

Supporting Information:

The Challenge of Small Energy Differences in Metal-Organic Framework Reactivity

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Contents

1	Catalytic Cycle of Ethylene Hydrogenation	S3
2	Table of $\Delta\Delta G$ Fits by Quasiharmonic Setting	S4
3	Table of $\Delta\Delta E$ Fits by Geometry	S5
4	Fits with $\Delta\Delta(H - E)$, and $\Delta\Delta(G - E)$	S6
4.1	$(G - E)$	S6
4.2	$(H - E)$	S7
5	Hirshfeld Charge Analysis	S8
6	Table of Quasiharmonic Settings	S9
	References	S10

1 Catalytic Cycle of Ethylene Hydrogenation

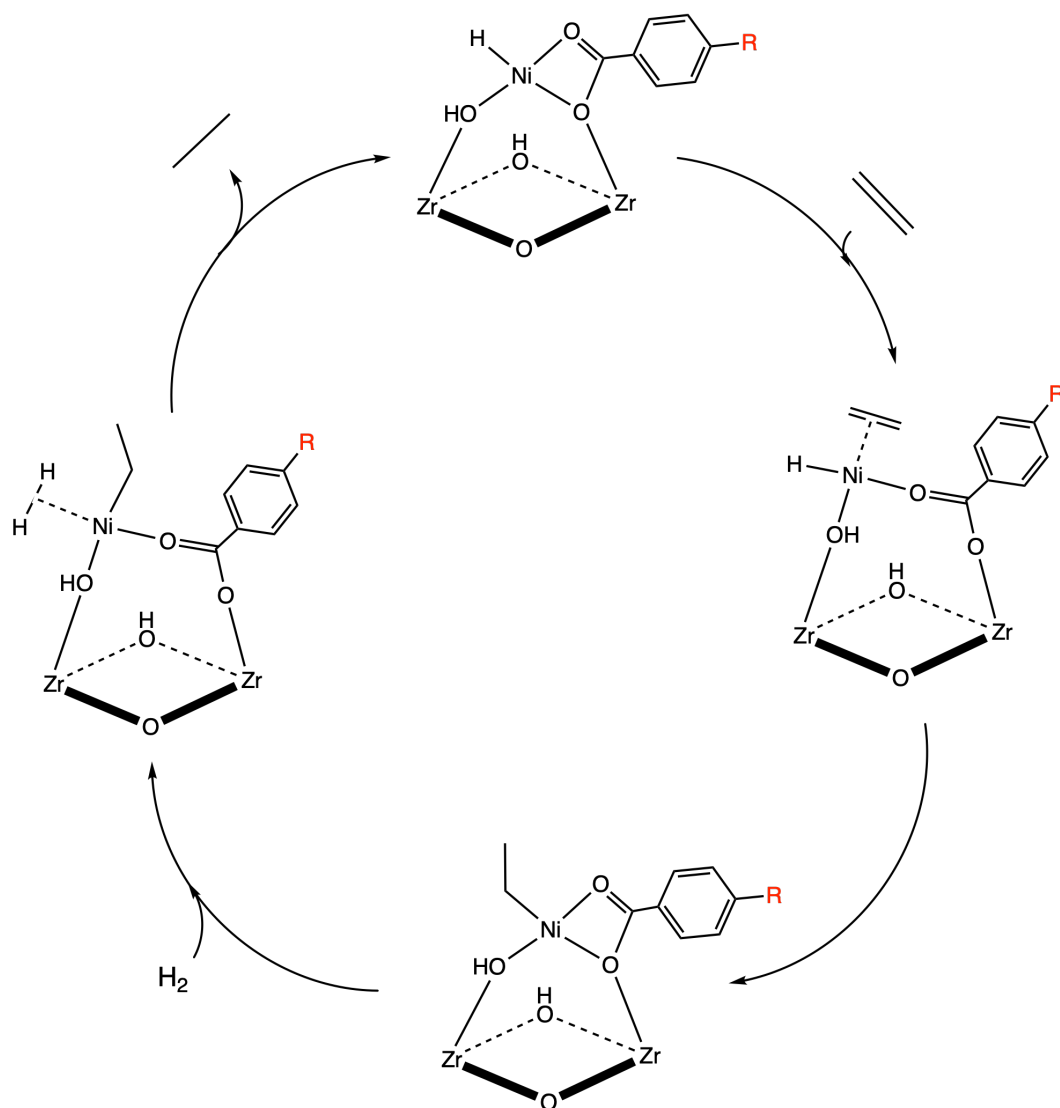


Figure S1. Catalytic cycle of ethylene hydrogenation to ethane on benzoate-modified NU-1000.

