A QUANTUM LEAP INTO THE FUTURE OF CHEMISTRY

Intermolecular Interactions

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Evaluation of Intermolecular Binding Energies

Analysis of Intermolecular Bindings

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▶ Traditional DFT methods are problematic for non-covalent interactions (NC): long-range electron correlation is missing.

▶ The application of dispersion corrections largely improves the description of NC with DFT methods.

▶ Two outstanding examples:
  1. Grimme's DFT-D
  2. Non-local correlation (NLC) functionals

All the benchmark results for density functionals included in this talk were generated by Dr. Narbe Mardirossian (unpublished work).

The merit of dispersion correction:

RMSD over 1744 non-covalent dimers:

RMSDs in kcal/mol for NCED
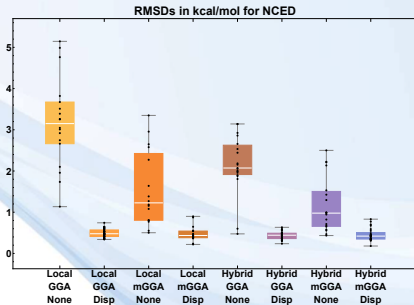
Benchmark results for non-covalent dimers (RMSD@1744 data points):

Functional	A24	DS14	HB15	HSG	NBC10	S22	X40	A21x12	BzDC215	HW30	NC15	S66	S66x8	3B-69-DIM	AlkBind12	CO2Nitrogen16	HB49	Ionic43
SPW92	1.66	1.96	4.60	2.01	0.77	3.18	2.46	1.11	1.28	1.57	0.77	2.51	2.16	2.17	1.23	1.03	4.60	5.40
PBE	0.48	1.13	0.78	1.72	2.98	3.63	1.74	0.24	1.16	0.55	0.18	2.66	2.27	1.82	3.53	2.71	1.06	1.33
TPSS	0.89	1.73	1.24	2.49	3.74	4.61	2.32	0.44	1.60	1.03	0.28	3.59	2.99	2.44	4.87	3.54	1.36	2.01
B3LYP	1.07	1.99	1.24	2.68	4.36	4.89	2.52	0.55	2.06	1.16	0.33	3.78	3.26	2.51	5.16	3.54	1.39	2.54
PBE-D3(BJ)	0.36	0.47	1.13	0.24	0.17	0.59	0.61	0.24	0.27	0.39	0.26	0.40	0.41	0.48	0.15	0.41	1.22	1.20
revPBE-D3(BJ)	0.28	0.30	1.07	0.60	0.57	0.62	0.55	0.19	0.33	0.33	0.19	0.49	0.40	0.52	0.25	0.63	0.87	1.37
