Supporting Information: A simple fragment-based method for van der Waals corrections over density functional theory

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1 Polarizability

1.1 α_{xx}

To calculate the dipole polarizability we should consider all the possible transition with one quanta excitation from ground state. Therefore the possible transitions are $(0_x 0_y 0_z \rightarrow n_x n_y n_z)$:

$$000 \rightarrow 100, 000 \rightarrow 010, 000 \rightarrow 001$$

The general expression for calculating the polarizability is:

$$\alpha_{\alpha\beta} = \sum_{n_x n_y n_z}{}^{'} \frac{\langle 000| \hat{\mu_\alpha} |n_x n_y n_z\rangle \langle n_x n_y n_z| \hat{\mu_\beta} |000\rangle}{E_n - E_0} + \frac{\langle n_x n_y n_z| \hat{\mu_\alpha} |000\rangle \langle 000| \hat{\mu_\beta} |n_x n_y n_z\rangle}{E_n - E_0} \quad (1)$$

Similarly the expression for α_{xx} is:

$$\alpha_{xx} = \sum_{n_x n_y n_z}{}^{'} \frac{\langle 000| \hat{\mu_x} |n_x n_y n_z\rangle \langle n_x n_y n_z| \hat{\mu_x} |000\rangle}{E_n - E_0} + \frac{\langle n_x n_y n_z| \hat{\mu_x} |000\rangle \langle 000| \hat{\mu_x} |n_x n_y n_z\rangle}{E_n - E_0} \quad (2)$$

Here μ in x-direction is:

$$\hat{\mu_x} = qx$$

The wavefunction for simple harmonic oscillator is:

$$\psi = \frac{1}{\sqrt{2^n n!}} \left[\frac{mw}{\pi\hbar}\right]^{\frac{1}{4}} e^{-\frac{\alpha^2 r^2}{2}} H_n(\alpha r)$$

$$\alpha_x = \left[\frac{m\omega_x}{\hbar}\right]^{\frac{1}{2}}, \qquad \alpha_y = \left[\frac{m\omega_y}{\hbar}\right]^{\frac{1}{2}}, \qquad \alpha_z = \left[\frac{m\omega_z}{\hbar}\right]^{\frac{1}{2}}$$

$$\alpha_x . x = \frac{H_1(\alpha_x x)}{2}, \qquad \alpha_y . y = \frac{H_1(\alpha_y y)}{2}$$

For solving the first term in α_{xx} expression

$$\langle 000| \hat{\mu_x} |n_x n_y n_z\rangle = q\langle 0_y n_y\rangle\langle 0_z n_z\rangle\langle 0| x |n_x\rangle$$

This expression can be written as:

$$= q\langle 0_y n_y\rangle\langle 0_z n_z\rangle\frac{\langle 0_x| H_1(\alpha_x x) |n_x\rangle}{2\alpha_x}$$

Out of three possible transition only ($n_x n_y n_z = 100$) is non-zero using orthogonality

$$q\langle 0_y n_y\rangle\langle 0_z n_z\rangle\langle 0| x |n_x\rangle = q\left[\int_{-\infty}^{\infty} dy\frac{\alpha_y}{\sqrt{\pi}}e^{-\alpha_y{}^2y^2}\int_{-\infty}^{\infty} dz\frac{\alpha_z}{\sqrt{\pi}}e^{-\alpha_z{}^2z^2}\int_{-\infty}^{\infty} dx\frac{1}{2\alpha_x}\frac{\alpha_x}{\sqrt{\pi}}e^{-\alpha_x{}^2x^2}H_1(\alpha_x x)H_{nx}(\alpha_x x)\right]$$

$$q\left[\frac{\alpha_y}{\sqrt{\pi}}\int_{-\infty}^{\infty} dye^{-\alpha_y{}^2y^2}\right]\left[\frac{\alpha_z}{\sqrt{\pi}}\int_{-\infty}^{\infty} dze^{-\alpha_z{}^2z^2}\right]\left[\frac{1}{2\alpha_x}\frac{\alpha_x}{\sqrt{\pi}}\frac{1}{\sqrt{2}}\int_{-\infty}^{\infty} dxe^{-\alpha_x{}^2x^2}H_1(\alpha_x x)H_1(\alpha_x x)\right]$$

$$\int_{-\infty}^{\infty} dye^{-\alpha_y{}^2y^2} = \frac{\sqrt{\pi}}{\alpha_y}$$

similarly for z component

$$\int_{-\infty}^{\infty} dze^{-\alpha_z{}^2z^2} = \frac{\sqrt{\pi}}{\alpha_z}$$

for x part

$$\int_{-\infty}^{\infty} dxe^{-\alpha_x{}^2x^2}H_{nx}(\alpha_x.x)H_1(\alpha_x x) = \frac{\sqrt{\pi}}{\alpha_x}2^{n_x}n_x!\delta_{n_x 1}$$

Therefore we get

$$q\left(\frac{\alpha_y}{\sqrt{\pi}}\frac{\sqrt{\pi}}{\alpha_y}\right)\left(\frac{\alpha_z}{\sqrt{\pi}}\frac{\sqrt{\pi}}{\alpha_z}\right)\left(\frac{1}{2\alpha_x}\frac{\alpha_x}{\sqrt{\pi}}\frac{1}{\sqrt{2}}\frac{\sqrt{\pi}}{\alpha_x}2\right)$$

Final expression for is :

$$\langle 000| \hat{\mu_x} |n_x n_y n_z\rangle = \frac{q}{\sqrt{2}\alpha_x} \tag{3}$$

$$\langle n_x n_y n_z| \hat{\mu_x} |000\rangle = \frac{q}{\sqrt{2}\alpha_x} \tag{4}$$

Therfore the equation 1 becomes

$$\alpha_{xx} = \frac{q^2}{2{\alpha_x}^2\hbar\omega} + \frac{q^2}{2{\alpha_x}^2\hbar\omega}$$

$$= \frac{q^2}{{\alpha_x}^2\hbar\omega}$$

subsituting the value of α_x, we get

$$\alpha_{xx} = \frac{q^2}{mw_x^2}$$

similarly

$$\alpha_{yy} = \frac{q^2}{mw_y^2}$$

and,

$$\alpha_{zz} = \frac{q^2}{mw_z^2}$$

For $\alpha_{xy}, \alpha_{xz}, \alpha_{zy}$:

$$\alpha_{xy} = 0, \qquad \alpha_{xz} = 0, \qquad \alpha_{yz} = 0$$

1.2 Dispersion in the Quantum drude oscillator

$$U_{Disp} = -\sum_{m_{xA}m_{yA}m_{zA}\neq 0 n_{xB}n_{yB}n_{zB}\neq 0} \frac{\langle 00| H' |mn\rangle \langle mn| H' |00\rangle}{W_{m0}^A + W_{n0}^B} \tag{5}$$

In general the dispersion energy $U_{disp}^{\alpha\beta}$ is given by considering,

$$m_{xA}m_{yA}m_{zA} = M, \qquad n_{xB}n_{yB}n_{zB} = N$$

$$U_{disp}^{\alpha\beta} = -\sum_{M\neq 0}\sum_{N\neq 0} \frac{\langle 000, 000|\, \hat{\mu}_{\alpha}^{A} T_{\alpha\beta} \hat{\mu}_{\beta}^{B}\, |M, N\rangle \langle m_{xA}m_{yA}m_{zA}, n_{xB}n_{yB}n_{zB}|\, \hat{\mu}_{\alpha}^{A} T_{\alpha\beta} \hat{\mu}_{\beta}^{B}\, |000, 000\rangle}{W_{m0}^{A} + W_{n0}^{B}} \tag{6}$$

$$U_{disp}^{xy} = -\sum_{m_{xA}m_{yA}m_{zA}\neq 0}\ \sum_{n_{xB}n_{yB}n_{zB}\neq 0} \frac{\langle 000, 000|\, \hat{\mu}_{x}^{A} T_{xy} \hat{\mu}_{y}^{B}\, |m_{xA}m_{yA}m_{zA}, n_{xB}n_{yB}n_{zB}\rangle \langle m_{xA}m_{yA}m_{zA}, n_{xB}n_{yB}n_{zB}}{W_{m0}^{A} + W_{n0}^{B}}$$

$$= -\left(\frac{W_{m0}^{A} W_{n0}^{B} T_{xy} T_{xy}}{E_A + E_B}\right) \sum_{m_{xA}m_{yA}m_{zA}\neq 0} \frac{|\langle 000|\, \hat{\mu}_{x}^{A}\, |m_{xA}m_{yA}m_{zA}\rangle|^2}{W_{m0}^{A}} \sum_{n_{xB}n_{yB}n_{zB}\neq 0} \frac{|\langle 000|\, \hat{\mu}_{y}^{B}\, |n_{xB}n_{yB}n_{zB}\rangle|^2}{W_{n0}^{B}}$$

$$\hat{\mu}_{x}^{A} = q_A x_A, \hat{\mu}_{y}^{B} = q_B y_B$$

$$|T_{xy}|^2 = \frac{(3R_x R_y - R^2\delta_{ij})^2}{(4\pi\epsilon_0)^2 R^{10}}$$

Therefore we get

$$|T_{xy}|^2 = \frac{(3R_x R_y)^2}{(4\pi\epsilon_0)^2 R^{10}}$$

$$E_A = \hbar\omega_{xA}, E_B = \hbar\omega_{yB}$$

Part 1st for U_{disp} The possible transition for molecule A is ($m_{xA}m_{yA}m_{zA} = 100, 010, 001$), similarly for molecule B also, $(n_{xB}n_{yB}n_{zB} = 100, 010, 001)$

$$\langle 000|\,\hat{\mu_x^A}\,|m_{xA}m_{yA}m_{zA}\rangle = q_A\langle 0|\,x\,|m_x\rangle_A\langle\, 0_y n_y\rangle_A\langle\, 0_z n_z\rangle_A$$

$$= q_A\frac{\langle 0_{xA}|\,H_1(\alpha_{x_A}x_A)\,|m_{xA}\rangle}{2\alpha_{x_A}}\langle\, 0_y n_y\rangle_A\langle\, 0_z n_z\rangle_A$$

$$\langle 000|\,\hat{\mu_y^B}\,|n_{xB}n_{yB}n_{zB}\rangle = q_B\langle\, 0_x n_x\rangle_B\langle 0|\,y\,|n_y\rangle_B\langle\, 0_z n_z\rangle_B$$

