Supporting Information for "Energy Decomposition Analysis with a Stable Charge-Transfer Term for Interpreting Intermolecular Interactions"

Ka Un Lao and John M. Herbert*
Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH 43210

1 Examination of Basis-Set Dependence

1.1 Set of 11 Charge-Transfer Complexes

In Fig. S1 we examine the basis-set dependence of CT energies for this set of complexes. For this comparison, we choose the 6-311++G(3df,3pd) basis set, which is used frequently in ALMO-EDA,[1] along with def2-TZVPPD and def2-QZVPPD, which have been recommended for the cDFT scheme.[2] The cDFT method exhibits essentially no basis set dependence, whereas the basis-set dependence of the ALMO and SAPT methods is significant for the four complexes where the extent of CT is large ($\delta q > 0.1\ e^-$). CT energies for ALMO and SAPT vary by as much as 26.7 kJ/mol (ALMO-EDA) and 16.5 kJ/mol (SAPT) for the $H_3N \cdots BH_3$ complex. For the ALMO-EDA and SAPT calculations, the maximum deviations amongst the three basis sets occurs between def2-TZVPPD and def2-QZVPPD, indicating once again the extreme dependence on basis set size associated with these definitions of CT.

1.2 Cation–Alkyl Radical Complexes

Using the same three basis sets for this set of 8 complexes, we once again find that the cDFT method exhibits very mild basis-set dependence, with CT energies that vary by no more than 1.4 kJ/mol amongst these three basis sets. ALMO-EDA results, in contrast, vary by as much as 27.3 kJ/mol across these basis sets and SAPT results vary by as much as 8.2 kJ/mol. The large basis-set dependence of the ALMO-EDA results cannot be explained by BSSE, as the counterpoise corrections are no larger than 2.5 kJ/mol.

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*`herbert@chemistry.ohio-state.edu`

1.3 Nucleophile–$C_6H_5^{\bullet+}$ Complexes

In most cases, CT energies calculated using B3LYP are greatly overestimated as compared to the those computed using ωB97X-D3. For example, the mean unsigned deviation for ALMO-EDA CT energies, comparing B3LYP/ and ωB97X-D3/6-311++G(3df,3pd) results is 9.3 kJ/mol, and the corresponding mean unsigned deviation for cDFT calculations is 6.0 kJ/mol. We attribute the larger B3LYP values of the CT energies to greater delocalization error with this functional, which is known to exaggerate the extent of CT.[3,4]

Examining the same three basis sets considered above for this set of 12 complexes, we find that the maximum basis-set deviation in the CT energy is 4.5 kJ/mol for ALMO-EDA and 2.1 kJ/mol for cDFT. For SAPT and SAPT+δSCF, the maximum deviations are 3.7 and 3.9 kJ/mol, respectively, for $C_6H_5^{\bullet+}\cdots HBr$ and $C_6H_5^{\bullet+}\cdots PH_3$. As in all of the results reported in this work, cDFT results are far less dependent on the choice of basis set as compared to orbital-based EDAs.

2 Exchange-Dipole Model for $C_6H_5^{\bullet+}\cdots H_2O$

The high-level SAPT2+3(CCD)/aug-cc-pVTZ method was used to estimate the dispersion energy (for use with dlDF) for the $C_6H_5^{\bullet+}\cdots H_2O$ complex. These calculations were performed using the Psi4 program,[5] and because this method is only available for closed-shell species, we substitute the closed shell $C_6H_6\cdots H_2O$ complex for these calculations. To assess the magnitude of this approximation, we turn to the Becke-Johnson exchange-dipole model (XDM),[6,7] a DFT-based way to compute dispersion interactions that is available for both closed- and open-shell species. At the B3LYP/aug-cc-pVTZ level of theory, we find that the XDM dispersion energy for the open-shell $C_6H_5^{\bullet+}\cdots H_2O$ complex is smaller than that of the closed-shell $C_6H_6\cdots H_2O$ complex, but only by 0.7 kJ/mol (on-top orientation) or 0.3 kJ/mol (side-on orientation). Assuming that these differences are transferable to SAPT calculations, they amount to only 3% of the SAPT2+3(CCD)/aug-cc-pVTZ dispersion energy for $C_6H_6\cdots H_2O$, in either orientation. This justifies our use of the closed-shell complex to obtain an accurate dispersion correction to augment the dlDF functional.

3 Charge-Transfer Interactions in Alkyl and Aryl complexes

CT energies in alkyl and aryl complexes are shown in Tables 3 and S2, respectively.