BLYP-D3(BJ)	0.15	0.21	0.57	0.40	0.43	0.32	0.34	0.12	0.21	0.27	0.14	0.25	0.21	0.34	0.20	0.28	0.63	1.23
B97-D3(BJ)	0.28	0.32	0.94	0.55	0.64	0.49	0.52	0.18	0.35	0.37	0.18	0.42	0.35	0.48	0.38	0.58	0.76	1.33
TPSS-D3(BJ)	0.15	0.20	0.80	0.26	0.30	0.47	0.49	0.14	0.28	0.21	0.17	0.34	0.34	0.47	0.35	0.57	0.86	0.85
SCAN-D3(BJ)	0.43	0.35	1.19	0.47	0.17	0.69	0.75	0.29	0.44	0.55	0.16	0.56	0.50	0.55	0.23	0.16	1.07	1.56
M06-L	0.35	0.43	0.58	0.63	0.61	0.83	0.59	0.22	0.34	0.51	0.26	0.61	0.52	0.72	0.38	1.16	0.72	1.02
B97M-rV	0.16	0.10	0.25	0.12	0.26	0.29	0.15	0.09	0.21	0.15	0.07	0.19	0.17	0.19	0.27	0.11	0.44	0.65
PBE0-D3(BJ)	0.25	0.32	1.11	0.18	0.18	0.61	0.53	0.18	0.35	0.34	0.16	0.41	0.42	0.48	0.12	0.30	0.87	1.25
B3LYP-D3(BJ)	0.15	0.22	0.75	0.21	0.24	0.43	0.34	0.09	0.20	0.23	0.10	0.34	0.31	0.36	0.17	0.07	0.59	0.80
ωB97X-D	0.16	0.24	0.51	0.35	0.25	0.24	0.55	0.10	0.31	0.31	0.18	0.41	0.34	0.39	1.00	0.81	0.37	1.07
ωB97X-V	0.08	0.11	0.28	0.16	0.33	0.27	0.24	0.05	0.21	0.14	0.06	0.13	0.21	0.20	0.12	0.10	0.29	0.78
TPSSh-D3(BJ)	0.13	0.18	0.79	0.23	0.33	0.44	0.46	0.13	0.31	0.19	0.14	0.31	0.34	0.43	0.33	0.48	0.73	0.80
M06-2X	0.26	0.25	0.36	0.52	0.56	0.54	0.32	0.14	0.34	0.37	0.14	0.33	0.38	0.52	0.30	0.36	0.56	1.16
MN15	0.31	0.25	0.66	0.28	0.34	0.84	0.36	0.19	0.53	0.44	0.12	0.64	0.48	0.48	1.18	0.36	0.58	0.73
ωB97M-V	0.09	0.15	0.20	0.11	0.16	0.28	0.22	0.05	0.19	0.17	0.05	0.15	0.11	0.16	0.13	0.09	0.23	0.70
Minimum	**0.08**	**0.10**	**0.20**	**0.11**	**0.12**	**0.24**	**0.15**	**0.05**	**0.17**	**0.11**	**0.05**	**0.13**	**0.11**	**0.16**	**0.11**	**0.07**	**0.23**	**0.54**
Best	ωB97X-V	B97M-rV	ωB97M-V	ωB97M-V	LC-VV10	ωB97X-D	B97M-rV	ωB97M-V	VV10	PWB6K	ωB97M-V	ωB97X-V	ωB97M-V	ωB97M-V	RPBE-D3(BJ)	B3LYP-D3(BJ)	ωB97M-V	M06-D2

