

# Supporting Information: Uncertainty Quantification for Quantum Chemical Models of Complex Reaction Networks

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## Reference Set

The reference set consists of relative energies between structures taken from Refs. [1, 2]. These energies were determined from density fitting local coupled cluster (DF-LCCSD(T0)-F12a/cc-pVTZ-F12) [3, 4] single-point calculations which were carried out with Molpro (version 2015) [5]. The cc-pVTZ/JKFIT basis [6] was employed for Fock matrix fitting and the aug-cc-pVTZ/MP2FIT basis [7] for the fitting of all other integrals. All DFT single-point calculations were carried out with the NWChem program package [8]. The following density functionals were employed: BP86 [9, 10], B3LYP [10–12], PBE [13], PBE0 [14], LC-PBE0, M06-2X [15], M06-L [16], TPSS [17], and TPSSh [18]. Furthermore, for BP86, B3LYP, PBE0, M06-2X, M06-L, TPSS, and TPSSh we considered Grimme’s third generation dispersion correction [19, 20], denoted as BP86-D3, B3LYP-D3, PBE0-D3, M06-2X-D3, M06-L-D3, TPSS-D3, and TPSSh-D3, respectively. For all DFT calculations a triple- $\zeta$  basis set (def2-TZVP) was chosen for all atoms [21].

In Table 1, the DF-LCCSD(T0)-F12 electronic energies and the norm of the T1 vector [22] for each structure in the reference set are given. The coordinates of each structure are provided in files named <ID>.xyz.

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Table 1: Electronic energies (in Hartree) and norm of T1 vector for structures in reference set.

ID	$E_H$	$\ t_1\ $
kua2013_4o	-457.65359	0.116
kua2013_4a	-457.67799	0.113
kua2013_2aTo2ha	-457.95053	0.111
kua2013_3eTo3k	-572.35235	0.123
kua2013_4aTo4f2	-610.41469	0.128
kua2013a_2To6+6	-610.40052	0.145
kua2013_4a3To4f4	-610.42607	0.123
kua2013_4f2	-457.68028	0.098
kua2013a_5	-457.68050	0.100
kua2013a_1	-457.67813	0.100
kua2013_4f4	-457.68220	0.098
kua2013a_4	-457.67702	0.100
kua2013a_2To8	-686.80671	0.127
kua2013_2e	-228.81298	0.086
kua2013_2o	-228.78407	0.072
kua2013a_2	-457.66650	0.114
kua2013a_3	-457.67897	0.101
kua2013a_6+7To8	-686.79515	0.130
kua2013_3hk	-419.64940	0.089
kua2013a_2To5	-610.40700	0.137
kua2013_4eTo4a	-686.77662	0.133
kua2013a_2To4	-610.40764	0.134
kua2013_3kTo3hk	-572.37984	0.118
kua2013_4k	-457.68365	0.115
kua2013_4aTo4f	-610.41766	0.125
kua2013_4f3	-457.68297	0.098
kua2013_3aTo3ha	-572.37943	0.119
kua2013_2a	-228.82488	0.091
kua2013a_9	-534.06369	0.105
kua2013_4f	-457.68098	0.099
kua2013_4aTo4ha	-686.80642	0.128
kua2013_3p	-419.62432	0.099
kua2013_4e	-457.66797	0.107
kua2013_2aTo2e	-457.92785	0.116
kua2013_4a3	-457.67680	0.113
kua2013_4kTo4e	-686.78600	0.134
kua2013_2p	-305.20672	0.082
kua2013_4p	-534.04188	0.114

Continued on next page

Table 1: Electronic energies (in Hartree) and norm of T1 vector for structures in reference set.

ID	$E_H$	$\ t_1\ $
kua2013_4ha	-534.07355	0.100
kua2013_3ha	-419.64614	0.090
kua2013a_1To2	-610.41076	0.130
kua2013a_8	-534.06776	0.104
kua2013_3o	-343.24019	0.097
kua2013_3a	-343.25211	0.103
kua2013_4hk	-534.07354	0.100
kua2013_3k	-343.25262	0.105
kua2013_3e	-343.23899	0.095
kua2013_4a3To4f3	-610.41926	0.131
kua2013_3eTo4k	-610.39293	0.144
kua2013_3aTo3e	-572.36210	0.123
kua2013_2ha	-305.21442	0.078
kua2013a_2To3	-610.41069	0.134

The dataset applied for the re-parametrization of LC\*-PBE0 consists of energy differences ( $D_i = B_i - A_i$ ) between two structures on the same PES, i.e., structures with the same number and type of atomic nuclei, the same number of electrons, and the same electronic spin state. In Tables 2 and 3, the IDs of the structures are listed between which energy differences  $D_i$  are calculated.

