Comparison of some dispersion-corrected and traditional functionals with CCSD(T) and MP2 *ab initio* methods: Dispersion, induction, and basis set superposition error

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(Received 4 January 2012; accepted 17 September 2012; published online 4 October 2012)

We compare dispersion and induction interactions for noble gas dimers and for Ne, methane, and 2-butyne with HF and LiF using a variety of functionals (including some specifically parameterized to evaluate dispersion interactions) with *ab initio* methods including CCSD(T) and MP2. We see that inductive interactions tend to enhance dispersion and may be accompanied by charge-transfer. We show that the functionals do not generally follow the expected trends in interaction energies, basis set superposition errors (BSSE), and interaction distances as a function of basis set size. The functionals parameterized to treat dispersion interactions often overestimate these interactions, sometimes by quite a lot, when compared to higher level calculations. Which functionals work best depends upon the examples chosen. The B3LYP and X3LYP functionals, which do not describe pure dispersion interactions, appear to describe dispersion mixed with induction about as accurately as those parametrized to treat dispersion. We observed significant differences in high-level wavefunction calculations in a basis set larger than those used to generate the structures in many of the databases. We discuss the implications for highly parameterized functionals based on these databases, as well as the use of simple potential energy for fitting the parameters rather than experimentally determinable thermodynamic state functions that involve consideration of vibrational states. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4755990>]

INTRODUCTION

In this paper, we focus on the ability of various functionals to properly account for interactions that involve a combination of inductive and dispersive interactions. To accomplish this, we have performed calculations using various functionals on model systems where pure dispersion interactions are expected and compare them in related systems where induction and dispersion operate together. Since several new functionals have been developed that have been specifically designed to describe dispersive interactions, we compare the performance of several of these with the more traditional functionals and with high level calculations (up to CCSD(T)/aug-cc-pV5Z, in some cases).

The importance of the contribution of dispersion to intermolecular and intramolecular interactions has received much recent attention in the literature. However, distinguishing dispersion from induction and basis set superposition error (BSSE) can sometimes be difficult. Rare gas van der Waals dimers exemplify true dispersion. The attractive interaction between these spherical, nonpolar atoms can be thought of as a time-dependent polarization process where electron density in both atoms are shifted in the same direction creating a dipole–dipole interaction. Since the probability of this shift coming in one direction is exactly the same as it occurring in the opposite direction, no permanent dipole–dipole inter-

action occurs. As this process requires correlated action between electrons, it cannot be described by molecular orbital (MO) methods that employ one-electron Hamiltonians, such as Hartree–Fock (HF) calculations. Induction occurs when an entity with a permanent dipole (or higher) moment induces a dipole (or higher) moment in another entity which may not have any permanent dipole (or higher) moments, itself. For simplicity, we shall restrict our discussion to dipole moments, hereafter. An example might be the interaction of a HF molecule with a rare gas atom. In this case, the permanent dipole of the HF will induce a permanent dipole in the rare gas atom next to it. In the cases both of dispersion and induction, the energy of interaction will depend upon the polarizability of the rare gas atom and the distance (r) between the entities as r^{-6} as the interaction between linearly aligned parallel dipoles is the product of the dipole moments (μ) $\times r^{-3}$. The induced dipole moment is the polarizability (ρ) times the field generated by the other dipole moment times r^{-3} . Thus, the inductive interaction of a permanent dipole, μ_p , with a nonpolar entity of polarizability ρ will be $\mu_p \rho r^{-6}$, while the dispersion interaction between two nonpolar entities, A and B, will depend upon $\rho_A \rho_B r^{-6}$. Clearly, the fact that an interaction has an r^{-6} dependence cannot distinguish between dispersion and induction. However, MO methods that are incapable of calculating dispersion, such as Hartree–Fock methods, can, in principle, properly calculate induction.

BSSE¹ can be confused with dispersion or induction interactions. In particular, if one attempts to calculate the

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interaction energy between two rare gas atoms via geometry optimization at the HF level with a moderate sized basis set, one finds a minimum on the potential energy surface despite the fact that HF calculations are incapable of describing the dispersion interaction. This minimum will disappear at the Hartree–Fock limit (complete basis set) or if the optimization be carried out on a surface that is corrected for BSSE using the counterpoise (CP) correction as in the CP-opt procedure.² Thus, optimizations on PESs that are not corrected for BSSE can lead to artefactual minima. The foregoing is especially true for weak interactions.³ A study of the interactions of pyrimidine and p-benzoquinone showed that the preference for stacked versus H-bonded dimers is inverted when BSSE is considered at the MP2/6-31++G** level of theory. According to this report, the π -stacked dimer is incorrectly predicted to be more stable than the experimentally determined H-bonding dimer before (but not after) CP correction.⁴ Cybulski and Sadlej have reinvestigated this result using MP2 and symmetry-adapted perturbation theory (SAPT).⁵ Their report shows the results depend upon the method of calculation and whether (or not) the geometry optimization uses a CP-corrected surface. We have addressed this particular problem in more detail elsewhere.⁶

Dispersion interactions can be influenced by induction. Let us compare the van der Waals dimer of neon with that between neon and HF. In the former, each neon is nonpolar on average, but the neon in the latter is not. The (time dependent) dispersion interaction in the former will have equal probability of involving on-axis polarization in either direction, as either will lower the energy by the same amount. For the Ne–HF dimer, time dependent on-axis polarization is no longer symmetrical. The energy will be lowered by a polarization that increases the dipole of the Ne that is already induced by the HF, but raised by one that decreases this induced dipole, thus increasing the probability of the former and decreasing that of the latter. Thus, the time-dependent (dispersion) interaction will tend to augment the inductive interaction. Will this dispersive interaction be greater or less than that of the Ne dimer?

Dipole moments can be induced in two molecules that are individually nonpolar in a vacuum. Consider the C_{3v} dimer of methane with C–H bonds pointing along the same axial direction (see Figure 1). A methane dimer with this symmetry must have a permanent dipole moment (however small) even though the isolated methane molecules do not. The extent to which this interaction is due to dispersion or induction needs clarification.