Recommended functionals:

▶ semi-local GGA:
BLYP-D3(BJ)

▶ semi-local meta-GGA:
B97M-rV

▶ hybrid GGA:
ωB97X-V, B3LYP-D3(BJ)

▶ hybrid meta-GGA:
ωB97M-V

Benchmark results for non-covalent clusters (RMSD@243 data points):

Functional	H2O6Bind8	HW6Cl	HW6F	FmH2O10	Shields38	SW49Bind345	SW49Bind6	WATER27	3B-69-TRIM	CE20	H2O20Bind10	H2O20Bind4
SPW92	27.39	21.14	22.28	66.21	33.36	9.51	19.39	26.70	4.74	20.47	122.42	125.52
PBE	0.90	0.86	2.47	6.22	1.55	1.28	2.62	3.08	4.78	2.35	11.61	4.47
TPSS	3.98	4.54	5.68	16.31	3.64	2.87	6.12	3.86	6.48	2.65	31.32	19.49
B3LYP	3.93	5.52	5.09	16.11	4.54	3.13	6.53	4.03	6.61	3.24	29.53	22.68
PBE-D3(BJ)	4.15	3.38	1.12	6.22	6.47	1.72	2.94	5.71	0.93	4.45	14.33	24.66
revPBE-D3(BJ)	4.64	2.78	6.90	14.98	3.51	1.08	2.41	3.17	1.25	2.04	24.72	13.12
BLYP-D3(BJ)	0.62	0.91	3.77	5.94	1.59	0.76	0.85	2.20	0.71	1.55	4.51	6.88
B97-D3(BJ)	3.32	1.90	5.04	10.34	2.75	0.82	1.57	2.66	1.11	1.78	17.87	10.62
TPSS-D3(BJ)	1.39	0.73	1.50	1.18	2.85	0.78	1.00	3.32	0.96	2.41	0.93	10.36
SCAN-D3(BJ)	6.52	5.78	6.61	19.08	7.77	2.47	4.70	6.69	1.16	4.83	28.71	28.81
M06-L	1.35	0.90	1.23	3.33	1.47	0.42	0.44	1.43	1.71	1.34	6.32	8.10
B97M-rV	0.33	0.20	0.50	0.71	0.45	0.24	0.54	1.26	0.43	0.77	1.26	1.64
PBE0-D3(BJ)	3.93	2.77	2.33	7.29	4.29	0.97	1.70	3.94	0.92	2.69	13.62	14.86
B3LYP-D3(BJ)	2.35	1.17	0.46	2.62	3.21	0.87	1.48	2.72	0.74	2.06	8.84	11.93
ωB97X-D	0.83	0.39	0.67	2.88	0.73	0.76	0.70	0.65	0.88	0.42	1.95	0.98
ωB97X-V	0.43	0.34	0.13	0.18	0.70	0.31	0.64	0.92	0.39	0.69	1.18	1.87
TPSSh-D3(BJ)	1.40	0.58	0.97	0.66	2.13	0.58	0.73	2.71	0.86	1.83	1.05	7.27
M06-2X	1.60	2.84	4.07	8.53	1.77	0.57	0.90	2.73	1.31	1.44	3.50	3.30
MN15	0.45	2.08	2.33	3.47	0.63	0.19	0.49	1.19	1.11	1.06	6.74	2.24
ωB97M-V	0.29	0.22	0.14	0.43	0.48	0.27	0.60	0.51	0.32	0.65	0.97	1.06
Minimum	**0.18**	**0.20**	**0.13**	**0.17**	**0.23**	**0.07**	**0.15**	**0.51**	**0.32**	**0.42**	**0.53**	**0.98**
Best	B97-D2	B97M-rV	ωB97X-V	B97M-V	PW6B95-D2	M05-2X	LC-ωPBE08-D3(0)	ωB97M-V	ωB97M-V	ωB97X-V	BP86-D3(BJ)	ωB97X-D

- The best-performing functional on each rung is roughly consistent with the tests for dimers.
- Overall, it is evident that B97M-rV is the best-performing semi-local functional, while ωB97M-V is the best hybrid.

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The D3 correction to KS-DFT energy only relies on the relative position of the nuclei:

$$E_{D3} = -\sum_{i<j} \sum_{n=6,8} s_n \frac{C_{n,ij}}{r_{ij}^n} f_{damp,n}(r_{ij})$$

There are various flavors of D3 tails, mainly due to the different choices for the damping function. These methods are accessible in Q-CHEM 5.0 via setting the DFT_D rem variable:

▶ D3_ZERO: the original "zero" damping

▶ D3_BJ: the Becke-Johnson damping

▶ D3_ZEROM & D3_BJM: the modified -D3(0) and -D3(BJ) tails

▶ D3_OP: the "optimal power" damping by Witte *et al.*

▶ D3_CSO: the "C_6 only" D3 tail

See the updated Q-CHEM manual for more details and the references.

- For most general cases, specify the XC functional and the D3 tail separately.
- For B97-D3(0)/ωB97X-D3/ωM06-D3, simply set `Method` to B97-D3/wB97X-D3/wM06-D3.

The combinatorially designed functionals developed by Mardirossian *et al.* (ωB97X-V, B97M-V, and ωB97M-V) use the VV10 NLC functional:

$$E_{\mathrm{c}}^{\mathrm{VV10}} = \int d\mathbf{r}\, \rho(\mathbf{r}) \left[\frac{1}{32} \left(\frac{3}{b^2} \right)^{3/4} + \frac{1}{2} \int d\mathbf{r}'\, \rho(\mathbf{r}') \Phi(\mathbf{r}, \mathbf{r}') \right],$$

which requires the evaluation of a double-integral.

B97M-rV employs the revised VV10 (rVV10), which involves a small modification to the NLC kernel $\Phi(\mathbf{r}, \mathbf{r}')$.