## Error Estimation

To increase the flexibility of the LC-PBE0 functional, parameters of the range-separation scheme, the exchange ( $E_x^{\text{PBE}}$ ) functional, and correlation ( $E_c^{\text{PBE}}$ ) functional were modified (see Ref. [23]).

In range-separated hybrid (RSH) functionals [24–29], the exchange functional is divided into short-range DFT exchange and long-range Hartree-Fock (HF) exchange by splitting the electron-electron interaction operator  $1/r_{12}$  into two parts:

$$\frac{1}{r_{12}} = \underbrace{\frac{1 - [\alpha + \beta \cdot \text{erf}(\gamma r_{12})]}{r_{12}}}_{\text{short-range}} + \underbrace{\frac{\alpha + \beta \cdot \text{erf}(\gamma r_{12})}{r_{12}}}_{\text{long-range}} \quad (1)$$

The exchange part of the PBE functional is given by

$$E_x^{\text{PBE}}[\rho] = \int \rho \epsilon_x^{\text{unif}}(\rho) F_x^{\text{PBE}}(s) d^3r, \quad (2)$$

where  $F_x^{\text{PBE}}(s) = 1 + \kappa - \kappa / (1 + \frac{\mu}{\kappa} s^2)$ ,  $\kappa = 0.804$ ,  $\mu = 0.21951$ , and the reduced gradient  $s = |\nabla\rho| / (2k_F\rho)$ .

Table 2: IDs of structures between which the energy difference  $D_i = B_i - A_i$  in the training set are calculated.

	A	B
D1	kua2013_2o	kua2013_2e
D2	kua2013_2e	kua2013_2a
D3	kua2013_2ha	kua2013_2p
D4	kua2013_3k	kua2013_3a
D5	kua2013_3a	kua2013_3o
D6	kua2013_3o	kua2013_3e
D7	kua2013_3hk	kua2013_3ha
D8	kua2013_3ha	kua2013_3p
D9	kua2013_4o	kua2013a_2
D10	kua2013a_2	kua2013a_4
D11	kua2013a_4	kua2013_4a3
D12	kua2013_4a3	kua2013_4k
D13	kua2013_4k	kua2013a_3
D14	kua2013a_3	kua2013_4f3
D15	kua2013_4f3	kua2013a_5
D16	kua2013a_5	kua2013_4f
D17	kua2013_4f	kua2013_4f2
D18	kua2013_4f2	kua2013a_1
D19	kua2013a_1	kua2013_4e
D20	kua2013_4e	kua2013_4a
D21	kua2013_4a	kua2013_4f4
D22	kua2013_2aTo2e	kua2013_2aTo2ha
D23	kua2013_4p	kua2013a_9
D24	kua2013a_9	kua2013a_8
D25	kua2013a_8	kua2013_4hk

The correlation part of the PBE functional reads

$$E_c^{\text{PBE}}[\rho_\uparrow, \rho_\downarrow] = \int \rho \left[ \epsilon_c^{\text{unif}}(r_s, \zeta) + H(r_s, \zeta, t) \right] d^3r, \quad (3)$$

with

$$H(r_s, \zeta, t) = \gamma_c \phi^3 \ln \left( 1 + \frac{\beta_c}{\gamma_c} \frac{t^2 + At^4}{1 + At^2 + A^2t^4} \right), \quad (4)$$

where  $\rho = \rho_\uparrow + \rho_\downarrow$  is the electron density (obtained as a sum of spin-up and spin-down densities),  $\epsilon_c^{\text{unif}}(r_s, \zeta)$  the correlation energy per particle of the uniform electron gas,  $r_s = [(4\pi/3)\rho]^{1/3}$  the local Wigner-Seitz radius,  $t = |\nabla\rho|/(2\phi k_s \rho)$  the correlation density gradient,  $\zeta = (\rho_\uparrow - \rho_\downarrow)/\rho$  the relative spin polarization, and  $\phi = ((1+\zeta)^{2/3} + (1-\zeta)^{2/3})/2$  a spin scaling factor. The factor  $A$  is a function of  $\phi$  and  $\epsilon_c^{\text{unif}}$  [13]. The parameters  $\beta_c = 0.066725$  and  $\gamma_c = (1 - \ln 2)/\pi^2$ .