2 Table of $\Delta\Delta G$ Fits by Quasiharmonic Setting

Table S1. Slopes of lines of best fit and R^2 value (in brackets) for 22 functionals calculated across the Hammett series of R = -NH₂, -H, -CF₃, and -NO₂ in the free energy G at the four different thermochemical settings given in Table S5.

	Hybrid?	RRHO	Ribero	Grimme	Li
APFD ^{S1}	x	-0.87 [0.92]	-0.92 [0.96]	-0.84 [0.94]	-0.91 [0.95]
B3LYP ^{S2}	x	0.32 [0.46]	0.66 [0.96]	0.45 [0.71]	0.52 [0.87]
B3LYP+D3 ^{S3}	x	0.09 [0.16]	-0.07 [0.11]	0.0 [0.0]	0.02 [0.02]
B98 ^{S4,S5}	x	0.61 [0.66]	0.45 [0.78]	0.6 [0.81]	0.52 [0.69]
BMK ^{S6}	x	1.27 [0.96]	0.38 [0.09]	0.74 [0.41]	0.86 [0.74]
CAM-B3LYP ^{S7}	x	0.7 [0.97]	0.71 [0.94]	0.76 [0.97]	0.72 [0.96]
LC- ω PBE ^{S8}	x	0.88 [0.96]	0.93 [0.93]	0.92 [0.95]	0.94 [0.95]
M06 ^{S9}	x	-1.54 [0.96]	-1.15 [0.94]	-1.16 [0.97]	-1.42 [0.96]
M06-2X ^{S10}	x	0.98 [0.78]	0.45 [0.54]	0.69 [0.66]	0.73 [0.7]
M06-HF ^{S11,S12}	x	0.91 [0.93]	1.2 [0.89]	1.04 [0.86]	1.1 [0.92]
M06-L ^{S9}		-0.45 [0.86]	-0.82 [1.0]	-0.69 [0.99]	-0.61 [0.98]
M11-L ^{S13}		0.31 [0.07]	1.11 [0.38]	0.75 [0.25]	0.71 [0.25]
MN12-L ^{S14}		-0.8 [0.45]	-0.73 [0.7]	-0.8 [0.63]	-0.75 [0.54]
MN15 ^{S15}	x	0.69 [0.47]	0.68 [0.68]	0.55 [0.61]	0.72 [0.65]
O3LYP ^{S16}	x	0.61 [0.87]	0.54 [0.92]	0.56 [0.89]	0.58 [0.9]
PBE0 ^{S17}	x	0.79 [0.99]	0.75 [0.95]	0.8 [0.98]	0.78 [0.98]
SOGGA11 ^{S18}		-0.36 [0.05]	0.07 [0.01]	-0.16 [0.04]	-0.15 [0.01]
SOGGA11-X ^{S19}	x	0.52 [0.95]	0.46 [0.97]	0.53 [0.97]	0.5 [0.97]
TPSSH ^{S20,S21}	x	0.69 [0.96]	0.7 [0.95]	0.69 [0.96]	0.7 [0.97]
ω B97 ^{S22}	x	0.31 [0.25]	0.01 [0.0]	0.16 [0.23]	0.17 [0.14]
ω B97X ^{S22}	x	-0.08 [0.04]	-0.06 [0.04]	-0.0 [0.0]	-0.08 [0.07]
ω B97X-D ^{S23}	x	0.22 [0.03]	0.13 [0.02]	0.12 [0.02]	0.19 [0.03]

3 Table of $\Delta\Delta E$ Fits by Geometry

Table S2. Slopes of lines of best fit and R^2 value (in brackets) for 22 functionals calculated across the Hammett series of $R = -\text{NH}_2$, $-\text{H}$, $-\text{CF}_3$, and $-\text{NO}_2$ in the electronic energy E at four different sets of geometries: those optimized by the functional in the row ("Self"), those optimized by APFD ("APFD"), those optimized by MN12-L ("MN12-L"), and those optimized by PBE0 ("PBE0").