For these functionals, the XC part is trained together with the NLC. Thus they are all specified through the `Method` rem variable.

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Choice of basis set

The quality of DFT results for intermolecular interactions heavily depends on the employed basis set.

Functional	Basis	NCED	NCEC	NCD	IE	ID	TCE	TCD	BH	EBL	EBE
PBE-D3(BJ)	6-31G*	2.52	51.38	5.43	2.09	6.06	13.00	21.98	15.88	0.056	2.24
	def2-SVPD	1.38	13.27	4.37	1.24	5.50	12.67	24.62	11.28	0.060	1.70
	def2-TZVPPD	0.49	5.99	3.72	0.73	5.13	9.76	17.51	10.09	0.048	0.45
	def2-QZVPPD	0.46	5.78	3.67	0.71	5.19	9.67	17.20	9.99	0.049	0.42
B3LYP-D3(BJ)	6-31G*	2.34	45.62	3.90	1.81	6.14	9.00	11.09	10.96	0.065	2.28
	def2-SVPD	1.32	10.58	2.53	1.08	5.50	7.66	11.53	6.29	0.070	1.75
	def2-TZVPPD	0.35	3.18	1.91	0.51	8.32	3.87	5.98	5.71	0.023	0.41
	def2-QZVPPD	0.31	3.02	1.88	0.49	8.51	3.72	5.97	5.65	0.022	0.37
ωB97M-V	6-31G*	2.12	41.92	3.20	1.62	4.26	9.00	11.94	8.84	0.073	1.99
	def2-SVPD	1.31	8.31	1.65	0.98	4.65	8.23	14.84	3.21	0.080	1.75
	def2-TZVPPD	0.20	0.74	1.15	0.31	2.06	2.65	4.45	1.78	0.018	0.20
	def2-QZVPPD	0.18	0.48	1.13	0.28	2.05	2.48	4.30	1.68	0.014	0.15
PBEh-3c	def2-mSVP	1.63	17.60	5.11	1.33	6.18	12.08	17.19	6.74	0.061	0.63

▶ For the relevant categories (NC and EB), def2-QZVPPD roughly represents the CBS limit and usually has the best performance.

▶ The performance of augmented triple-ζ (def2-TZVPPD) is close.

▶ The direct use of smaller basis sets (*e.g.* def2-SVPD) introduces much larger errors, mostly due to basis set superposition error (BSSE).

▶ BSSE arises from the inconsistent treatment of the supersystem and the monomers in a calculation of interaction energy via

$$E_{\text{int}} = E(AB) - E(A) - E(B).$$

▶ Due to BSSE, overbinding results could be obtained when insufficiently large basis sets are employed.

▶ Conventionally, counterpoise corrections can be applied to improve the results when small basis sets are employed, *i.e.*, we compute the monomer energies using the supersystem basis.

Evaluate monomer energy in the supersystem basis:

```
$molecule
0 1
  O   -1.5186150    0.1207555    0.0000000
  H   -1.9235996   -0.7477512    0.0000000
  H   -0.5659945   -0.0420030    0.0000000
 @O    1.3918540   -0.1089394    0.0000000
 @H    1.7518409    0.3476125   -0.7639214
 @H    1.7518409    0.3476125    0.7639214
$end

$rem
   BASIS  =  def2-SVPD
   GUI  =  2
   METHOD  =  wB97M-V
   SCF_CONVERGENCE  =  8
   THRESH  =  12
$end
```

"ghost" atoms

"ghost" atoms have no nuclei but only the associated AO basis functions. They are specified by "@" in the $molecule section.