For *ab initio* calculations that use basis sets that describe nucleocentric hydrogen-like atomic orbitals, both polarization and dispersion (which is simply electron correlated instantaneous polarization) should yield larger stabilizations as the basis sets increase. The foregoing follows from the fact that each atomic orbital is a spherical harmonic which cannot be individually polarized. Thus, the polarization must derive from the atomic orbital overlap populations which have flexibility that increases with the size of the basis set. If one allows the orbitals to move off the nucleus (as in floating Gaussian calculations), polarization becomes much easier.⁷ Accurate evaluation of all of the interactions discussed above require

FIG. 1. Methane dimer in C_{3v} symmetry.

very large basis sets when nucleocentric basis functions are used with *ab initio* calculations. This makes high level *ab initio* calculations of these interactions very costly. For large systems, the costs of such calculations becomes prohibitive. For these reasons, various groups have endeavored to develop new functionals that can better describe these interactions than do the commonly used functionals such as B3LYP. Density functional theory generally depends less on basis-set size than do correlated wavefunction methods, as it operates via a non-interacting system.

The functionals in density functional theory need not explicitly depend on atomic orbitals or basis sets. The older functionals such as $X\alpha$ and LSDA do not explicitly depend upon these. In Kohn–Sham (KS) DFT, the density is the sum of the densities of the KS molecular orbitals, which are obtained by solution of the non-interacting KS equation and so depend on the basis set employed in the calculation. The total energy (E) is given as

$$E = \text{kinetic energy} + \text{mean-field Coulomb interaction term} \\ + \text{exchange correlation energy } (E_{xc}), \quad (1)$$

where

$$E_{xc} = E_x + E_c \text{ (conventionally separable exchange and correlation terms)} \quad (2)$$

and

$$E_{xc}^{\text{GGA}} = \int d^3r \rho(r) \varepsilon_x(\rho) F_{xc}(\rho, s), \quad (3)$$

where $\rho(r)$ = total density, $\varepsilon_x(\rho)$ = the exchange energy density in the uniform electron gas of density ρ , $F_{xc}(\rho, s)$ is the GGA enhancement factor and depends on a dimensionless density gradient term. Many other recent functionals are meta-GGAs, meaning the enhancement factor is a functional of the density, its dimensionless gradient, and the kinetic energy density (usually spin-decomposed versions of these quantities are used). Others like M06-2X are hybrid meta-GGAs, as they mix in a fraction of Hartree–Fock exchange with a local part depending on the local density, its dimensionless gradient, and the kinetic energy density. Table I lists the functionals we consider in the present work.

When basis sets are used for the description of the electron gas and/or for the Hartree–Fock part of the exchange–correlation terms, BSSE will affect the result. Both the energy and distance between two interacting entities will be affected.

TABLE I. Description of functionals with number of fitted parameters.

Functional	Type	Parameters fitted
PBE1PBE	Hybrid GGA	- ^a
B3LYP	Hybrid GGA	3
X3LYP	Hybrid GGA	4
M06	Hybrid meta-GGA	38
M06-2X	Hybrid meta-GGA	35
M06-L	Pure meta-GGA	39
M05	Hybrid meta-GGA	22
M05-2X	Hybrid meta-GGA	22
B97-D	Hybrid GGA with dispersion correction	5 ^b
ω B97x-D	Range corrected hybrid with dispersion correction	18
B2PLYP	Double hybrid	2
B2PLYP-D	Double hybrid with dispersion correction	5 ^b

^aThere are parameters that are fixed to satisfy boundary conditions, but not against training set.

^bOne of them is a scaling factor and vdW-radii are computed and scaled using ROHF/TZV level.

For this reason correction for BSSE, such as the counterpoise (CP) method should be used when optimizing the geometries rather than simply as an *a posteriori* single point calculation.

Early functionals did not properly describe dispersion interactions such as those between rare gases.⁸ The developers of several recent functionals have attempted to include dispersion interactions in the applications for which these functionals can be used. Sherrill and co-authors⁹ and Zhao and Truhlar¹⁰ have recently compared several of these, and the number of available functionals continues to grow as improvements continue.¹¹ Most of these functionals depend upon fitting several (up to 39, see Table I) parameters to data sets that include interactions thought to exemplify dispersion. The dispersive interactions in these data sets are generally obtained by high level *ab initio* calculations for which BSSE has often but not always been addressed. Table II reviews the data sets and evaluations of DFT results that have appeared. From it one sees that most databases used contain a mixture of results some of which are CP-corrected, others not. Only five of these databases contain only CP-corrected values. Experimental measurements of dispersive interactions have not been used to parametrize these functionals. Some of these databases have been updated since the methods that we consider have been developed;¹² however, these updates were not available at the time of parametrization and the parametrizations were not consequently updated.

We present new tests of these newer functionals designed to include dispersion (DFs) and the older, traditional functionals not specifically parametrized (TFs), in comparison with high level *ab initio* calculations in several cases where pure dispersion might be expected (i.e., rare gas dimers) and other related cases where dispersion might be mixed with induction such as interactions between HF or LiF and Ne, methane, or 2-butyne. We have presented similar comparisons with good experimental data for larger systems including peptides elsewhere.¹³

METHODS

All calculations were performed using the GAUSSIAN 09 suite of computer programs.¹⁴ Except where explicitly indicated, all structures were optimized with respect to all internal coordinates. Harmonic frequencies were calculated for these optimizations to confirm the existence of a minimum (no imaginary frequencies) and to obtain the gas phase enthalpies that correspond to these structures. Counterpoise (CP) corrections¹⁵ were calculated either on the CP-corrected surface² or as single point *a posteriori* calculations or both. When a CP-corrected surface was used, the frequencies were calculated on this surface.² We considered the following DFs: B97D,¹⁶ ω B97X-D,¹⁷ M06, M06-2X, M06L,¹⁸ B2PLYP,¹⁹ and B2PLYP-D²⁰ and the following TFs: B3LYP,²¹ PBE1PBE,²² and X3LYP²³ for comparisons. While X3LYP uses the neon dimer as a reference point, it is basically a small modification of B3LYP, with the values of the three parameters adjusted and one additional parameter that mixes in B88 and PW91 exchange functionals so we include it among the TFs. Some calculations were also carried out at various *ab initio* levels such as Hartree–Fock, MP2, and CCSD(T) where useful and practical for comparison. As we found the default grids and convergence criteria of the GAUSSIAN 09 program to be inadequate to properly describe many of these systems, we performed all the DFT calculations reported in this paper using the finest grid available in the GAUSSIAN 09 program (the “99974” grid) and the “very tight” convergence criteria. The “very tight” convergence criteria require geometric convergence of 2, 1, 6, and 4 (all $\times 10^{-6}$) on the maximum and RMS force and maximum and RMS displacements, respectively. In many cases, especially where the CP-corrected interaction energy was expected to be close to zero, we performed energy scans where partial optimizations were performed at several fixed increasing distances between the entities. All geometric parameters other than the fixed distances were optimized. This procedure prevented false minima when the gradient approached zero on a completely flat surface. Using this procedure uncovered several anomalies for several potential energy surfaces calculated using some (but not all) functionals. In the cases of HF and LiF interacting with methane and 2-butyne, we enforced C_{3v} symmetry.

