D3BJ[HF]	69.4896 26.4396	00.4129 49 5025	42.0033 31.0231	24.1047	18.2301	13.9758	10.5021	8.0239	6.5081	4.7875	3.8145	1 6000	1.0300	2.0123	18.7777	.47:	D3BJ[HF] 33.5647	27.6918	23.2049	15.7132	12.4440 7.1710	1 3606	0.6190	0.8428	0.5228 0.2463	11.2165	.48:	D3BJ[HF]	41.8636	32.3996	24.0080	11.6512	4.3867	0.7526	0.4241	14.8051
le D	Das	26.2665 27.2565	20.0738	22.1748	19.6761	14.3805	8.8109	4.1606	0.8018	1.3868	3.6427	5.0545 6 F 000	0.0299	6716.1	2110.0	11.4129	le D	D_{as} 44.0412	25.8453	14.5971	3.0801	0.2251	1 8023	1.0713	4.2617	7.0667 9.2726	10.3416	le D	Das	14.6182	5.1502	0.9527	4.0167 6.0152	6.5574	5.1686	2.7616	5.1551
Tab	R	2.3100	2.0100	3.2100	3.5100	4.0100	4.5100	5.0100	5.5100	6.0100	6.5100	7.0100	0.000.1	0:0000 8 5050	9.0050	MAPE	Tab	R = 3.2000	3.5000	3.7600	4.2500	4.5000	0000.0	7.0000	8.0000	9.0000	MAPE	Tab	R	3.0000	3.5000	4.0000	5 0000	6.0000	7.0000	8.0000	MAPE