Solving the integration the way we did for polarization

$$q_A\left[\frac{\alpha_y}{\sqrt{\pi}}\int_{-\infty}^{\infty} dy e^{-\alpha_y{}^2y^2}\right]\left[\frac{\alpha_z}{\sqrt{\pi}}\int_{-\infty}^{\infty} dz e^{-\alpha_z{}^2z^2}\right]\left[\frac{1}{2\alpha_x}\frac{\alpha_x}{\sqrt{\pi}}\frac{1}{\sqrt{2}}\int_{-\infty}^{\infty} dx e^{-\alpha_x{}^2x^2}H_1(\alpha_x x)H_{nx}(\alpha_x x)\right]$$

$$\int_{-\infty}^{\infty} dy e^{-\alpha_y{}^2y^2} = \frac{\sqrt{\pi}}{\alpha_y}$$

similarly for z component

$$\int_{-\infty}^{\infty} dz e^{-\alpha_z{}^2z^2} = \frac{\sqrt{\pi}}{\alpha_z}$$

for x part

$$\int_{-\infty}^{\infty} dx e^{-\alpha_x{}^2x^2}H_{nx}(\alpha_x.x)H_1(\alpha_x x) = \frac{\sqrt{\pi}}{\alpha_x}2^{n_x}n_x!\delta_{n_x 1}$$

For this we get

$$\langle 000|\,\hat{\mu_x^A}\,|m_{xA}m_{yA}m_{zA}\rangle = \frac{q_A}{\sqrt{2}\alpha_{xA}}$$

Similarly for y

$$\langle 000|\,\hat{\mu_y^B}\,|n_{xB}n_{yB}n_{zB}\rangle = \frac{q_B}{\sqrt{2}\alpha_{xB}}$$

Therfore we get

$$-|T_{xy}|^2 \frac{q_A q_B}{2\alpha_{xA}\alpha_{xB}}$$

So,

$$U_{disp} = -|T_{xy}|^2 \frac{q_A^2 q_B^2}{4\alpha_{xA}^2 E_A \alpha_{xB}^2 E_B} \left(\frac{E_A E_B}{E_A + E_B}\right)$$

$$U_{disp} = -|T_{xy}|^2 \left(\frac{q_A^2}{\hbar\omega_{xA}\alpha_{xA}^2}\right) \left(\frac{q_B^2}{\hbar\omega_{yA}\alpha_{yB}^2}\right) \left(\frac{\hbar\omega_{xA}\omega_{yB}}{4(\omega_{xA} + \omega_{yB})}\right)$$

or we ca write

$$U_{disp} = -|T_{xy}|^2 (\alpha_{xx}^A \alpha_{yy}^B) \left(\frac{\hbar\omega_{xA}\omega_{yB}}{4(\omega_{xA} + \omega_{yB})}\right)$$

$$|T_{xy}|^2 = \frac{(3xy)^2}{(4\pi\epsilon_0)^2 R^{10}}$$

U_{disp} for T_{xx}

$$U_{disp}^{xx} = -|T_{xx}|^2 (\alpha_{xx}^A \alpha_{xx}^B) \left(\frac{\hbar\omega_{xA}\omega_{xB}}{4(\omega_{xA} + \omega_{xB})}\right)$$

$$|T_{xx}|^2 = \frac{(3x^2 - R^2)^2}{(4\pi\epsilon_0)^2 R^{10}}$$

U_{disp} for T_{yy}

$$U_{disp}^{yy} = -|T_{yy}|^2 (\alpha_{yy}^A \alpha_{yy}^B) \left(\frac{\hbar\omega_{yA}\omega_{yB}}{4(\omega_{yA} + \omega_{yB})}\right)$$

$$|T_{yy}|^2 = \frac{(3y^2 - R^2)^2}{(4\pi\epsilon_0)^2 R^{10}}$$

U_{disp} for T_{zz}

$$U_{disp}^{zz} = -|T_{zz}|^2 (\alpha_{zz}^A \alpha_{zz}^B) \left(\frac{\hbar\omega_{zA}\omega_{zB}}{4(\omega_{zA} + \omega_{zB})}\right)$$

$$|T_{zz}|^2 = \frac{(3z^2 - R^2)^2}{(4\pi\epsilon_0)^2 R^{10}}$$

U_{disp} for T_{xz}

$$U_{disp}^{xz} = -|T_{xz}|^2(\alpha_{xx}^A \alpha_{zz}^B)\left(\frac{\hbar\omega_{xA}\omega_{zB}}{4(\omega_{xA} + \omega_{zB})}\right)$$

$$|T_{xz}|^2 = \frac{(3xz)^2}{(4\pi\epsilon_0)^2 R^{10}}$$

U_{disp} for T_{yz}

$$U_{disp}^{yz} = -|T_{yz}|^2(\alpha_{yy}^A \alpha_{zz}^B)\left(\frac{\hbar\omega_{yA}\omega_{zB}}{4(\omega_{yA} + \omega_{zB})}\right)$$

$$|T_{yz}|^2 = \frac{(3yz)^2}{(4\pi\epsilon_0)^2 R^{10}}$$

U_{disp} for T_{yx}

$$U_{disp}^{yx} = -|T_{yx}|^2(\alpha_{yy}^A \alpha_{xx}^B)\left(\frac{\hbar\omega_{yA}\omega_{xB}}{4(\omega_{yA} + \omega_{xB})}\right)$$

$$|T_{yx}|^2 = \frac{(3yx)^2}{(4\pi\epsilon_0)^2 R^{10}}$$

U_{disp} for T_{zx}

$$U_{disp}^{zx} = -|T_{zx}|^2(\alpha_{zz}^A \alpha_{xx}^B)\left(\frac{\hbar\omega_{zA}\omega_{xB}}{4(\omega_{zA} + \omega_{xB})}\right)$$

$$|T_{zx}|^2 = \frac{(3zx)^2}{(4\pi\epsilon_0)^2 R^{10}}$$

U_{disp} for T_{zy}

$$U^{zy}_{disp} = -|T_{zy}|^2(\alpha^A_{zz}\alpha^B_{yy})\left(\frac{\hbar\omega_{zA}\omega_{yB}}{4(\omega_{zA}+\omega_{yB})}\right)$$

$$|T_{zy}|^2 = \frac{(3zy)^2}{(4\pi\epsilon_0)^2R^{10}}$$

$$U_{disp} = -\sum_{ab}^{xyz}|T_{ab}|^2(\alpha^A_{aa}\alpha^B_{bb})\left(\frac{\hbar\omega_{aA}\omega_{bB}}{4(\omega_{aA}+\omega_{bB})}\right) \tag{7}$$

2 Monomer Fragmentation

The monomer fragmentation scheme for all the monomers (except Ethene, Water, Ethyne) are given below.

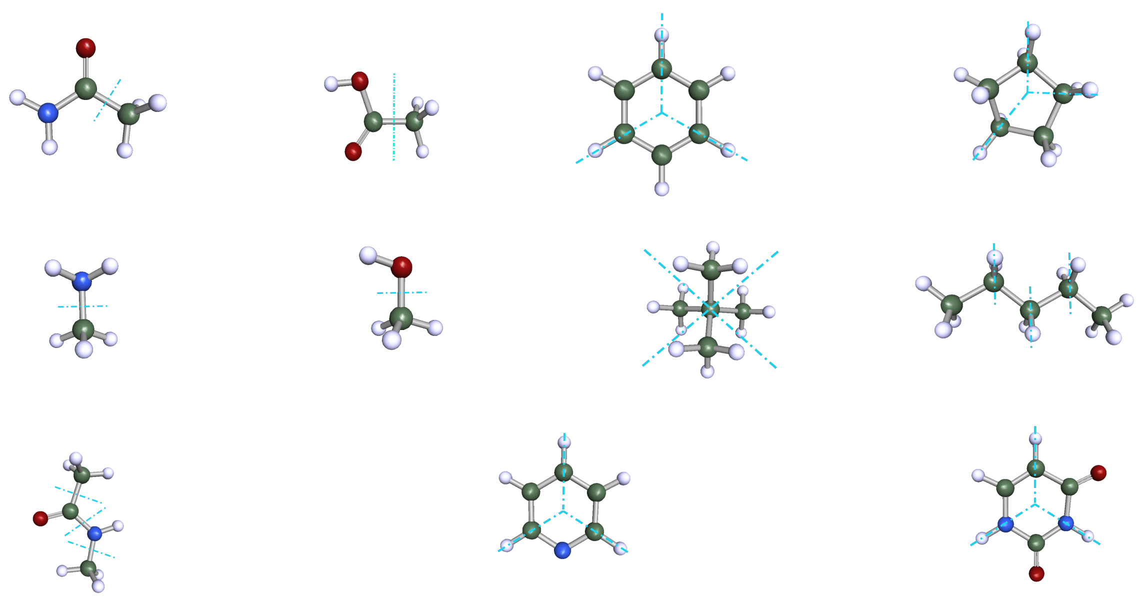
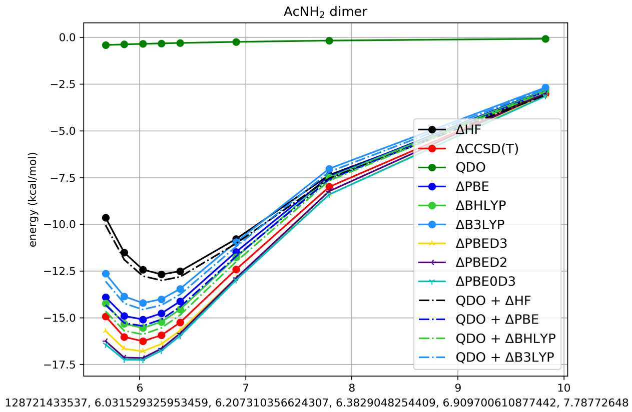


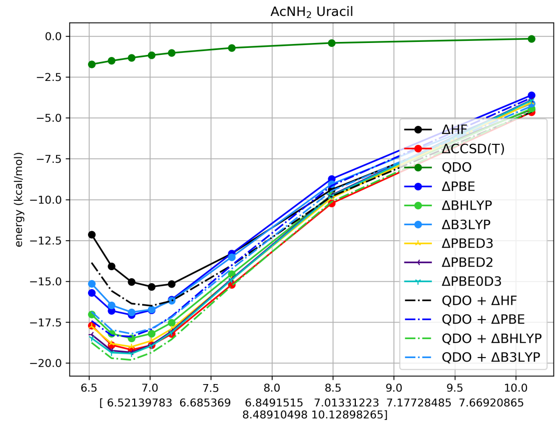
Figure S1: Fragmentation scheme for monomers. Color Code: Green: C, White: H, Red: O, Blue: N

3 Interaction energy curves for Complexes

3.1 Interaction energy curves for all complexes of S66x8 dataset

The Following Figures show the interaction energy curve for all the 66 complexes obtained with HF, CCSD(T) and DF methods.