GAUSSIAN 09 uses the SCF orbitals to calculate both dipoles and Mulliken populations as the default. We obtained the MP2 dipoles using the “density” keyword. CCSD(T) dipole moments cannot be calculated explicitly using GAUSSIAN 09. We projected the orbitals to a minimum basis set for calculation of the charge transfers.²⁴ We corrected these values for CP by removing the transfer to ghost orbitals from the uncorrected values. While MP2 densities can be obtained using the “density” keyword, the projection to minimum basis set reverts to Hartree–Fock densities.

RESULTS

Noble gas dimers

We present the interaction energies together with the relevant interatomic distances optimized using several different

TABLE II. Representative databases and studies used for DFT parameterization/performance evaluation.

Database	Functional(s)	Type of interaction	Use of CP and basis set	Reference
HB6/04 database	Modified PW and B97 functionals	Hydrogen bonding	CP and no-CP (MG3S, and 6-31+G** basis set)	41
WI7/05 database	Modified PW and B97 functionals	Weak interaction	CP and no-CP (MG3S, and 6-31+G** basis set)	41
PPS/05	Modified PW and B97 functionals	Pi-Stacking	CP and no-CP (MG3S, and 6-31+G** basis set)	41
Nucleic acids and small peptides	M08-HX, M08-SO	H-bond, stacking (?)	CP, no-CP for Uracil dimer (different basis set for different database)	42
H2S-benzene dimer	B3LYP, M06-L, PWB6K, MPWB1K	Dissociation energy and geometry	No-CP (DFT/MG3S, aug-cc-pVDZ; and MP2/aug-cc-pVTZ, aug-cc-pVQZ)	43
Water-hexamer	16 functionals including M06-series	Relative energy	No-CP (MG3S, 6-31+G**, aug-cc-pVTZ, 6-311+G(2d,2p))	44
S22	M06-2X	Noncovalent interaction of biological importance, graphene systems	CP, CCSD(T)/CBS; CP, no-CP (MIDI!, 6-31+G**, MG3S basis sets)	12, 45, and 46
S66	SCS-MPn and SAPT	Extended S22; cyclic H-bond, pi-pi, X-pi, H-bonding, aliphatic dispersion, interaction with water	CP (aug-cc-pVXZ, X = D, T, Q)	47
GMTKN30	DFT-D/DFT-D3	(Basis set dependence too)	CP	48
Mixed database	w-B97 series	CT,DD, IGD, DNA-base pairs, interstand base pairs, stacked base pairs	CP (6-311++G(df,3pd) basis)	49
Pi-conjugated polyenes	Double hybrids	Stacking and H-bond	No-CP (cc-pVTZ basis)	50
Alkane isomerization energy	DFT and basis sets	Ionization, isomerization	...	51
Bis-thiophene derivative	DFT-D	Stacking, geometry	...	52
Mixed training set	ω -B97X-D	All	...	17
F1	DFT	Vibrational frequencies	...	53
JSCH2005	DFT-D	DNA base pairs, amino acid pairs and other small complexes	CP	45 and 54
Alkanes	DFT	Isodesmic stabilization energy	...	55

methods on both normal (CP-uncorrected) and CP-corrected surfaces for the noble gas dimers He_2 , Ne_2 , and Ar_2 , as well as the effects of BSSE upon the energies and interatomic distances in Table III. We begin with the high level *ab initio* calculations. The experimental value for the binding energy of He_2 is 0.002 cal/mol.²⁵ As the He...He distance was reported in the same paper (52 Angstroms), this dissociation appears to be from the zero-point vibrational level. The reported values for the potential wells (not affected by zero point vibrations) for Ne_2 are 86²⁶ or 84²⁷ and for Ar_2 is 262²⁸ cal/mol. The calculated values appear in Table III. Our best values resemble those previously reported.²⁹ Clearly, the calculated values for He_2 do not resemble the reported experimental values even at the highest levels of theory used. This observation might be

due to the inadequacy of the basis sets used or some problem with the experimental determination. At the reported interatomic distance of 52 Angstroms,²⁵ even the largest basis set considered would have almost no amplitude. While this might not affect the depth of the well, the shape might be poorly described. We should arguably dismiss the He_2 dimer as unsuitable for calculations by common *ab initio* methods. Nevertheless, we shall include it in the discussion as the trends predicted by the various methods might be of interest.

Ne_2 represents the 2nd row of the periodic table, so is probably the most relevant to organic and biochemical systems. For Ne_2 , the CCSD(T)/aug-cc-pV5Z value (−74 cal/mol) is smaller than the experimentally determined values mentioned above (−86 and −84 cal/mol),^{26,27} but

TABLE III. Interaction energies (cal/mol) interatomic distances (Angstroms) and BSSE (cal/mol) for dimers of He, Ne, and Ar optimized on CP-corrected surfaces using the aug-cc-pVXZ basis sets ($X = D, T, Q, \text{ or } 5$). Functionals marked with an asterisk (*) produced more than one minimum on some or all of the PESs.