Table 3: IDs of structures between which the energy difference  $D_i = B_i - A_i$  in the test set are calculated.

	A	B
D26	kua2013_4hk	kua2013_4ha
D27	kua2013_3kTo3hk	kua2013_3aTo3ha
D28	kua2013_3aTo3ha	kua2013_3aTo3e
D29	kua2013_3aTo3e	kua2013_3eTo3k
D30	kua2013_3eTo4k	kua2013a_2To6+6
D31	kua2013a_2To6+6	kua2013a_2To5
D32	kua2013a_2To5	kua2013a_2To3
D33	kua2013a_2To3	kua2013a_1To2
D34	kua2013a_1To2	kua2013_4aTo4f2
D35	kua2013_4aTo4f2	kua2013_4aTo4f
D36	kua2013_4aTo4f	kua2013_4a3To4f4
D37	kua2013_4a3To4f4	kua2013_4a3To4f3
D38	kua2013_4a3To4f3	kua2013a_2To4
D39	kua2013_4eTo4a	kua2013_4kTo4e
D40	kua2013_4kTo4e	kua2013a_6+7To8
D41	kua2013a_6+7To8	kua2013_4aTo4ha
D42	kua2013_4aTo4ha	kua2013a_2To8

The parameters  $\alpha$ ,  $\gamma$ ,  $\kappa$ , and  $\mu$  were re-optimized employing the reference set. We emphasize that complete long-range correction is always maintained, i.e.  $\alpha + \beta = 1$ .

The optimized parameter values for LC\*-PBE0 are:  $\alpha = 0.346$  ( $\sigma = 0.121$ ),  $\gamma = 0.039$ ,  $\kappa = 0.794$ ,  $\mu = 0.498$ . It is important to note that  $\alpha$  as a linear parameter is the only parameter included in the error estimation scheme [23].

The set of parameters employed for  $\alpha$  in the LC\*-PBE0 functional is: {0.5590, 0.3943, 0.4642, 0.6166, 0.5715, 0.2280, 0.4607, 0.3277, 0.3335, 0.3956, 0.3634, 0.5216, 0.4379, 0.3607, 0.3996, 0.3863, 0.5264, 0.3212, 0.3838, 0.2429, 0.0377, 0.4249, 0.4504, 0.2564, 0.6201, 0.1704, 0.3515, 0.3234, 0.5311, 0.5235, 0.3647, 0.3917, 0.2388, 0.1068, 0.3040, 0.3649, 0.4946, 0.4912, 0.2992, 0.3095, 0.2194, 0.1745, 0.1399, 0.5816, 0.2845, 0.2931, 0.1947, 0.4399, 0.1511, 0.3203}

In this work, we calculate the electronic energy of the ensemble non-selfconsistently employing the electron density obtained from a selfconsistent calculation with the best-fit parameters  $a_0$  [30, 31].

Data analysis and visualization were carried out with the software packages Pandas [32], Matplotlib [33], and IPython [34].

## Formose Reaction Network

In our model network, intermediates were obtained by perturbing the transition states taken from Ref. [1] along the reaction coordinate followed by a structure optimization.

The transition states in our network were obtained by refining the transition states reported in Ref. [1] with a trust-radius of at most 0.15 Å. All structure optimizations were carried out with the exchange-correlation functional B3LYP [10–12] and a 6-311G\*\* [35] basis set employing TURBOMOLE (version 7.0.2) [36] in its shared-memory parallelized implementation. The maximum norm of the Cartesian structure gradient was considered to be converged when it dropped below  $10^{-4}$  hartree/bohr. Harmonic frequencies were obtained with the TURBOMOLE module `aoforce`, which evaluates the molecular Hessian analytically.