AcNH$_2$ dimer
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
128721433537, 6.031529325953459, 6.207310356624307, 6.3829048254409, 6.909700610877442, 7.78772648


AcNH$_2$ Uracil
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
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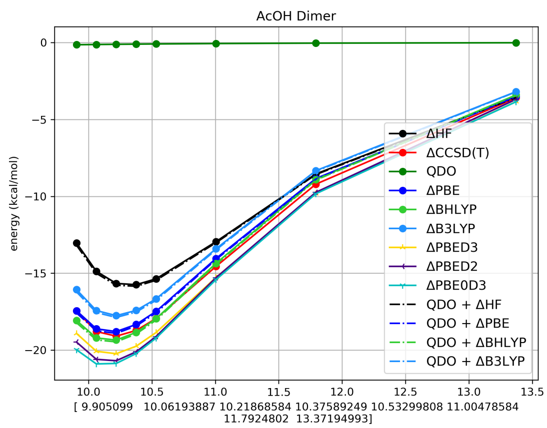
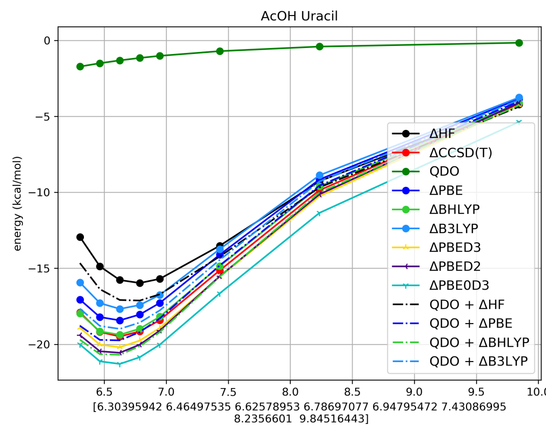
8.48910498 10.12898265]


AcOH Dimer
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[9.905099 10.06193887 10.21868584 10.37589249 10.53299808 11.00478584
11.7924802 13.37194993]


AcOH Uracil
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
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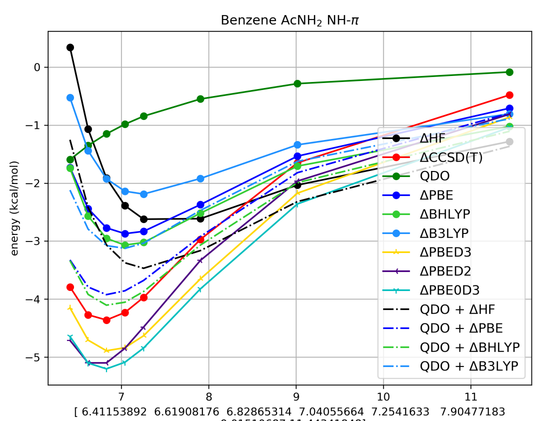
8.2356601 9.84516443]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energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
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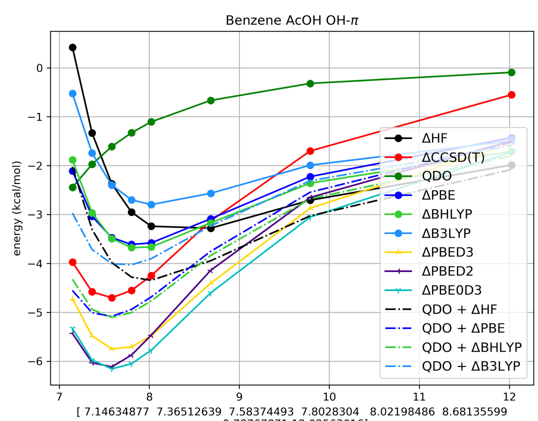
9.01510687 11.44341848]


Benzene AcOH OH-π
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
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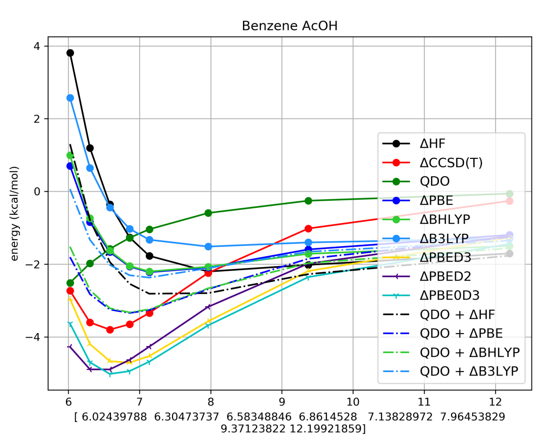
9.78767871 12.02563016]


Benzene AcOH
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
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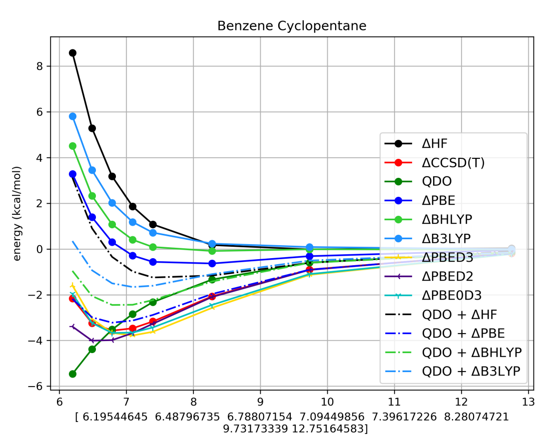
9.37123822 12.19921859]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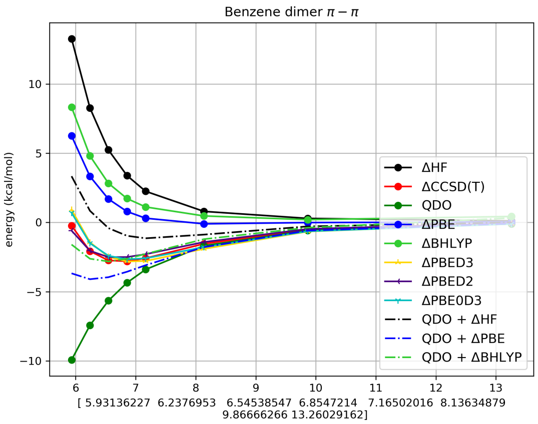
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[6.19544645 6.48796735 6.78807154 7.09449856 7.39617226 8.28074721
9.73173339 12.75164583]


Benzene dimer $\pi-\pi$
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
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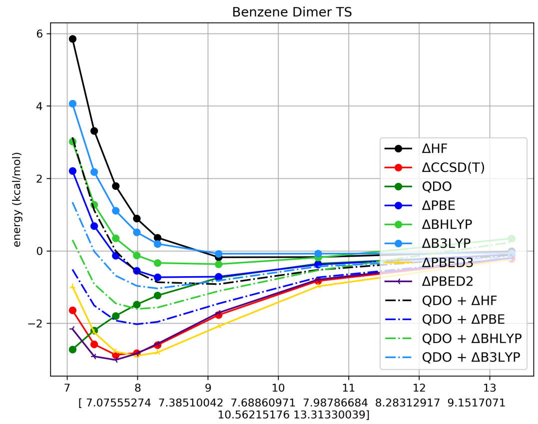
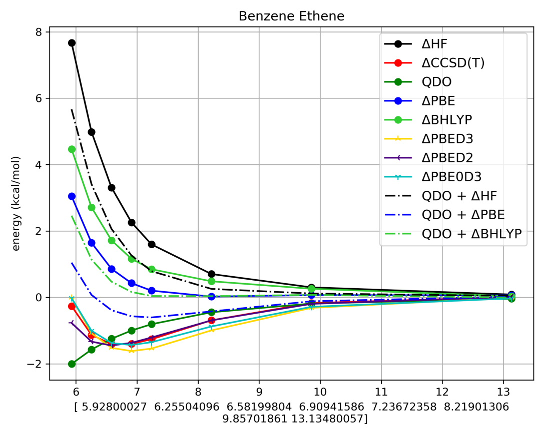
9.86666266 13.26029162]


Benzene Dimer TS
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[7.07555274 7.38510042 7.68860971 7.98786684 8.28312917 9.1517071
10.56215176 13.31330039]


Benzene Ethene
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
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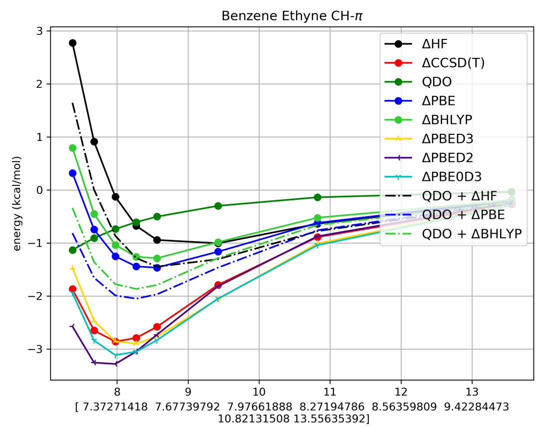
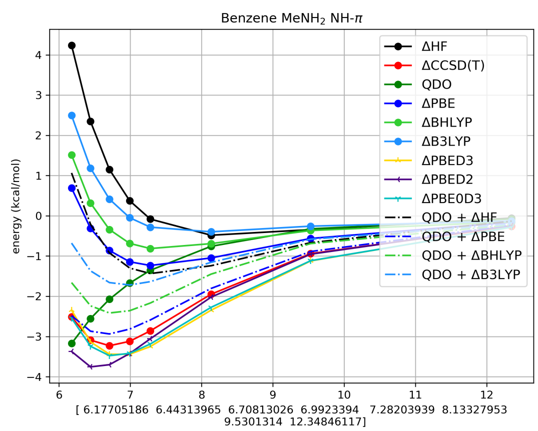
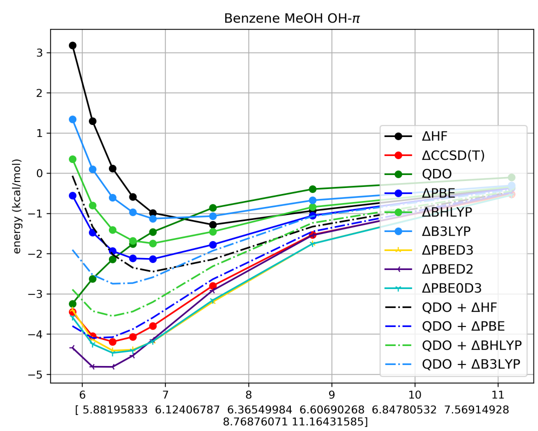
9.85701861 13.13480057]