$X = \rightarrow$	He				Ne				Ar			
	D	T	Q	5	D	T	Q	5	D	T	Q	5
CCSD(T)	-12	-17	-19	-20	-28	-51	-66	-74	-124	-204	-238	-260
MP2	-8	-11	-12	-13	-23	-37	-45	-49	-159	-242	-279	-302
B2PLYP*	0	0	0	0	-5	-2	0	-6	-5	-11	-23	-30
PBE0	-34	-41	-43	-42	-69	-62	-65	-72	-71	-81	-87	-88
X3LYP	-18	-23	-27	-26	-98	-69	-58	-73	-4	-1	-11	-16
B3LYP	0	0	0	0	0	0	0	0	0	0	0	0
M05	-71	-74	-83	-79	-161	-165	-161	-176	-233	-197	-205	-208
M05-2X	-23	-21	-14	-14	-69	-150	-152	-118	-224	-237	-194	-190
M06*	-126	-114	-114	-116	-149	-138	-64	-128	-125	-160	-135	-138
M06-2X	-110	-113	-113	-114	-173	-178	-174	-165	-202	-194	-181	-181
M06L*	-47	-27	-14	-15	-55	-127	-106	-69	-152	-169	-121	-106
B97-D	-48	-47	-51	-52	-204	-154	-138	-156	-229	-227	-250	-256
ω B97xD	-16	-18	-18	-18	-77	-67	-65	-69	-138	-146	-141	-140
B2PLYP-D*	-1	-1	-1	-2	-106	-108	-108	-108	-137	-174	-196	-206
Interatomic distance												
CCSD(T)	3.2	3.0	3.1	3.0	3.5	3.5	3.2	3.1	4.1	3.9	3.8	3.8
MP2	3.3	3.2	3.1	3.1	3.6	3.3	3.3	3.3	4.0	3.9	3.8	3.8
B2PLYP	∞	∞	∞	∞	3.3	3.2	5.4	3.1	5.5	4.2	4.1	4.1
PBE0	2.9	2.8	2.8	2.8	3.2	3.2	3.2	3.2	4.1	4.1	4.1	4.1
X3LYP	2.8	2.7	2.7	2.7	3.0	3.0	3.0	3.0	4.3	4.2	4.2	4.2
B3LYP	∞	∞	∞	∞	∞	∞	∞	∞	∞	∞	∞	∞
M05	2.6	2.7	2.7	2.7	2.8	2.9	2.9	2.9	3.7	3.8	3.8	3.7
M05-2X	2.7	2.8	2.8	2.8	2.9	2.9	2.9	2.9	3.8	3.8	3.9	3.8
M06	3.0	3.0	3.0	3.0	3.5	3.5	3.2	3.5	3.9	4.2	4.3	4.3
M06-2X	3.0	2.9	2.9	2.9	3.1	3.1	3.1	3.1	3.9	4.2	4.2	4.3
M06L	3.0	3.0	3.0	3.3	3.2	3.1	3.4	3.5	3.9	4.2	4.2	4.2
B97-D	3.1	3.1	3.0	3.0	3.2	3.3	3.3	3.2	4.2	4.1	4.1	4.1
ω B97xD	3.3	3.3	3.3	3.3	3.5	3.5	3.5	3.5	4.2	4.2	4.3	4.3
B2PLYP-D	4.3	4.7	5.1	2.9	3.0	3.0	2.9	2.9	3.9	3.8	3.8	4.0
BSSE												
CCSD(T)	12	3	2	1	71	52	28	12	95	63	35	29
MP2	12	3	2	1	51	41	26	12	93	70	42	39
B2PLYP	0	0	0	0	37	25	1	6	12	19	11	8
PBE0	5	1	1	0	21	16	8	3	43	11	2	0
X3LYP	5	1	1	0	30	20	8	1	34	9	3	1
B3LYP	0	0	0	0	0	0	0	0	0	0	0	0
M05	8	1	9	5	50	33	10	5	60	17	4	5
M05-2X	4	3	1	0	30	28	25	3	44	31	15	4
M06	10	3	1	3	12	20	24	12	57	32	12	2
M06-2X	3	1	0	0	18	24	14	1	36	16	5	1
M06L	15	8	1	2	16	36	42	23	57	45	34	23
B97-D	3	2	1	0	23	14	7	2	40	11	3	4
ω B97xD	2	1	1	1	13	13	14	4	40	16	4	1
B2PLYP-D	1	0	0	1	50	34	19	8	57	31	15	12

the internuclear distance predicted by CCSD(T) agrees with the experimentally determined 3.1 Angstroms.²⁷ MP2 predicts a larger separation, but the energy is somewhat less (-49 cal/mol). One should note that the CP corrections for the CCSD(T) calculation is 12 cal, close to the difference between the calculated and experimental interaction energy. Using the aug-cc-pV5Z basis for Ar_2 , CCSD(T) predicts an interaction very close to the experimental report (262 cal). MP2 predicts a stronger interaction (-302 cal/mol) than the -260 cal/mol

of CCSD(T) (the reverse of He_2 and Ne_2 , where CCSD(T) predicts the stronger interaction).

As noted above, we expect the orbital methods to predict larger interactions as the basis set increases. The BSSE should decrease as the quality of the basis set improves and disappear completely for an infinite basis. One also expects the internuclear distance to *decrease* with increasing basis set size as the interaction energies become more negative. Again, all *ab initio* methods follow this trend. From Table III one sees

FIG. 2. Comparison of scans for Ar_2 using different methods. All calculations used the aug-cc-pVQZ basis set. The DFT calculations used the 99 974 grid and very tight convergence.

that both the expectation that the interaction energies increase and the interatomic distances decrease are met by the *ab initio* (MP2 and CCSD(T)) calculations.

None of the DFT methods follow all three of these qualitative expectations. As B3LYP predicts essentially no interactions for these dimers, one cannot usefully comment on this functional. Only B2PLYP-D followed the expected trend of increasing interactions with larger basis sets, but not the trend for interatomic distance. The B2PLYP, M05, and M06 functionals do not follow the expected trends for BSSE (neglecting the very slight deviations for M06L, B97-D, and B2PLYP-D).

Scans of energy versus interatomic distance for some of the DFs showed unexpected features and sometimes include multiple minima. Cases where this occurred are noted in the appropriate tables. The scans can be found in the supplementary material.³⁰ The interatomic distances calculated using most functionals proved to be less sensitive to basis set than the orbital methods, as expected especially for He_2 and Ne_2 .