Automatic evaluation of binding energy and BSSE in Q-CHEM:

```
$molecule
0 1
--
0 1
  O   -1.5186150    0.1207555    0.0000000
  H   -1.9235996   -0.7477512    0.0000000
  H   -0.5659945   -0.0420030    0.0000000
--
0 1
  O    1.3918540   -0.1089394    0.0000000
  H    1.7518409    0.3476125   -0.7639214
  H    1.7518409    0.3476125    0.7639214
$end

$rem
   JOBTYPE  =  BSSE
   METHOD  =  wB97M-V
   BASIS  =  def2-SVPD
   GUI  =  0
   SCF_CONVERGENCE  =  8
   THRESH  =  12
$end
```

fragment charge/multiplicity

set jobtype to "BSSE"

```
-----------------------------------------------------------------
*                    Fragment's binding energy                   *
-----------------------------------------------------------------
  Fragment       E(TOTAL)         E(CP-CORR)         DE(BSSE)

     1        -76.3452780955     -76.3454943484     0.0002162529
     2        -76.3453674461     -76.3457468263     0.0003793803
  Complex     -152.6995431218
-----------------------------------------------------------------
DE, kJ/mol    -23.3608741583     -21.7970206162
```

Another important practical aspect is the integration grid for XC (and NLC if applicable).

Mean absolute percentage grid errors over 15 NC complexes:

Functional	SG-1	(50,194)	(75,302)	(99,590)	(250,770)
SPW92	9.10	2.14	0.18	0.03	0.00
PBE-D3(BJ)	11.87	3.14	0.31	0.05	0.00
BLYP-D3(BJ)	63.56	17.04	1.29	0.52	0.00
B97-D3(BJ)	26.22	6.51	0.62	0.35	0.01
PBE0-D3(BJ)	12.99	3.36	0.39	0.07	0.00
B3LYP-D3(BJ)	41.80	12.08	0.62	0.28	0.00
ωB97X-V	13.62	3.32	0.46	0.09	0.00
ωB97X-D	94.89	16.74	2.62	1.06	0.08
TPSS-D3(BJ)	15.66	4.37	0.84	0.26	0.00
SCAN-D3(BJ)	20.05	6.98	2.11	0.73	0.09
B97M-rV	22.92	5.66	0.96	0.23	0.01
M06-L	70.37	51.50	17.31	11.96	0.60
MN15-L	65.67	26.46	8.91	3.68	0.04
TPSSh-D3(BJ)	16.01	4.45	0.82	0.26	0.00
ωB97M-V	17.78	4.08	0.46	0.28	0.02
PW6B95-D3(BJ)	21.14	7.52	2.79	2.34	0.12
M06	75.94	81.65	33.75	29.39	0.77
M06-2X	10.96	5.97	1.64	0.51	0.09
M11	98.82	54.47	18.76	6.85	0.08
MN15	11.11	12.54	3.84	1.42	0.01

Q-CHEM's new default for XC grid (Saswata *et al.*, JCC, **38**, 869 (2017)):

▶ SG-2 for meta-GGAs and B97-based functionals (*e.g.* ωB97X-D, B97M-V)

▶ SG-3 for Minnesota functionals

▶ SG-1 for all the other functionals (*e.g.* B3LYP, PBE)

Usage of ωB97M-V:

▶ For accurate results:
def2-QZVPPD / (99, 590) / SG-1

▶ For quick calculations:
def2-TZVPPD / (75, 302) / SG-0

Evaluate the interaction energy of the water dimer at the equilibrium geometry with BLYP-D3(0), B3LYP-D3(BJ), B97M-V and ωB97M-V.

Requirements and Hints:

- Use the def2-SVPD with CP correction.
- Use the default integration grids.
- Use fragment inputs and the "BSSE" job type.
- Set integral thresh to 10^{-12}, SCF convergence criterion to 10^{-8}.

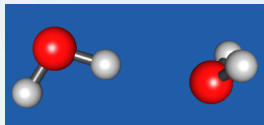Note: use a larger basis set and a finer grid in reality!

Functional	E_{int} (kJ/mol)
BLYP-D3(0)	-20.81
B3LYP-D3(BJ)	-21.92
B97M-V	-21.30
ωB97M-V	-21.80
Ref.	-21.25

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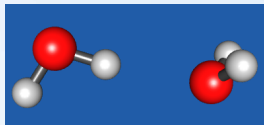
Answer:

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B3LYP-D3(BJ)	-21.92
B97M-V	-21.30
ωB97M-V	-21.80
Ref.	-21.25

Analysis of Intermolecular Bindings

Energy decomposition analysis (EDA): a category of methods that can separate intermolecular interactions obtained from electronic structure calculations into physically meaningful terms.