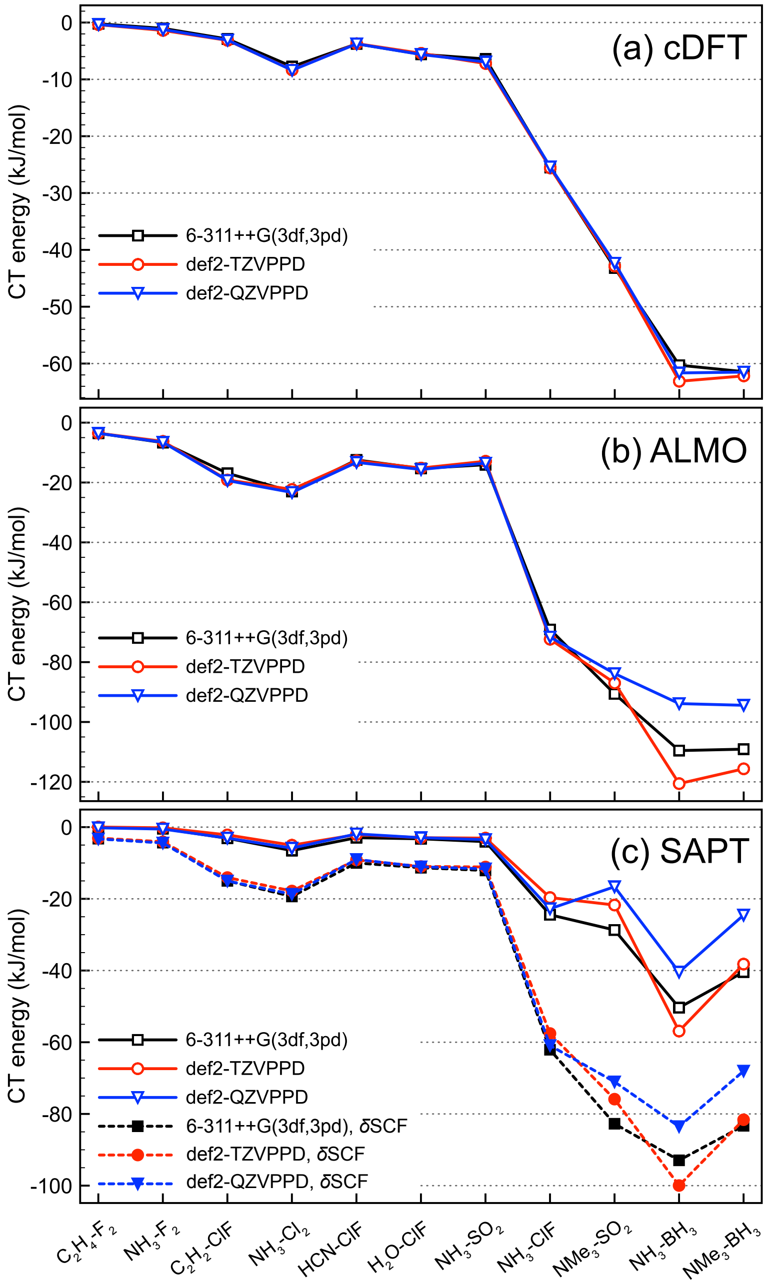

Figure S1: CT energies computed in a variety of basis sets using (a) cDFT with the ωB97X-D3 functional, (b) ALMO-EDA using the ωB97X-D3 functional, and (c) SAPT with and without the $\delta E_{\text{int}}^{\text{HF}}$ ("δSCF") correction, using the LRC-ωPBE functional.

Cation	Alkyl Species	$(\mathrm{IE} - \mathrm{EA})^{-1}$/ eV^{-1}	CT Energy / kJ mol^{-1}			
			cDFT	ALMO	SAPT	SAPT+δSCF
H_3O^+	CH_4	0.12	−30.30	−22.05	−2.73	−17.50
	$(CH_3)_3CH$	0.16	−41.55	−32.42	−3.37	−28.80
	$CH_3^\bullet$	0.18	−45.46	−48.84	−7.34	−41.75
	$(CH_3)_3C^\bullet$	0.42	−122.52	−96.96	−13.89	−124.98
NH_4^+	CH_4	0.13	−11.22	−7.11	−0.78	−5.21
	$(CH_3)_3CH$	0.17	−14.06	−10.06	−1.05	−7.80
	$CH_3^\bullet$	0.20	−16.91	−20.97	−2.84	−14.81
	$(CH_3)_3C^\bullet$	0.51	−33.71	−37.53	−4.92	−32.16

Table S1: CT energies for the cation–alkyl complexes.

Orientation	Nucleophile	$(\mathrm{IE} - \mathrm{EA})^{-1}$/ eV^{-1}	CT Energy / kJ mol^{-1}			
			cDFT	ALMO	SAPT	SAPT+δSCF
On-Top	PH_3	1.59	−80.34	−118.69	−9.10	−93.07
	NH_3	1.20	−63.45	−88.72	−10.05	−77.17
	CH_3COOH	0.71	−28.76	−30.69	−3.04	−27.33
	CH_3OH	0.63	−24.14	−29.69	−2.64	−22.48
	CH_3Cl	0.50	−17.49	−23.73	−1.79	−15.46
	HBr	0.41	−17.93	−27.44	−2.00	−16.76
	CH_3CN	0.34	−14.53	−16.65	−1.82	−17.89
	H_2O	0.30	−10.14	−11.86	−1.34	−10.78
Side-On	CH_3COOH	0.71	−4.60	−3.00	−0.65	−3.54
	CH_3OH	0.63	−5.28	−5.13	−1.05	−5.85
	CH_3CN	0.34	−5.55	−6.16	−1.31	−7.18
	H_2O	0.30	−3.95	−4.27	−0.91	−4.36

Table S2: CT energies for $C_6H_5^{\bullet+} \cdots$ nucleophile complexes, considering two orientations.

References

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