For Ne_2 and He_2 (but not Ar_2), the DF, $\omega\text{B97x-D}$, gives numerically reasonable results when compared to CCSD(T)/aug-cc-pV5Z, but it underestimates all three interactions. M05-2X, PBE0, B2PLYP-D, X3LYP, $\omega\text{B97x-D}$, and M06L also give reasonable results. In descending order, M06, M06-2X, M05, B3LYP, B2PLYP, and B97-D do the worst. Of these, the DFs significantly overestimate, while the two TFs significantly underestimate the interactions.

We note the smaller errors for the DFT calculations on Ne_2 than for He_2 or Ar_2 may be due to the fact that Ne_2 is included in some of the databases to which the functionals are parameterized and/or to the fact that Ne belongs to the second row of the periodic table which contains most of the atoms (other than H) in the molecules in these databases.

The M06, M06L, and M06-2X did not produce smooth curves for scans of ΔE_{int} versus interatomic distance. The first two had multiple minima and the last inflections where the

others had minima, even with the 99974 grid (the finest grid available in GAUSSIAN 09). Figure 2 illustrates this for Ar_2 . Illustrations for the other dimers can be found in the supplementary material. Such oscillations have been reported to be typical for meta-GGAs in other cases, but generally disappear when finer grids are used.³¹

Interactions of polar and nonpolar species

We determined the CCSD(T) interaction energies as a function of basis set size for the interaction of HF and LiF with Ne, methane, and 2-butyne. The calculations used basis sets up to aug-cc-pV5Z for interactions with Ne. However, the cost of the calculations required that we stop at QZ for methane and 2-butyne. We performed single point calculations at the optimized geometries at the TZ levels in these cases. While this procedure can test for basis set convergence, it will always underestimate the magnitude of the interaction energies, as the geometries will be slightly different from those optimized with the method used. As seen from Table IV, the interaction energies converge much faster than does the BSSE trend toward zero. If one considers the percent change in the interactions, the interaction energies converge more rapidly for the larger systems. The slower convergence of the interactions with Ne might be due to its low polarizability, which suggests that dispersion contributes more to the induction/dispersion mix for Ne than for the others. The results suggest that TZ should be reasonably adequate for interactions with larger (e.g., more polarizable) entities. The large BSSEs for the TZ calculations compared to the others do not greatly affect the interaction energies with optimizations performed using a CP-corrected surface, as we previously noted for water clusters.³²

We calculated the interactions of Ne, CH_4 , and 2-butyne with HF and LiF in conformations which had the F either

TABLE IV. Interaction energies and BSSE (kcal/mol) for complexes of Ne, methane, and 2-butyne with HF and LiF using CCSD(T)/aug-cc-pVXZ with different values of X. Geometries are fixed at the MP2/aug-cc-pVTZ optimized structures on CP-corrected surfaces.

X = -->	HF						LiF					
	F-facing			H-facing			F-facing			Li-facing		
	T	Q	5	T	Q	5	T	Q	5	T	Q	5
	ΔE_{int}											
Ne	-0.10	-0.12	-0.13	-0.21	-0.22	-0.23	-0.14	-0.17	-0.18	-0.62	-0.65	-0.68
Methane	-0.26	-0.27		-1.56	-1.62		-0.43	-0.45		-3.74	-3.76	
2-Butyne	-0.71	-0.73		-0.43	-0.45		-2.10	-2.15		-1.24	-1.24	
	BSSE											
Ne	0.07	0.04	0.01	0.23	0.12	0.04	0.08	0.04	0.02	0.45	0.29	0.10
Methane	0.11	0.05		0.36	0.18		0.17	0.06		0.57	0.18	
2-Butyne	0.19	0.08		0.41	0.17		0.34	0.11		0.67	0.21	

facing or distant from the nonpolar entity (see Figures 3 and 4 and Tables IV–VI). In each of these situations, the dipole moments of the polar entity (HF or LiF) will induce a permanent dipole moment in the nonpolar entity. Furthermore, some covalent interaction measured by charge-transfer might also occur. Charge-transfer is not possible for noble gas dimers or other symmetrical systems where charge-transfer is equally probable in each direction. The effects of the dipole/induced dipole interaction and charge-transfer should be reproducible by methods that use one-electron Hamiltonians (such as Hartree–Fock) and by functionals not specifically designed to reproduce dispersion. Whatever dispersive interactions exist should increase the stabilizing interactions. We estimated the induced dipole moments using the assumption that the dipoles of HF and LiF do not appreciably change in the presence of the neutral species. Since the dipole moment of the complex will be the vector sum of the individual dipoles and the molecules are aligned along an axis, the induced dipole can be estimated as the difference between the dipoles of the complex and HF or LiF. As seen from Table VII, the induced dipoles increase in the order Ne < methane < 2-butyne, and are greater for LiF than HF, as expected. The MP2 induced dipole moments do not change appreciably as the basis sets are improved from aug-cc-pVTZ to aug-cc-pVQZ or aug-cc-pV5Z (see Table VII). They are larger than those calculated using Hartree–Fock methods, but mostly smaller than those calculated using DFT. We observed smaller induced dipoles when F-faces, consistent with the longer equilibrium separations.

The concept of charge transfer cannot be correctly defined using quantum mechanical calculations as the electron density of the complex must be arbitrarily partitioned. The large overlap populations that give rise to the induced dipoles and dispersion interactions complicate the calculation of charge-transfer using Mullikan populations which equally divide these populations between the atoms involved. This sometimes gives physically unreasonable negative populations on the ghost atoms during CP calculations. We reduced this problem by projecting the large basis set calculations onto a minimum basis set to reduce the overlap populations.²⁴ Table VIII lists the charge transfers calculated using this method and corrected for artefactual transfer due to BSSE to the ghost orbitals. All the transfers are negative indicating transfer from the polar molecule to the neutral (-0.0 indicates a negative value less than 1×10^{-4} electrons). Without correction for the density on the ghost orbitals, the numbers vary over a considerably larger range which includes positive values. The apparent charge transfers when H or Li faces the neutral exceed those for when F- faces. Charge transfer to methane exceeds that to 2-butyne when H- or Li- faces. We note that charge-transfers calculated using either MP2 or CCSD(T) at the optimized MP2/aug-cc-pVTZ geometries are the same as GAUSSIAN 09 uses the SCF orbitals to do these calculations when projecting to a minimal basis set.