Benzene Ethyne CH-π
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
[7.37271418 7.67739792 7.97661888 8.27194786 8.56359809 9.42284473
10.82131508 13.55635392]


Benzene MeNH$_2$ NH-π
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[6.17705186 6.44313965 6.70813026 6.9923394 7.28203939 8.13327953
9.5301314 12.34846117]


Benzene MeOH OH-π
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
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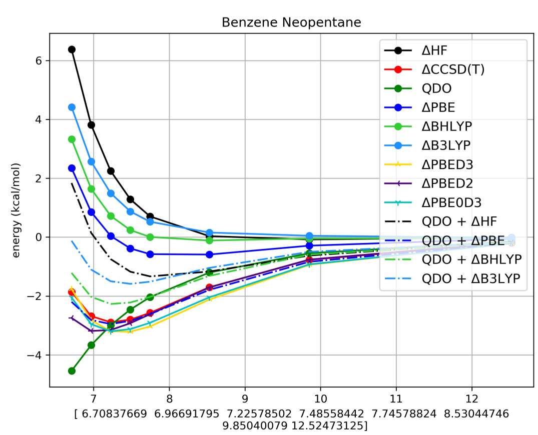
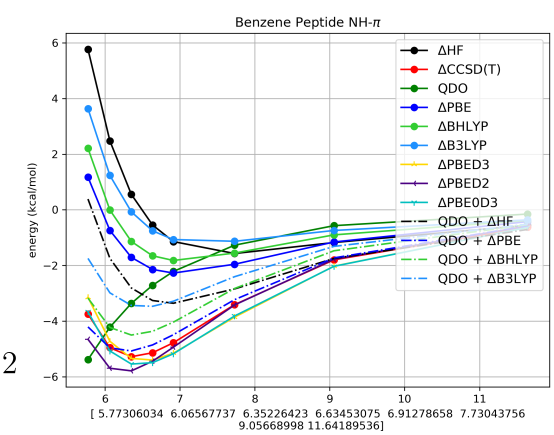
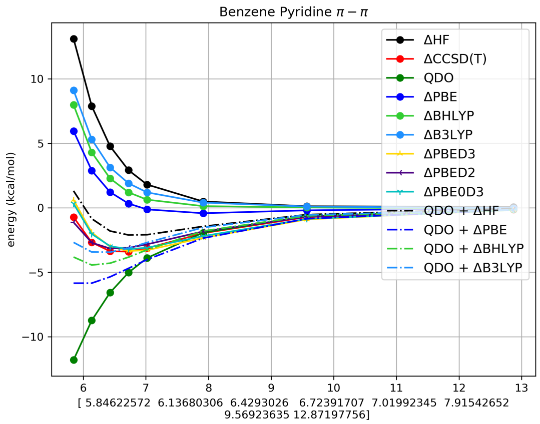
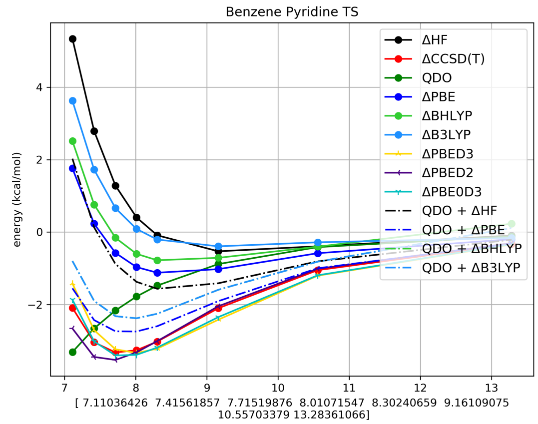
8.76876071 11.16431585]


Benzene Neopentane
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[6.70837669 6.96691795 7.22578502 7.48558442 7.74578824 8.53044746
9.85040079 12.52473125]


Benzene Peptide NH-π
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[5.77306034 6.06567737 6.35226423 6.63453075 6.91278658 7.73043756
9.05668998 11.64189536]


Benzene Pyridine $\pi-\pi$
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[5.84622572 6.13680306 6.4293026 6.72391707 7.01992345 7.91542652
9.56923635 12.87197756]


Benzene Pyridine TS
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
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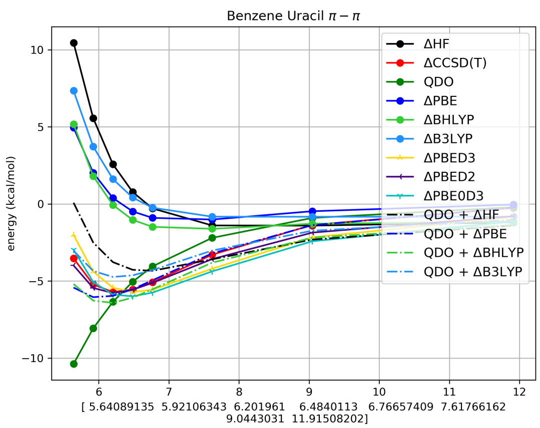
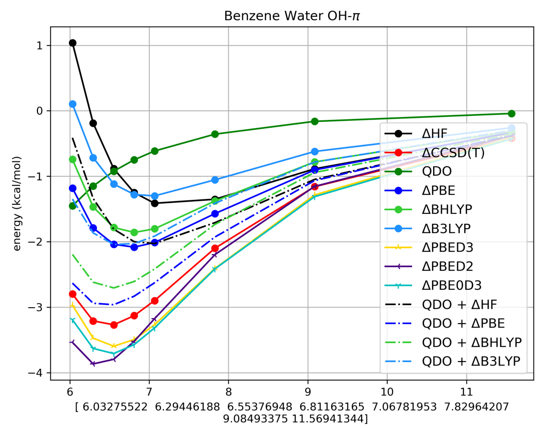
10.55703379 13.28361066]


Benzene Uracil $\pi-\pi$
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[5.64089135 5.92106343 6.201961 6.4840113 6.76657409 7.61766162
9.0443031 11.91508202]


Benzene Water OH-π
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
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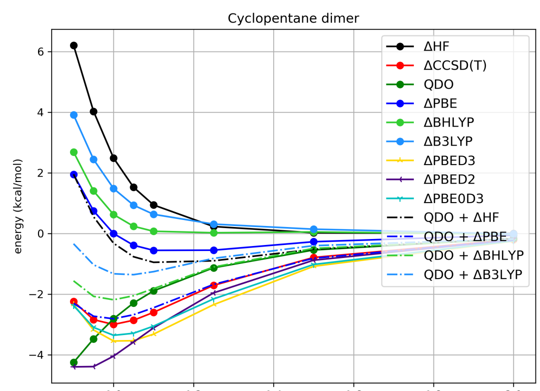
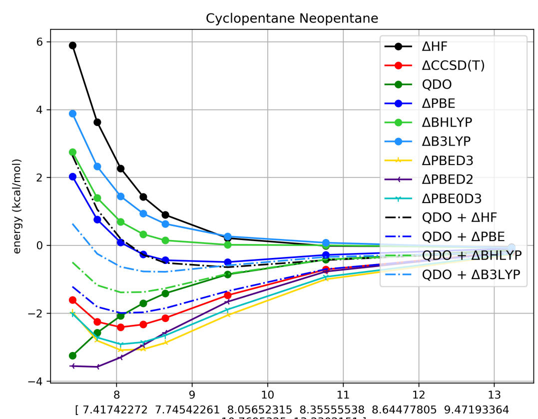
9.08493375 11.56941344]


Cyclopentane dimer
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP


Cyclopentane Neopentane
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
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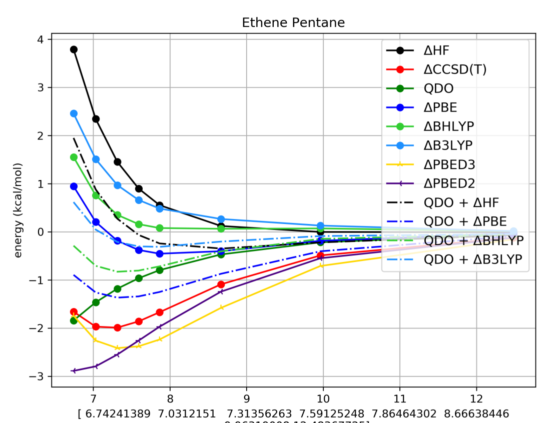
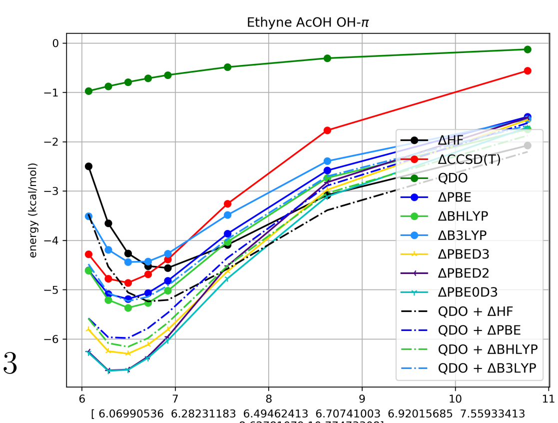
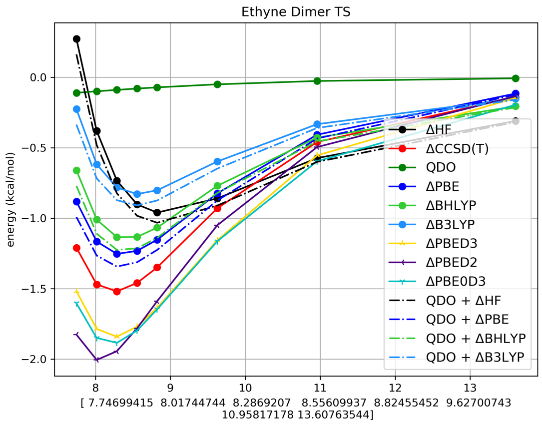
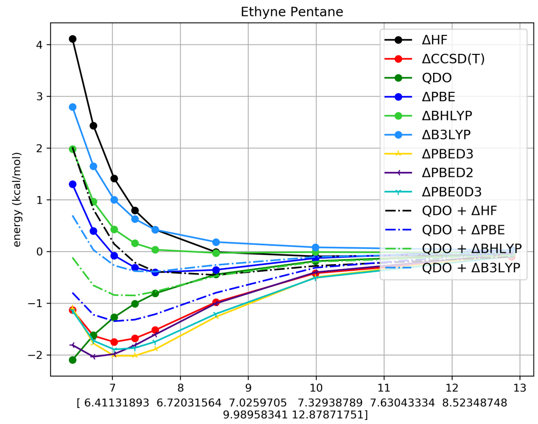
10.7695325 13.2302151]