Such a separation is not unique but can be greatly useful:

▶ Unraveling the origin of interactions in intermolecular complexes.

▶ Providing references for the development of empirical models of intermolecular interactions (*e.g.* MM force field).

The original absolutely localized molecular orbitals (ALMO)-EDA decomposes the intermolecular binding energy as follows:

$$E_{int} = E_{gd} + E_{frz} + E_{pol} + E_{ct}$$

▶ Geometry distortion (GD): energy difference between the monomers at their geometries in the complex and at their fully relaxed structures.

▶ Frozen interaction (FRZ): energy change associated with bringing the infinitely separated fragments into the complex geometry without relaxing their MOs

▶ Polarization (POL): energy lowering associated with the intramolecular relaxation of each fragment's ALMOs due to the presence of other fragments.

The ALMO constraint requires each fragment's MOs to be expanded by the AO basis functions on the same fragment only.

▶ Charge transfer (CT): energy lowering when the ALMO constraint is removed, which is largely due to the electron transfer from one fragment's occupied orbitals to another's empty levels.

R. Khaliullin *et al. J. Phys. Chem. A* **111**, 8753 (2007)

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The ALMO-EDA method has seen several recent advances:

1. The partitioning of POL and CT now has a well-defined basis set limit, by using the fragment electrical response functions (FERFs) to compute E_{pol}.

2. Further decomposition of the FRZ term (into contributions from permanent electrostatics, Pauli repulsion and dispersion) is enabled:

$$E_{frz} = E_{elec} + E_{pauli} + E_{disp}$$

An alternative "classical" decomposition of the FRZ term is also reported (using the dispersion energy computed above):

$$E_{frz} = E_{elec}^{cls} + E_{pauli}^{mod} + E_{disp}$$

These improvements define the second-generation ALMO-EDA method.

P. R. Horn *et al. Phys. Chem. Chem. Phys.* **18**, 23067 (2016)

The "EDA2" set of methods in Q-CHEM supports the new ALMO-EDA scheme and several related methods.

The use of preset options largely simplifies the job control:

▶ EDA2 = 1: nDQ-FERF + FRZ decomp

▶ EDA2 = 2: old ALMO + FRZ decomp

Option 1 is recommended when large basis sets (*e.g.* def2-QZVPPD) are used.

Option 2 is still useful when large basis sets are unaffordable.

Other rem variables:
EDA_BSSE, DISP_FREE_X/DISP_FREE_C

Example: ALMO-EDA calculation (op. 2) for the water-Cl⁻ complex.

Model chemistry:
ωB97X-V/def2-SVPD(CP)


```
$molecule
-1 1
--
-1 1
  Cl   -1.1242249    0.0179827    0.0000000
--
0 1
  O     1.9940516   -0.0909265    0.0000000
  H     1.0163933   -0.2184602    0.0000000
  H     2.0588108    0.8652887    0.0000000
$end

$rem
  JOBTYPE   =  EDA
  EDA2      =  2
  BASIS     =  def2-SVPD
  METHOD    =  wB97X-V
  THRESH    =  12
  EDA_BSSE  =  TRUE
  SCF_CONVERGENCE  =  8
$end
```