The difference in zero-point energy  $\Delta\text{ZPE}^\ddagger$  and the difference in thermal contributions to the free energy in the gas phase  $\Delta A_{\text{therm}}^{\ddagger,*}$  were evaluated with the TURBOMOLE program `freeh`, which employs the rigid rotor-harmonic oscillator approximation discussed in the main article. For the difference in free energies of solvation  $\Delta\Delta A_{\text{solv}}^{\ddagger,*}$  we employed SM12 [37] as an implicit solvent model which is implemented in QCHEM (version 4.3) [38]. The free energies of solvation  $\Delta A_{\text{solv}}^{\ddagger,*}$  were evaluated from B3LYP/6-311G\*\* single-point calculations, in which water was specified as the solvent and the CM5 partial-charge representation was employed.

The standard-state Helmholtz free energy of activation  $\Delta A^{\ddagger,*}$  is calculated from the following contributions:

$$\Delta A_{\text{sol}}^{\ddagger,*} = \Delta E_{\text{elec}}^\ddagger + \Delta\text{ZPE}^\ddagger + \Delta A_{\text{therm}}^{\ddagger,*} + \Delta\Delta A_{\text{solv}}^{\ddagger,*} \quad (5)$$

In Table 4, the individual contributions are listed for each reaction in the network.

Table 4: Contributions to the standard-state Helmholtz free energy of activation,  $\Delta A^{\ddagger,*}$ , for the reactions in the network (in kJ/mol): electronic energy  $\Delta E_{\text{elec}}^\ddagger$  (with error estimate  $\sigma$ ), zero-point energy  $\Delta\text{ZPE}^\ddagger$ , thermodynamic corrections  $\Delta A_{\text{therm}}^{\ddagger,*}$ , and free energy of solvation  $\Delta A_{\text{solv}}^{\ddagger,*}$ .

	Reactant(s)	Product(s)	$\Delta E_{\text{elec}}^\ddagger$	$\sigma$	$\Delta\text{ZPE}^\ddagger$	$\Delta A_{\text{therm}}^{\ddagger,*}$	$\Delta\Delta A_{\text{solv}}^{\ddagger,*}$	$\Delta A^{\ddagger,*}$
R1	1	2	88.4	4.8	-9.7	12.6	4.1	95.4
R2	2	1	138.1	13.2	-23.7	6.2	4.3	124.9
R3	1 + 1	3	237.4	14.2	-12.2	14.3	-24.1	215.4
R4	3	1 + 1	343.6	23.0	-27.2	3.8	-9.1	311.1
R5	3	4	154.8	11.6	-17.1	15.2	4.4	157.3
R6	4	3	148.3	10.2	-24.2	8.2	-1.5	130.8
R7	3	5	87.0	3.2	-8.3	18.3	3.3	100.3
R8	5	3	136.0	12.3	-22.2	5.2	0.2	119.2
R9	4 + 1	6	92.6	13.4	-8.8	19.1	9.6	112.5
R10	6	4 + 1	180.7	23.1	-16.6	6.2	15.1	185.4

In Table 5, the IDs of the structures are listed between which  $\Delta A^{\ddagger,*}$  is calculated. The coordinates of each structure are provided in files named <ID>.xyz.

Table 5: IDs of intermediate and transition state between which  $\Delta A^{\ddagger,*}$  are calculated.

	Intermediate	Transition State
R1	I1	TS1
R2	I2	TS1
R3	I3	TS2
R4	I4	TS2
R5	I5	TS3
R6	I6	TS3
R7	I7	TS4
R8	I8	TS4
R9	I9	TS5
R10	I10	TS5
R11	I11	TS6
R12	I12	TS6
R13	I13	TS7
R14	I14	TS7
R15	I15	TS8
R16	I16	TS8
R17	I19	TS10
R18	I20	TS10