Ethene Pentane
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[6.74241389 7.0312151 7.31356263 7.59125248 7.86464302 8.66638446
9.96319008 12.48367725]


Ethyne AcOH OH-π
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[6.06990536 6.28231183 6.49462413 6.70741003 6.92015685 7.55933413
8.62781079 10.77473308]


Ethyne Dimer TS
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[7.74699415 8.01744744 8.2869207 8.55609937 8.82455452 9.62700743
10.95817178 13.60763544]


Ethyne Pentane
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
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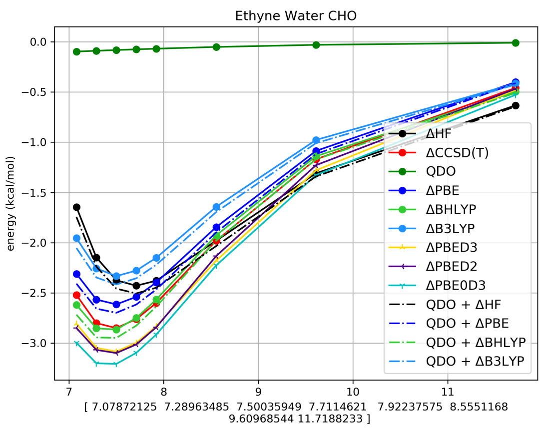
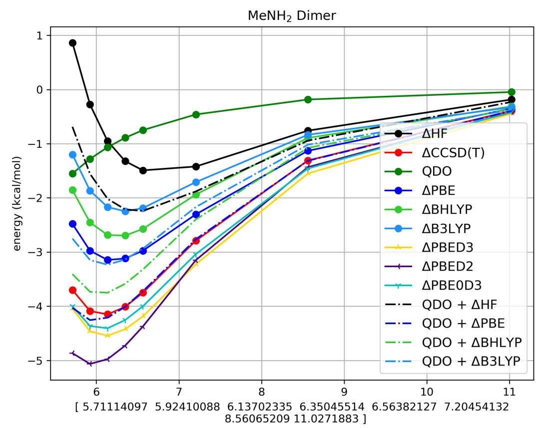
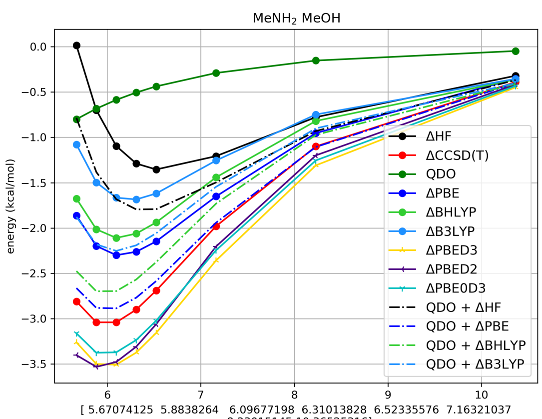
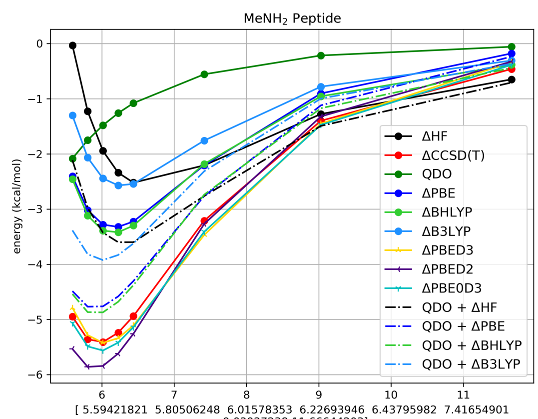
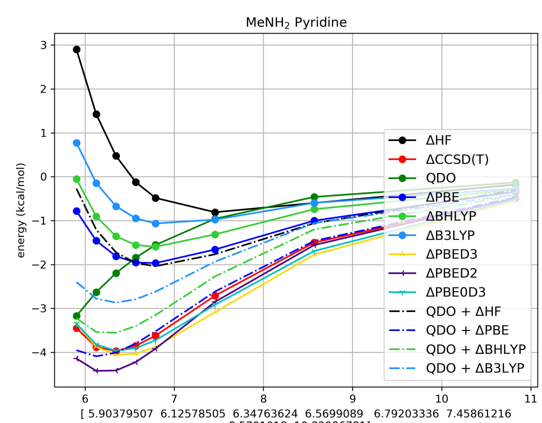
9.98958341 12.87871751]

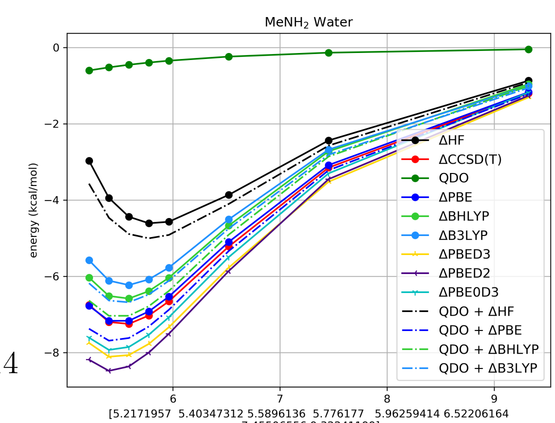

Ethyne Water CHO
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[7.07872125 7.28963485 7.50035949 7.7114621 7.92237575 8.5551168
9.60968544 11.7188233]

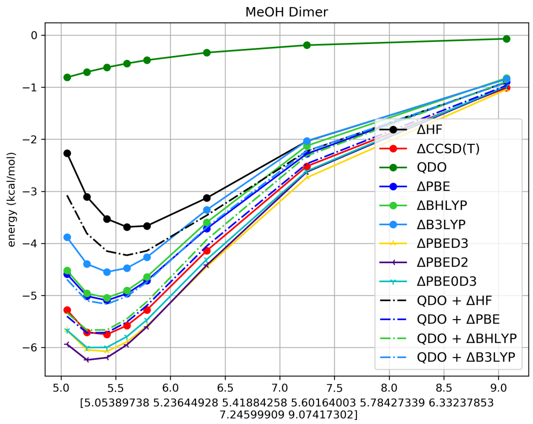

$MeNH_2$ Dimer
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[5.71114097 5.92410088 6.13702335 6.35045514 6.56382127 7.20454132
8.56065209 11.0271883]


$MeNH_2$ MeOH
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[5.67074125 5.8838264 6.09677198 6.31013828 6.52335576 7.16321037
8.23015145 10.36525316]

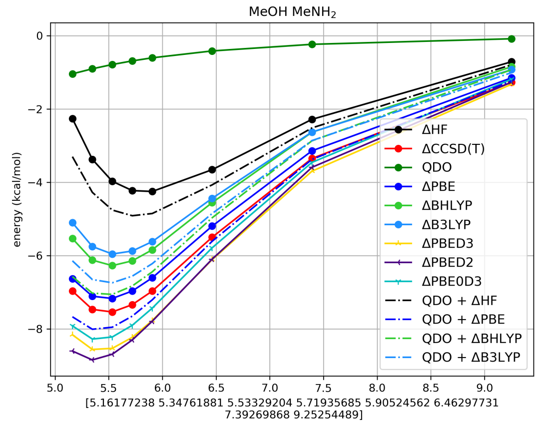

$MeNH_2$ Peptide
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[5.59421821 5.80506248 6.01578353 6.22693946 6.43795982 7.41654901
9.02927238 11.66644203]


$MeNH_2$ Pyridine
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[5.90379507 6.12578505 6.34763624 6.5699089 6.79203336 7.45861216
8.5701018 10.82986781]


$MeNH_2$ Water
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[5.2171957 5.40347312 5.5896136 5.776177 5.96259414 6.52206164
7.45506556 9.32241199]



MeOH Dimer
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[5.05389738 5.23644928 5.41884258 5.60164003 5.78427339 6.33237853
7.24599909 9.07417302]



MeOH MeNH$_2$
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
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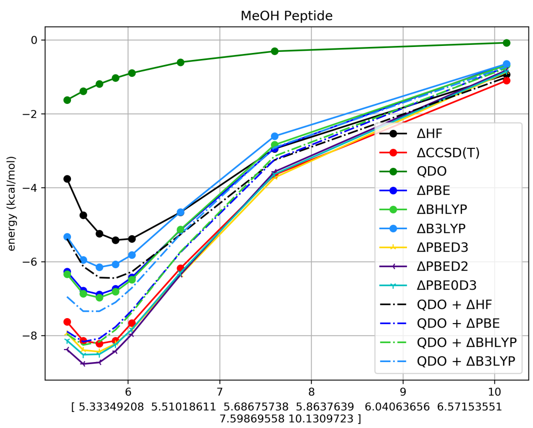
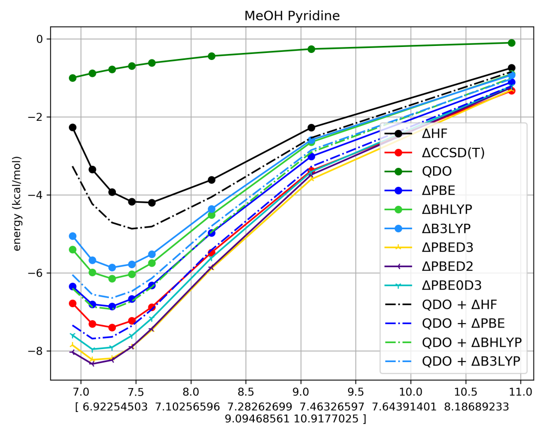
7.39269868 9.25254489]



MeOH Peptide
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[5.33349208 5.51018611 5.68675738 5.8637639 6.04063656 6.57153551
7.59869558 10.1309723]