set "Jobtype = eda" and the option set number

apply CP correction

```
==============================
     Results of EDA2
==============================
Basic EDA Quantities
--------------------
Fragment Energies (Ha):        monomer energies
1 -460.0529423830
2  -76.3470870254
--------------------
  E_frz (kJ/mol) = -32.8997
  E_pol (kJ/mol) = -15.0940
  E_vct (kJ/mol) = -16.6776 (CP-corrected)
  E_int (kJ/mol) = -64.6714 (CP-corrected)      FRZ, POL, and CT
--------------------


Initial Wavefunction Decomposition
----------------------------------
  --------------------
  Orthogonal Fragment Subspace Decomposition:
  --------------------
    E_elec   (ELEC)  (kJ/mol) = -119.8483        Frozen energy decomposition
    E_pauli  (PAULI) (kJ/mol) =   99.4947
    E_disp   (DISP)  (kJ/mol) =  -12.5461
    --------------------
    Terms summing to E_pauli:
    --------------------
      E_kep_pauli       (kJ/mol) =  124.7322
      E_disp_free_pauli (kJ/mol) =  -25.2376

  Classical Frozen Decomposition:
  --------------------                           "Classical" frozen
    E_cls_elec  (CLS ELEC)  (kJ/mol) = -81.5198   decomposition
    E_cls_pauli (CLS PAULI) (kJ/mol) =  48.6200
   [E_mod_pauli (MOD PAULI) (kJ/mol) =  61.1661 (CLS PAULI - DISP from orthogonal decomposition)
```
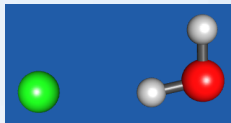
For this system:

► FRZ is the most favorable term, due to the strongly attractive PERM ELEC.

► POL and CT make similar contributions (roughly 25% of the total interaction).
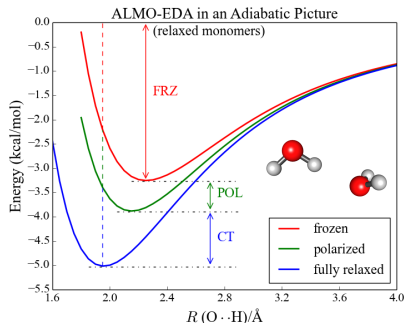
Q·CHEM

Limitations of a "vertical" EDA method:

1. Usually performed at equilibrium: too unfavorable FRZ and overly emphasized roles of POL and CT.

2. Partitioning of a "single-point" interaction energy: the effects on structural and vibrational properties are not directly characterized.

The adiabatic ALMO-EDA:

▶ It searches for the stationary point on each PES first, then the energy components are computed as the differences between them.

▶ Vibrational frequencies (and other properties) can be evaluated at the stationary point on each PES.

Illustration of frozen, polarized and fully relaxed PESs:

Analytical gradients for the frozen and polarized PESs are available in Q-CHEM 5.0.

Perform geometry optimization on the frozen PES:

Compute vibrational frequency at the optimal geometry on the polarized PES:

Note: `GEN_SCFMAN = TRUE` is required for these jobs.

1. ALMO-EDA for water-Cl$^-$ at the equilibrium geometry:
   - Use the old ALMO scheme for polarization
   - Functionals: ωB97M-V, B97M-V
   - Basis set: def2-SVPD (CP-correction needed)
   - Use revPBE as the dispersion-free functional for the latter functional (Hint: set `DISP_FREE_X` = revPBE, `DISP_FREE_C` = PBE).
   - Report ELEC, PAULI, DISP, POL, CT and TOTAL

2. Optimize the geometry of this complex on the polarized and frozen PESs. Report the resulting O··Cl$^-$ distance and $\angle$O-H$_1$-Cl.
   - Model chemistry: B3LYP-D3(BJ)/def2-SVPD
   - Hint: use the optimal geometry on the polarized PES as the starting point of the optimization on the frozen PES.

Note: larger basis sets and finer grids should be used for real calculations!

Question 1:

ALMO-EDA results for the water-Cl^- complex at equilibrium geometry (kJ/mol):

	ωB97M-V	B97M-V
ELEC	-121.32	-117.69
PAULI	101.43	95.23
DISP	-12.42	-7.86
POL	-15.19	-15.17
CT	-17.21	-17.39
TOTAL	-64.72	-62.89

Question 2:

O··Cl^- distance (Å) and $\angle$O-H_1-Cl (°) on the frozen, polarized and fully relaxed PESs:

	$d_{O··Cl}$	$\angle$O-H_1-Cl
Frozen	3.40	120.45
Polarized	3.33	149.54
Fully relaxed	3.12	166.26