We investigated the interaction of both HF and LiF with Ne using several (but not all) of the same methods that we used for the rare gas dimers with the aug-cc-pVTZ basis set. Table V displays the results for HF/Ne using many methods

FIG. 3. Interaction geometries for HF with Ne, methane, and 2-butyne.

FIG. 4. Interaction geometries for LiF with Ne, methane, and 2-butyne.

while Table VI displays HF and LiF interactions with Ne, methane, and 2-butyne using several of the more popular methods.

Let us first consider HF/Ne (Table V), where charge transfer is minimal. When calculated on a CP-corrected PES, CCSD(T)/aug-cc-pVTZ predicts interaction energies of -102 or -212 cal/mol, respectively, for F- and H facing interactions, while MP2 predicts -80 and -168 cal/mol (slightly larger interactions were calculated using larger basis sets, see Table IV). Hartree–Fock and B3LYP predict very small inter-

actions when F faces Ne, but the interactions become significant (although still too weak) when H- faces Ne. Comparing all methods, the order of the stability predicted when F faces Ne is $M06-2X > M05 > M05-2X > M06L > B97-D > M06 > B2PLYP-D \gg CCSD(T) > MP2 = X3LYP \gg B2PLYP > HF > B3LYP$. When H- faces Ne, the interactions become stronger for all methods used and the equilibrium distances between Ne and the nearest atom of HF become shorter. The order of the stabilizations when H- faces Ne becomes $B97-D \gg M05 = B2PLYP-D \gg M05-2X > X3LYP > M06-2X \gg$

TABLE V. Calculated interaction energies for Ne/HF using different methods. All calculations used the aug-cc-pVTZ basis set. Energies (and BSSE) in cal/mol, and distances in Angstroms. The $\mu\mu$ ratios are calculated from the ratios of the $\Delta E_{int} r^3$ (where r is the Ne...H or Ne...F distance). Functionals marked with an asterisk (*) produced more than one minimum on the PES.

	CP-optimized			No-CP				Ratio $\mu\mu$ interaction
	F-facing							
	ΔE_{int}	Ne—F	BSSE	ΔE_{int}	Ne—F	$\Delta\Delta E_{\text{int}}$	$\Delta(\text{Ne—F})$	
CCSD(T)	− 102	3.10	73	− 178	3.02	76	0.08	1.0
MP2	− 80	3.17	61	− 145	3.08	65	0.10	1.0
HF	− 2	4.20	7	− 11	3.75	9	0.45	0.2
B2PLYP	− 20	3.12	31	− 51	3.08	31	0.04	0.3
X3LYP	− 79	3.03	18	− 97	3.01	18	0.02	0.7
B3LYP	0	∞		0	∞			
M05	− 208	2.87	31	− 239	2.86	31	0.00	1.0
M05-2X	− 200	2.88	29	− 229	2.87	29	0.01	1.3
M06*	− 160	3.48	34	− 183	3.47	23	0.01	0.8
M06-2X	− 215	3.09	20	− 235	3.08	20	0.01	1.6
M06L*	− 196	3.09	34	− 230	3.09	34	0.00	2.4
B97-D	− 174	3.32	16	− 190	3.29	16	0.03	0.9
B2PLYP-D	− 150	2.92	39	− 190	2.89	39	0.02	0.7
H-facing								
		Ne—H			Ne—H			
CCSD(T)	− 212	2.40	253	− 506	2.23	294	0.17	
MP2	− 168	2.47	210	− 422	2.28	254	0.19	
HF	− 31	2.94	28	− 70	2.66	39	0.28	
B2PLYP	− 169	2.34	122	− 299	2.26	130	0.08	
X3LYP	− 295	2.25	71	− 368	2.22	73	0.03	
B3LYP	− 98	2.37	59	− 160	2.31	62	0.06	
M05	− 415	2.27	96	− 515	2.22	100	0.05	
M05-2X	− 306	2.28	107	− 418	2.23	112	0.05	
M06	− 176	2.95	31	− 207	2.94	31	0.01	
M06-2X	− 251	2.50	65	− 327	2.34	76	0.16	
M06L*	− 123	2.71	65	− 193	2.56	70	0.15	
B97-D	− 454	2.46	63	− 519	2.43	64	0.03	
B2PLYP-D	− 412	2.31	127	− 543	2.27	131	0.04	

TABLE VI. Interaction energies (kcal/mol) of HF and LiF with Ne, methane, and 2-butyne for structures optimized on CP-corrected surface using the aug-cc-pVTZ basis set for HF and the functionals. MP2 and CCSD(T) single point at MP2/aug-cc-pVTZ geometries using higher levels as indicated.

	F-facing			H or Li-facing		
	Neon	Methane	2-Butyne	Neon	Methane	2-Butyne
Hydrogen fluoride						
B3LYP	0	0	−0.19	−0.10	−1.00	0
HF	0	0	−0.28	−0.03	−0.49	0
X3LYP	−0.08	0	−0.39	−0.30	−1.33	−0.10
M06-2X	−0.22	−0.24	−0.73	−0.25	−1.99	−0.58
B97-D	−0.17	−0.26	−0.68	−0.45	−2.20	−1.05
MP2	−0.09 ^a	−0.19 ^b	−0.66 ^b	−0.18 ^a	−1.50 ^b	−0.38 ^b
CCSD(T)	−0.13 ^a	−0.27 ^b	−0.73 ^b	−0.23 ^a	−1.62 ^b	−0.45 ^b
LiF						
B3LYP	−0.02	0	−1.28	−0.76	−3.81	−1.33
HF	−0.03	0	−1.34	−0.48	−3.08	−0.49
X3LYP	−0.16	−0.09	−1.58	−1.01	−4.24	−1.71
M06-2X	−0.28	−0.41	−2.33	−0.84	−4.32	−1.69
B97-D	−0.21	−0.32	−1.78	−2.54	−8.64	−6.62
MP2	−0.13 ^a	−0.29 ^b	−1.92 ^b	−0.64 ^a	−3.64 ^b	−1.20 ^b
CCSD(T)	−0.18 ^a	−0.45 ^b	−2.15 ^b	−0.68 ^a	−3.76 ^b	−1.24 ^b
% error compared to CCSD(T)						
	F-facing		H or Li-facing		overall	
	MSE	MUE	MSE	MUE	MSE	MUE
B3LYP	40	40	17	24	29	32
HF	38	38	57	57	47	47
X3LYP	27	27	−11	34	8	30
M06-2X	−5	7	−28	28	−17	18
B97-D	15	18	−225	225	−105	121
MP2	11	10	7	7	9	9

^aaug-cc-pV5Z.