MeOH Pyridine
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
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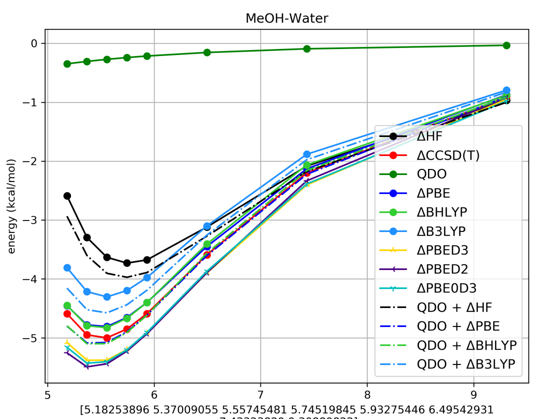
9.09468561 10.9177025]



MeOH-Water
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
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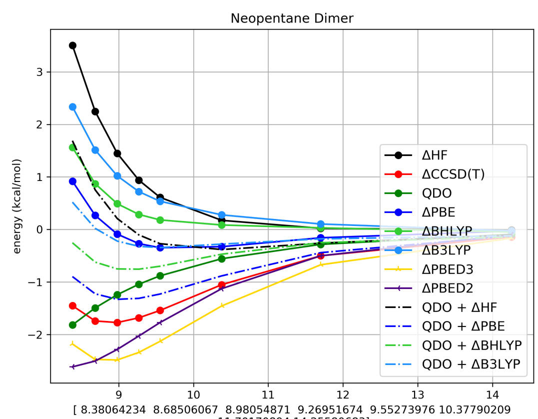
7.43323829 9.30889822]



Neopentane Dimer
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
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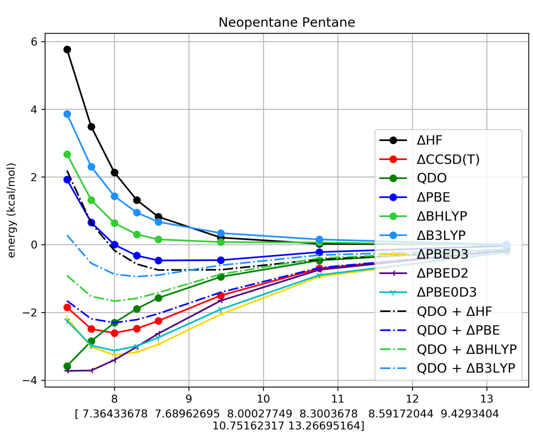
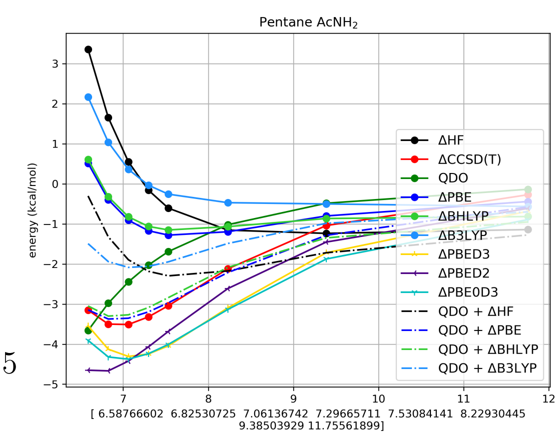
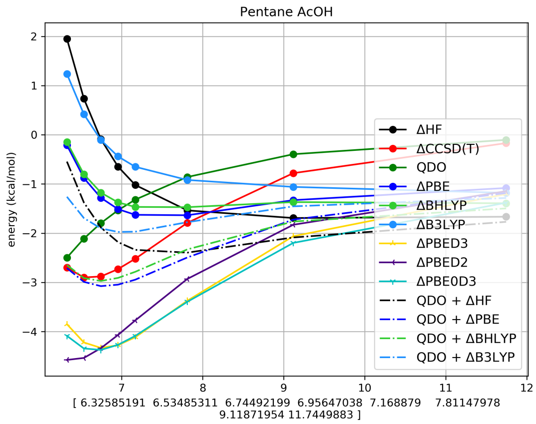
11.70170894 14.25580683]

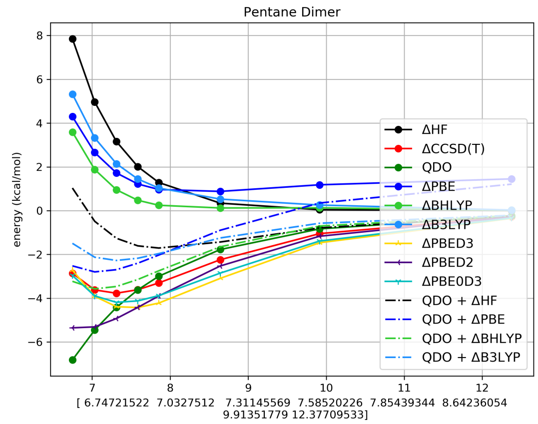


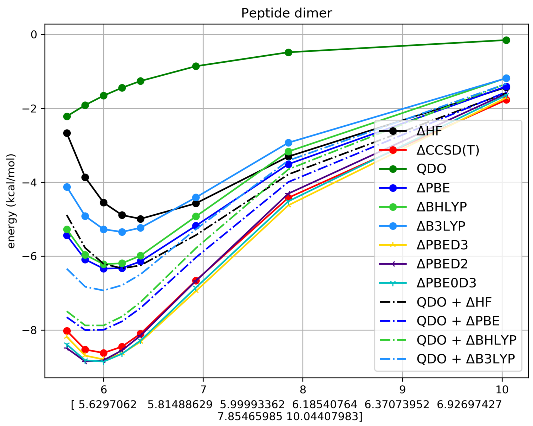
Neopentane Pentane
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[7.36433678 7.68962695 8.00027749 8.3003678 8.59172044 9.4293404
10.75162317 13.26695164]

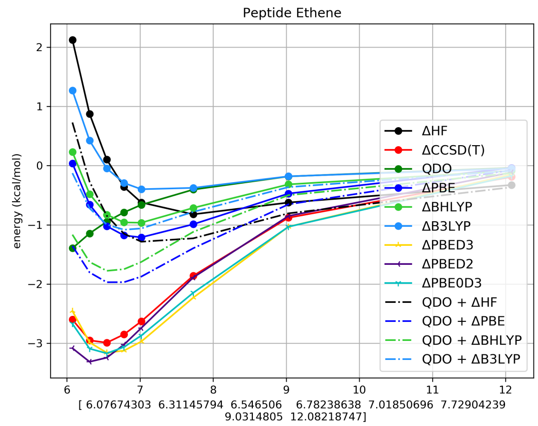


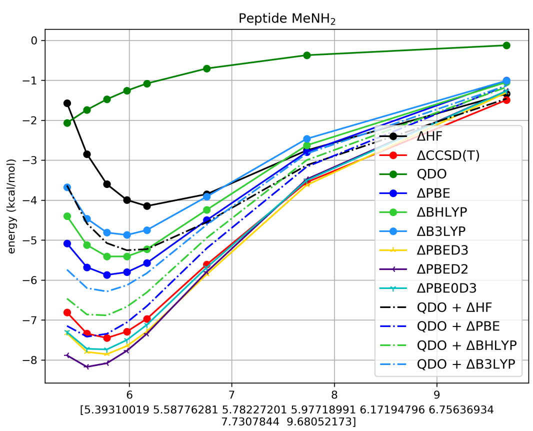
Pentane AcNH$_2$
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[6.58766602 6.82530725 7.06136742 7.29665711 7.53084141 8.22930445
9.38503929 11.75561899]

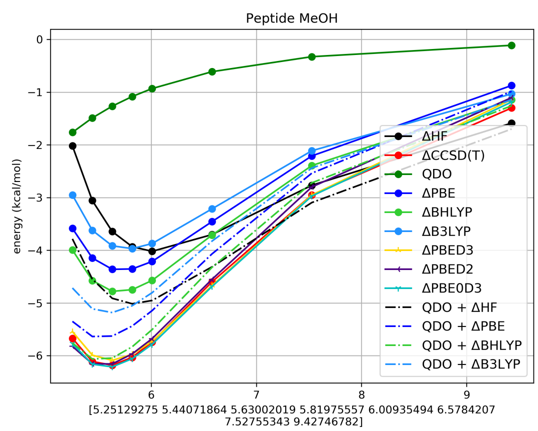

Pentane AcOH
energy (kcal/mol)
[6.32585191 6.53485311 6.74492199 6.95647038 7.168879 7.81147978
9.11871954 11.7449883]
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP

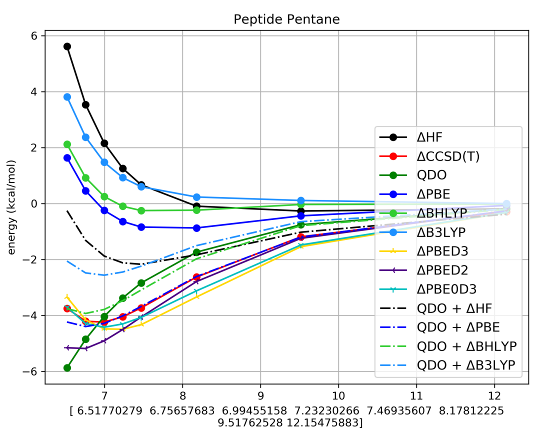

Pentane Dimer
energy (kcal/mol)
[6.74721522 7.0327512 7.31145569 7.58520226 7.85439344 8.64236054
9.91351779 12.37709533]
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP


Peptide dimer
energy (kcal/mol)
[5.6297062 5.81488629 5.99993362 6.18540764 6.37073952 6.92697427
7.85465985 10.04407983]
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP


Peptide Ethene
energy (kcal/mol)
[6.07674303 6.31145794 6.546506 6.78238638 7.01850696 7.72904239
9.0314805 12.08218747]
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP


Peptide $MeNH_2$
energy (kcal/mol)
[5.39310019 5.58776281 5.78227201 5.97718991 6.17194796 6.75636934
7.7307844 9.68052173]
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP


Peptide MeOH
energy (kcal/mol)
[5.25129275 5.44071864 5.63002019 5.81975557 6.00935494 6.5784207
7.52755343 9.42746782]
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP


Peptide Pentane
energy (kcal/mol)
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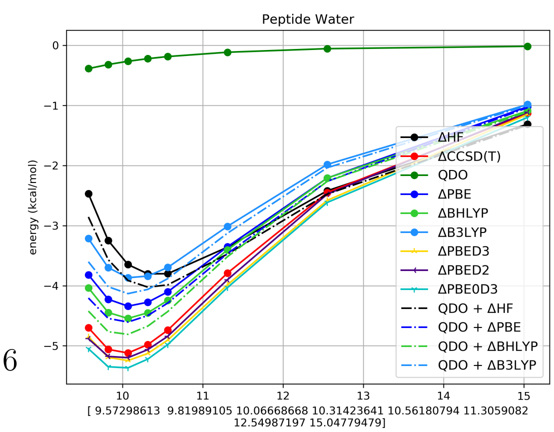
9.51762528 12.15475883]
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP


Peptide Water
energy (kcal/mol)
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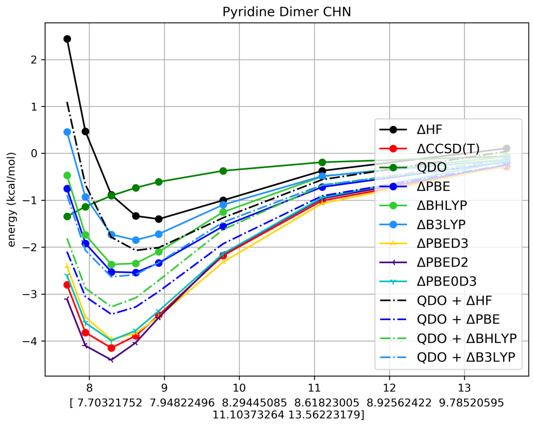
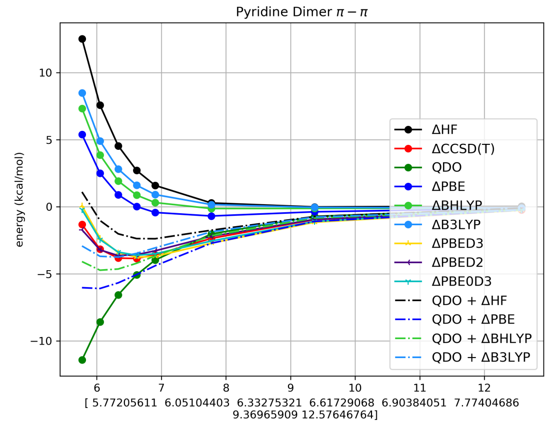
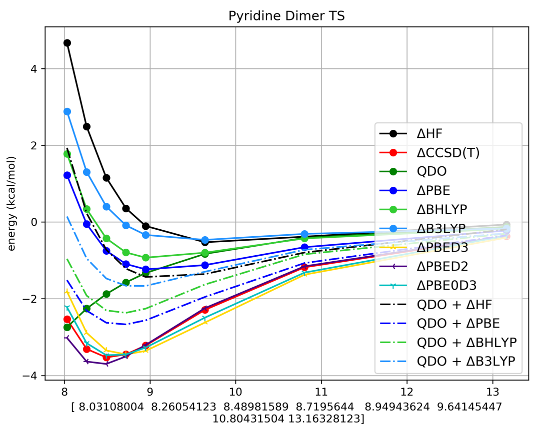
12.54987197 15.04779479]
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP


Pyridine Dimer CHN
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[7.70321752 7.94822496 8.29445085 8.61823005 8.92562422 9.78520595
11.10373264 13.56223179]


Pyridine Dimer $\pi-\pi$
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[5.77205611 6.05104403 6.33275321 6.61729068 6.90384051 7.77404686
9.36965909 12.57646764]


Pyridine Dimer TS
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
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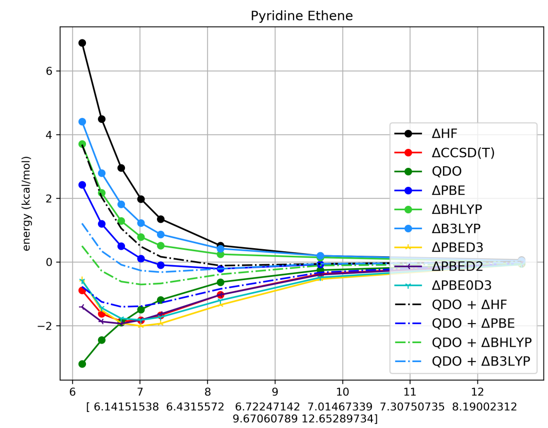
10.80431504 13.16328123]


Pyridine Ethene
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
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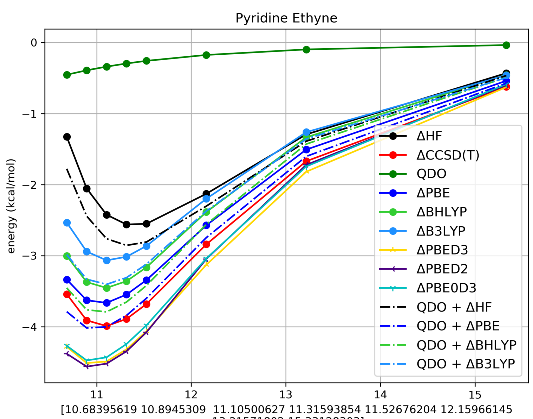
9.67060789 12.65289734]


Pyridine Ethyne
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
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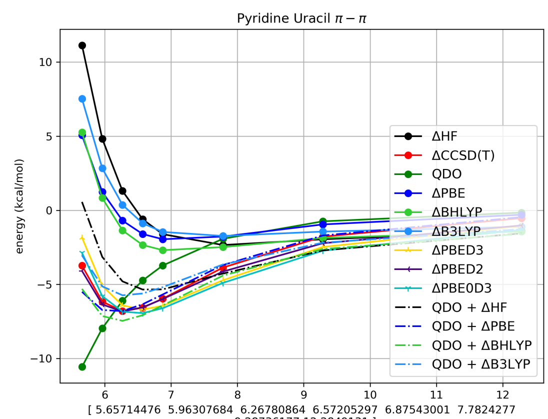
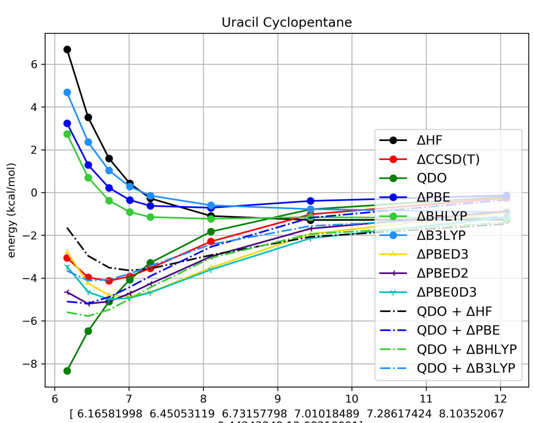
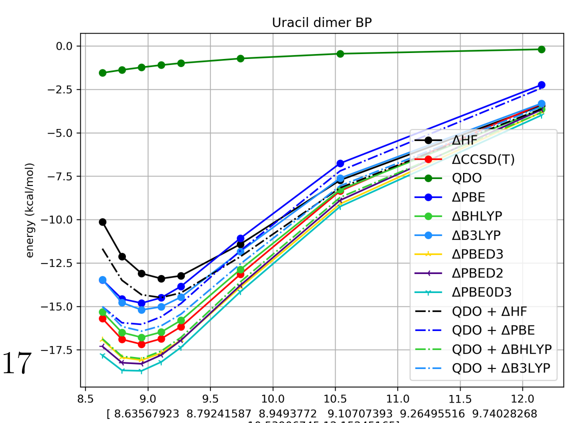
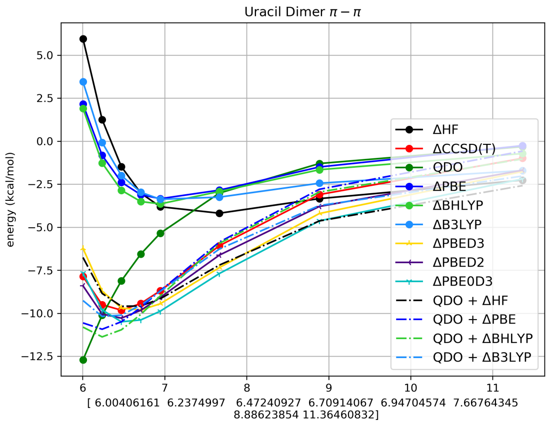
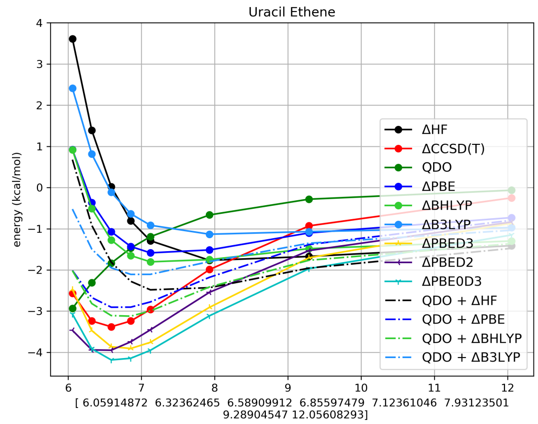
13.21571802 15.33128303]


Pyridine Uracil $\pi-\pi$
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[5.65714476 5.96307684 6.26780864 6.57205297 6.87543001 7.7824277
9.28736177 12.2849131]


Uracil Cyclopentane
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[6.16581998 6.45053119 6.73157798 7.01018489 7.28617424 8.10352067
9.44243249 12.08218091]


Uracil dimer BP
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[8.63567923 8.79241587 8.9493772 9.10707393 9.26495516 9.74028268
10.53906745 12.15245165]


Uracil Dimer $\pi-\pi$
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[6.00406161 6.2374997 6.47240927 6.70914067 6.94704574 7.66764345
8.88623854 11.36460832]


Uracil Ethene
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
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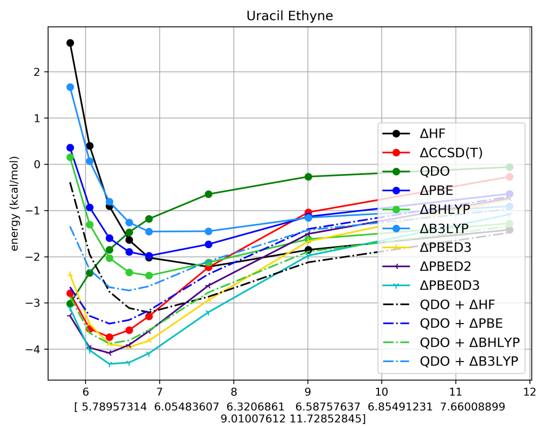
9.28904547 12.05608293]