## Kinetic Modeling

The kinetic model is constructed from 6 vertices (species) and 5 edges (elementary reactions). Since the concentration of water is essentially constant over the course of the reaction, elementary processes including water are assumed to be of pseudo-first order. Then, the stoichiometry matrix and the reaction pair vector read as follows,

$$\mathbf{S} = \begin{bmatrix} -1 & -2 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & -1 & -1 & 0 \\ 0 & 0 & 1 & 0 & -1 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix},$$

and

$$\mathbf{f} = \begin{bmatrix} k_{R1}y_1 - k_{R2}y_2 \\ k_{R3}(y_1)^2 - k_{R4}y_3 \\ k_{R5}y_3 - k_{R6}y_4 \\ k_{R7}y_3 - k_{R8}y_5 \\ k_{R9}y_1y_4 - k_{R10}y_6 \end{bmatrix},$$

respectively. From these mathematical objects, the Jacobian can be constructed,

$$\mathbf{J} = \begin{bmatrix} -k_{R1} - 4k_{R3}y_1 - k_{R9}y_4 & k_{R2} & k_{R4} & -k_{R9}y_1 & 0 & k_{R10} \\ k_{R1} & -k_{R2} & 0 & 0 & 0 & 0 \\ 2k_{R3}y_1 & 0 & -k_{R4} - k_{R5} - k_{R7} & k_{R6} & k_{R8} & 0 \\ -k_{R9}y_4 & 0 & k_{R5} & -k_{R6} - k_{R9}y_1 & 0 & k_{R10} \\ 0 & 0 & k_{R7} & 0 & -k_{R8} & 0 \\ k_{R9}y_4 & 0 & 0 & k_{R9}y_1 & 0 & -k_{R10} \end{bmatrix} .$$

We validated the time step for the simulation of the slow processes, which is determined automatically by studying the largest modulus of eigenvalues of the Jacobian corresponding to the slow sub-network (Figure 8 in the main text). We selected the mean of the ensemble of free reaction energies (see below), 1 mol/L of formaldehyde as feed, an absolute temperature of 298.15 K, and a time-gap criterion of  $\epsilon = 10^{-3}$ . Even a hundredfold decrease of the automatically determined time step did not change the concentration trajectories. Therefore, we assume that our time-discrete propagation of concentrations according to Eq. (1) in the main text is equivalent to a stable numerical integration.

To examine the validity of our simulations, we recorded two quantities over the entire course of the reaction. Firstly, the number of atomic nuclei must be conserved in closed systems. Here, we simply chose the concentration of carbon atoms  $z$ ,

$$z \equiv y_1 + y_2 + 2(y_3 + y_4 + y_5) + 3y_6 . \quad (6)$$

Secondly, due to detailed balance, the quotient of a corresponding pair of forward and backward reactions equals one at thermodynamic equilibrium. We set this convergence criterion to 1.001 for every reaction pair.

Reduction of the kinetic model to a single differential equation,

$$\frac{d}{dt}\Delta = -3k_{R3}(\alpha r(\Delta))^2 + 3k_{R4}\gamma(r(\Delta) - \Delta) , \quad (7)$$

is possible due to the time-scale separation determined with the CSP algorithm (see Figure 7 in the main text). In Eq. (7) in this Supporting Information,  $r(\Delta)$  is defined as

$$r(\Delta) \equiv -\frac{p(\Delta)}{2} + \sqrt{\left(\frac{p(\Delta)}{2}\right)^2 + q(\Delta)} , \quad (8)$$

$$p(\Delta) \equiv \frac{1}{k\alpha\beta} - \Delta , \quad (9)$$

$$q(\Delta) \equiv \frac{2\Delta + z}{3k\alpha\beta} , \quad (10)$$

where  $\alpha$ ,  $\beta$  and  $\gamma$  are Boltzmann probabilities,

$$\alpha \equiv \frac{\exp\left(-\frac{A_1^*}{RT}\right)}{\sum_{i=1}^2 \exp\left(-\frac{A_i^*}{RT}\right)} , \quad (11)$$



$$\beta \equiv \frac{\exp\left(-\frac{A_4^*}{RT}\right)}{\sum_{i=3}^5 \exp\left(-\frac{A_i^*}{RT}\right)}, \quad (12)$$

$$\gamma \equiv \frac{\exp\left(-\frac{A_3^*}{RT}\right)}{\sum_{i=3}^5 \exp\left(-\frac{A_i^*}{RT}\right)}, \quad (13)$$

and  $A_i^*$  refers to the standard-state Helmholtz free energy of the  $i$ -th chemical species.

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