^baug-cc-pVQZ.

CCSD(T) > M06 > B2PLYP = MP2 ≫ M06L > B3LYP ≫ HF, which is significantly different. For comparison, we include the interaction energies and the distances between the Ne and the nearest atom of the HF for optimizations on surfaces that do not reflect the CP corrections. The increases in these equilibrium distances upon going from a normal to CP-corrected surface are particularly large for Hartree–Fock when F- faces Ne.

Since the interaction between two dipoles arranged in a linear geometry varies as r^{-3} , where r is the distance between their charge centers, and since the distances between the species are shorter when H- faces Ne, we thought it interesting to compare the $\Delta E_{\text{int}} \times r^3$ for the two kinds of interaction (H- and F-facing). If these interactions be proportional to the dipole–dipole interactions, the ratio of these values should be 1.0. From the last column of Table V, one sees this to be the case for CCSD(T) and MP2. Among the functionals, only B97-D (0.9) comes close to this value. All of those functionals optimized for dispersion, except B97-D and B2PLYP-D, have ratios significantly larger than 1.0, with M06L have the highest (3.3), while the more traditional functionals have ratios that are lower, with that for X3LYP (0.7) closest to 1.0.

We examined the interactions of HF and LiF with Ne, methane, and 2-butyne (Table VI) in somewhat less detail. Here charge-transfer may play an important role in the in-

teractions. From the error analysis of the table, we see that X3LYP actually provides the best MSE with the CCSD(T) results, while its MUE is somewhat higher. Surprisingly, B3LYP and even HF do not do badly either. B97-D works well for those cases where F-faces, but very poorly when H or Li faces the neutral. M06-2X follows the same trend as B97-D, but does not suffer the extreme error of the former for F-facing. Even Hartree–Fock gives errors similar to those of the functionals, although it always underestimates the interaction. Interestingly, MP2 consistently underestimates the interaction despite reports that it overestimates pure dispersion interactions, particularly those involving π -stacking.^{5,6,33}

We should note that for the cases where H- or Li- faces 2-butyne, we observed unexpected maxima in relaxed scans of the distance between the entities. The energies at these maxima exceeded that of the fully dissociated species. At first we thought this might be an artefact of the DFT calculations. However, we found similar behavior for MP2 and HF calculations. This behavior does not occur when F-faces the neutral. We intend to look into this problem further.

DISCUSSION

The results show that all of the DFs except M06L and ω B97xD overestimate dispersion interactions for He and Ne

TABLE VII. Induced dipole moments (Debyes). Positive induced dipoles increase the dipole of the complex over that of HF or LiF alone using aug-cc-pVXZ.

Facing >	X	HF F	H	LiF F	Li
Ne					
HF	T	0.01	0.04	0.04	0.19
X3LYP	T	0.03	0.12	0.08	0.26
B3LYP	T		0.11	0.06	0.25
M06-2X	T	0.02	0.08	0.07	0.22
B97-D	T	0.02	0.10	0.06	0.26
MP2	T	0.02	0.08	0.06	0.22
MP2	Q	0.02	0.08	0.07	0.22
MP2	5	0.02	0.08	0.07	0.22
Methane					
HF	T		0.29	0.21	0.87
X3LYP	T	0.09	0.50	0.34	0.95
B3LYP	T		0.45		0.95
M06-2X	T	0.10	0.54	0.41	0.94
B97-D	T	0.10	0.51	0.33	0.94
MP2	T	0.11	0.46	0.36	0.87
MP2	Q	0.11	0.46	0.36	0.88
2-Butyne					
HF	T	0.17		0.78	1.40
X3LYP	T	0.26	0.62	0.89	1.68
B3LYP	T	0.23	0.56	0.87	1.64
M06-2X	T	0.29	0.73	1.00	1.61
B97-D	T	0.27	0.66	0.91	1.84
MP2	T	0.27	0.57	0.89	1.51
MP2	Q	0.27	0.57	0.89	1.51

dimers, but all DFs underestimate these interactions of Ar dimer, even using aug-cc-pV5Z, when compared to high level *ab initio* methods. They perform better with respect to high level calculations when larger (aug-cc-pV5Z) are used primarily due to the expected and observed increase in the dispersion interactions for the higher level (MP2 and (CCSD(T)) calculations. However, several of the DFs (but none of the TFs) we investigated predicted smaller negative interactions with the 5Z set than with the TZ or QZ sets. Since the DFs tend to overestimate the interactions within He₂ and Ne₂, these smaller interactions became closer to the benchmarks. For Ar₂, where the DFs all underestimate the interaction, the reverse holds. The most significant changes of this type occurred for M05-2X and M06L. The functionals behave quite differently from each other in several ways. They do not generally follow the expected patterns for interaction energies, BSSE, and interaction distances when basis sets are increased, although some do some of the time.

The effects of interaction of HF and LiF with nonpolar entities (Ne, methane, and 2-butyne) are significantly different for interactions with the F or H/Li ends of the polar molecule compared to MP2 and CCSD(T). However, the interactions suggest that dispersion interactions enhance induction as the time dependent electron density fluctuations are more favorable, therefore more likely, when they are in a direction that lowers the energy. The fact that methods that do not specifically account for dispersion interactions provide reasonable estimates of the interaction energies for several of

TABLE VIII. Charge transfer in electrons $\times 10^3$. All values are negative indicating transfer from the neutral to the HF or LiF. Values use Mulliken charges projected to a minimum basis set starting from aug-cc-pXZ and are corrected for BSSE (charge-transfer to ghost orbitals).