Uracil Ethyne
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
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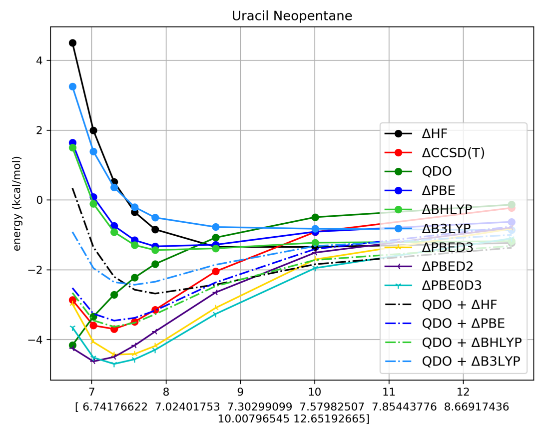
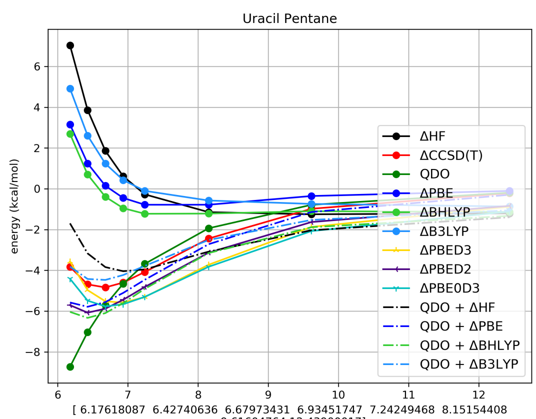
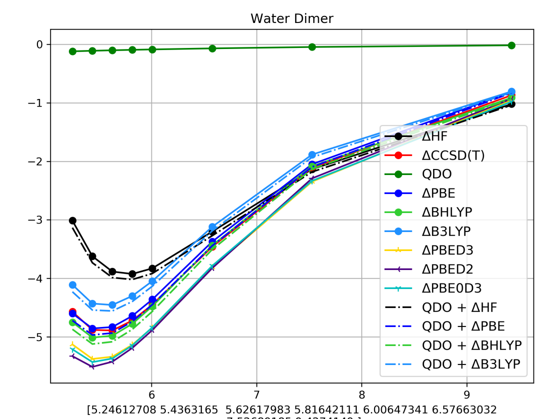
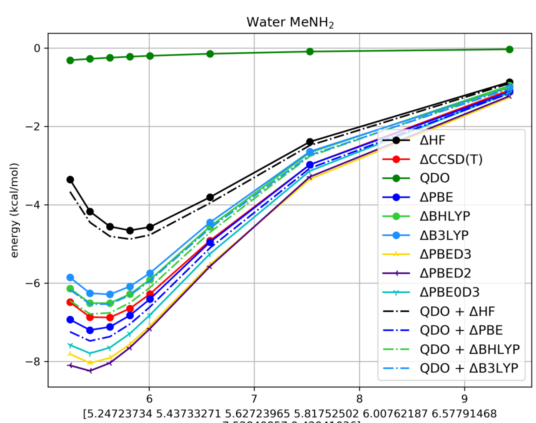
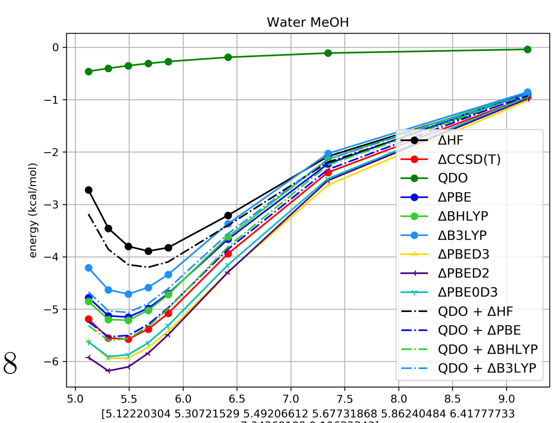
9.01007612 11.72852845]


Uracil Neopentane
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[6.74176622 7.02401753 7.30299099 7.57982507 7.85443776 8.66917436
10.00796545 12.65192665]


Uracil Pentane
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[6.17618087 6.42740636 6.67973431 6.93451747 7.24249468 8.15154408
9.61604764 12.43900017]


Water Dimer
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[5.24612708 5.4363165 5.62617983 5.81642111 6.00647341 6.57663032
7.52689185 9.4274149]


Water $MeNH_2$
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[5.24723734 5.43733271 5.62723965 5.81752502 6.00762187 6.57791468
7.52840857 9.42941036]


Water MeOH
energy (kcal/mol)
ΔHF
ΔCCSD(T)
QDO
ΔPBE
ΔBHLYP
ΔB3LYP
ΔPBED3
ΔPBED2
ΔPBE0D3
QDO + ΔHF
QDO + ΔPBE
QDO + ΔBHLYP
QDO + ΔB3LYP
[5.12220304 5.30721529 5.49206612 5.67731868 5.86240484 6.41777733
7.34369192 9.19622343]

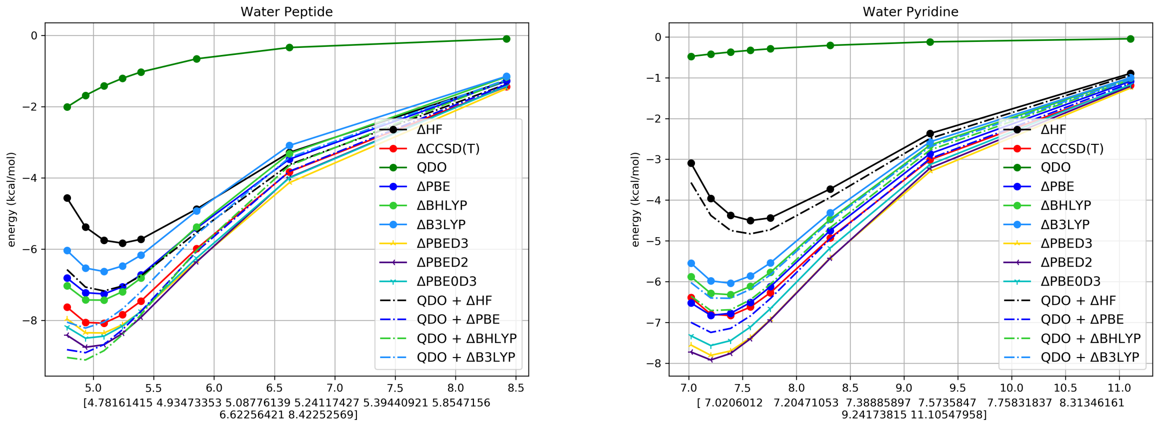


Figure S2: Interaction energy curves for 66 complexes with 66x8 data points.

3.2 Interaction energy curves for different fragmentation scheme of Uracil dimer base-pair and $AcNH_2$ dimer

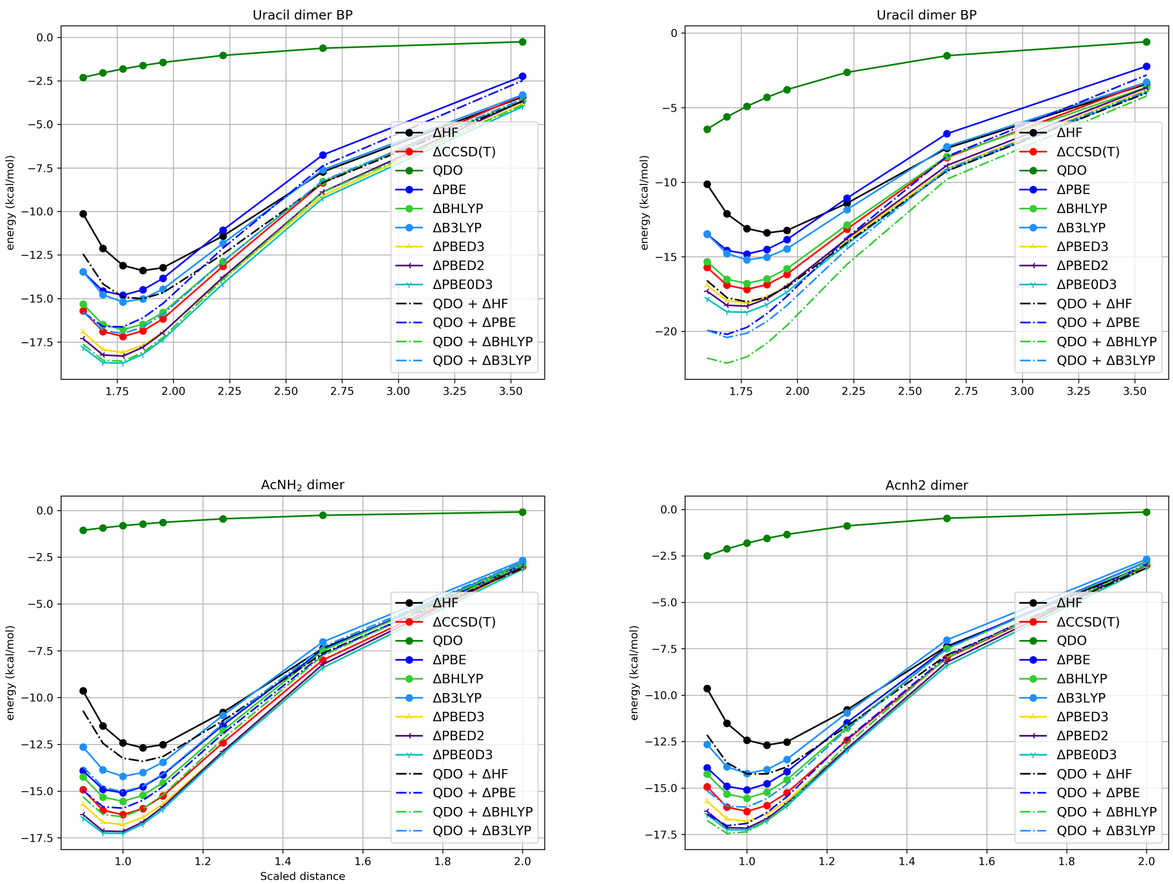


Figure S3: Interaction energy curves for Uracil dimer base-pair and $AcNH_2$ dimer. Top-left: Uracil spliced into 3 fragments, top-right: Uracil spliced into 6 fragments, bottom-left: $AcNH_2$ spliced into 2 fragments and bottom-right: $AcNH_2$ spliced into 3 fragments