Facing >	X	HF F	H	LiF F	Li
Ne					
HF	T		-0.0	-0.0	-8.0
X3LYP	T	-0.0	-2.7	-0.2	-12.8
B3LYP	T		-2.0	-0.1	-12.2
M06-2X	T	-0.0	-0.6	-0.1	-10.1
B97-D	T	-0.0	-1.7	-0.1	-12.1
MP2/CCSD(T)	T	-0.0	-0.3	-0.0	-7.7
MP2/CCSD(T)	Q	-0.0	-0.3	-0.0	-8.0
MP2/CCSD(T)	5	-0.0	-0.3	-0.0	-8.0
Methane					
HF	T		-1.9	-0.0	-38.5
X3LYP	T	-0.1	-13.3	-1.3	-51.9
B3LYP	T		-10.6		-51.5
M06-2X	T	-0.3	-14.0	-3.0	-49.4
B97-D	T	-0.2	-15.5	-1.0	-49.7
MP2/CCSD(T)	T	-0.4	-6.4	-1.3	-39.5
MP2/CCSD(T)	Q	-0.4	-6.4	-1.3	-39.4
2-Butyne					
HF	T	-0.1		-1.9	-34.9
X3LYP	T	-0.6	-6.5	-4.1	-52.8
B3LYP	T	-0.2	-5.0	-3.5	-50.0
M06-2X	T	-1.3	-9.5	-6.6	-46.9
B97-D	T	-0.6	-8.5	-3.5	-55.6
MP2/CCSD(T)	T	-0.8	-3.1	-3.8	-37.4
MP2/CCSD(T)	Q	-0.8	-3.1	-3.8	-37.3

the interactions considered in Table VI suggests that these methods either somehow account for dispersion in certain cases where it accompanies induction, or that dispersion does not significantly contribute to these interactions. The forgoing could be part of the explanation for the successes of B3LYP and X3LYP for describing H-bonding in water dimer³⁴ and peptides.³⁵ We compare the behavior of the various functionals in evaluating peptide interactions elsewhere.¹³

We found the differences between the interactions calculated using the two *ab initio* methods (CCSD(T) and MP2) to change sign depending upon the situation. MP2 underestimates the energies for neon dimer, but overestimates them for argon dimer. MP2 consistently underestimates the interactions for HF and LiF and the nonpolar entities. We did *not* find that MP2 calculations *consistently* overestimate the dispersion interactions when compared to DFT, as suggested in the literature.³⁶

The current results suggest that the physical model(s) used in the parameterized methods might be compromised. Peverati and Truhlar have recognized some problems in recent papers describing improvements to their series of functionals.^{11,37}

The development of semiempirical molecular orbital theories provides a useful comparison to the methods used to parametrize the functionals. Dewar *et al.* used gas phase enthalpies of formation taken from reliable experimental data as their primary source of data. Until they developed AM1,³⁸

semiempirical methods of Dewar *et al.* did not provide reasonable descriptions of molecules and reactions. Even then, the method only worked well for molecules containing atoms for which there were good data in differing molecular environments. For example, molecules containing halogens were not as well described as those containing only C, H, O, and N, probably due to the combination of their mono-valency and relative lack of reliable experimental heats of formation. Furthermore, Dewar *et al.* used a training set of molecules to parametrize and a large set to test. They insisted that the parameters for each atom follow a logical progression expected from their positions in the periodic table. Thus, they did not simply use the best fit to the data. Perhaps, parametrized functionals could be constructed that use better data and be tested so that they follow physically expected trends. Hopefully, the data in this paper will contribute to the efforts in this direction.

We also note that in real molecules containing dispersive interactions between entities, the distances between these entities might be constrained by other structural factors. Also, ΔE is not as an appropriate measure as ΔH , for most larger systems. Dispersion interactions could affect the vibrational modes of molecules that contribute to the ΔH . All these factors need to be considered for the construction of a truly useful semiempirical functional. For example, if one were to compare the energies of *cis* and *trans* stilbene (1,2-diphenylethene), one might expect a dispersive attraction between the phenyls in the *cis* (but not *trans*) isomer. However, this would be opposed by a steric interaction that would be due to the difficulty of the phenyls to independently rotate about the bonds to the ethenes in the *cis* isomer. To properly describe such systems, a functional must correctly describe the dispersive interactions as a function of distance (as the distance between the phenyls is constrained by the molecular framework) and correctly describe the vibrational frequencies that contribute to the calculation of the enthalpies of the two isomers.

Using functionals that eschew fitted parameters might be the other route to take. This has the advantage of preserving the theoretical nature of DFT, rather than using it as a sophisticated method of curve fitting. There has been intense recent progress in this area: some functionals have no fitted parameters at all,³⁹ while others have only slight empiricism.⁴⁰ In our view, both approaches have their places, but they might be useful in different ways. For example, empirical methods can often provide useful information in systems where enough good data are available and no unexpected effects occur. However, such methods cannot be relied upon to evaluate situations where such effects do occur. The obvious difficulty of knowing when to expect the unexpected argues for the development of better non-parametrized functions.

CONCLUSIONS

When compared to CCSD(T) calculations, the functionals designed to treat dispersion interactions behave rather erratically, but with a tendency to overestimate the strength of these interactions for most of the cases that studied here. The functionals do not follow the expected trends with respect to increasing size of basis sets and dispersion interactions and

BSSE. In several cases, the distances between the interacting entities increased when the interaction energies became stronger (as the basis set was varied). All of these observations suggest that these functionals do not provide reasonable physical models for the non-bonded interactions that they aim to assess. Erratic results involving apparent anomalous multiple minima on potential energy surfaces can arise with some these functionals with normal and even relatively fine integrations grids. In the present work, we found this problem with B2PLYP, M06, M06L, and B2PLYP-D. Even with the finest grid available in GAUSSIAN 09 (99974) the anomalies do not completely disappear. Sherrill and co-authors have reported the ability of several of these (and other) functionals to reproduce the values of many interactions in the datasets which were used to parametrize many of them.⁹

The high level calculations on the systems where induction occurs tend to support the idea that induction enhances dispersion since the induced permanent dipole will more likely be increased than diminished by the time dependent electron correlated motions that lead to dispersion. The B3LYP and X3LYP functionals can describe the interactions in several of these systems as well or better than some of the functionals specifically designed to address dispersion.

We suggest using better data sets that are based on good experimental data, and using fewer parameters that are chosen with preservation of the physical model in mind when designing better functionals.

ACKNOWLEDGMENTS

Mr. Jonathan Levy performed many preliminary calculations. The work described was supported by Award No. SC1AG034197 from the National Institute on Aging. N.T.M. was supported, in part, by the National Science Foundation.

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