	Hybrid?	Geometry Self	Geometry APFD	Geometry MN12-L	Geometry PBE0
APFD	x	-0.69 [0.75]	-0.69 [0.75]	0.52 [0.91]	-0.28 [0.82]
B3LYP	x	0.25 [0.48]	1.15 [0.96]	0.82 [0.93]	0.67 [0.99]
B3LYP+D3	x	-0.14 [0.81]	0.75 [0.94]	0.37 [0.8]	-0.16 [0.98]
B98	x	0.59 [0.99]	1.1 [0.96]	0.85 [0.94]	0.6 [0.99]
BMK	x	0.58 [0.93]	1.2 [0.95]	1.02 [0.93]	0.62 [0.96]
CAM-B3LYP	x	0.7 [0.99]	1.12 [0.97]	0.91 [0.94]	0.7 [0.99]
LC- ω PBE	x	0.66 [0.99]	1.02 [0.97]	0.93 [0.95]	0.68 [0.99]
M06	x	-0.05 [0.58]	0.79 [0.94]	0.48 [0.88]	0.07 [0.18]
M06-2X	x	0.2 [0.35]	0.99 [0.96]	0.96 [0.91]	0.41 [0.99]
M06-HF	x	0.79 [0.3]	1.02 [0.93]	1.35 [0.94]	0.69 [1.0]
M06-L		-0.61 [0.8]	0.28 [0.53]	-0.3 [0.57]	-0.37 [0.76]
M11-L		1.59 [0.56]	0.41 [0.91]	0.25 [0.91]	0.49 [0.96]
MN12-L		-0.84 [0.92]	0.12 [0.18]	-0.84 [0.92]	-0.14 [0.47]
MN15	x	0.1 [0.11]	0.54 [0.84]	0.34 [0.86]	0.38 [0.97]
O3LYP	x	0.39 [0.92]	1.23 [0.98]	0.92 [0.92]	0.68 [0.96]
PBE0	x	0.65 [0.99]	0.92 [0.96]	0.77 [0.95]	0.65 [0.99]
SOGGA11		-0.37 [0.37]	0.55 [0.77]	-0.31 [0.21]	0.07 [0.08]
SOGGA11-X	x	0.64 [1.0]	1.24 [0.98]	1.04 [0.93]	0.65 [1.0]
TPSSh	x	0.55 [0.93]	0.65 [0.85]	0.37 [0.77]	0.6 [0.96]
ω B97	x	0.06 [0.68]	1.06 [0.96]	0.68 [0.85]	0.14 [0.98]
ω B97X	x	0.28 [0.99]	1.11 [0.97]	0.81 [0.9]	0.31 [1.0]
ω B97X-D	x	0.15 [0.94]	0.96 [0.97]	0.63 [0.91]	0.06 [0.98]

4 Fits with $\Delta\Delta(H - E)$, and $\Delta\Delta(G - E)$

4.1 ($G - E$)

Table S3. Comparison in ($G - E$) regressions across thermodynamic settings. m values with R^2 in brackets.

	Hybrid?	RRHO	Ribero	Grimme	Li
APFD	x	-0.18 [0.56]	-0.23 [0.36]	-0.15 [0.26]	-0.22 [0.45]
B3LYP	x	0.07 [0.1]	0.41 [0.92]	0.2 [0.81]	0.27 [0.81]
B3LYP+D3	x	0.23 [0.75]	0.07 [0.26]	0.15 [0.63]	0.17 [0.63]
B98	x	0.02 [0.0]	-0.14 [0.19]	0.01 [0.0]	-0.07 [0.03]
BMK	x	0.69 [0.96]	-0.2 [0.02]	0.17 [0.03]	0.28 [0.17]
CAM-B3LYP	x	0.01 [0.0]	0.01 [0.01]	0.07 [0.33]	0.02 [0.05]
LC-WHPBE	x	0.23 [0.7]	0.27 [0.67]	0.26 [0.74]	0.28 [0.75]
M06	x	-1.49 [0.95]	-1.1 [0.91]	-1.11 [0.95]	-1.36 [0.95]
M062X	x	0.78 [0.82]	0.25 [0.51]	0.49 [0.73]	0.53 [0.74]
M06HF	x	0.12 [0.01]	0.41 [0.2]	0.24 [0.08]	0.3 [0.09]
M06L		0.16 [0.1]	-0.2 [0.31]	-0.08 [0.04]	0.01 [0.0]
M11L		-1.27 [0.69]	-0.48 [0.98]	-0.83 [0.81]	-0.88 [0.78]
MN12L		0.04 [0.0]	0.11 [0.07]	0.04 [0.01]	0.09 [0.03]
MN15	x	0.58 [0.34]	0.58 [0.81]	0.45 [0.53]	0.61 [0.59]
O3LYP	x	0.21 [0.7]	0.15 [0.92]	0.17 [0.78]	0.18 [0.81]
PBE0	x	0.14 [0.69]	0.1 [0.54]	0.14 [0.87]	0.13 [0.8]
SOGGA11		0.01 [0.0]	0.44 [0.13]	0.22 [0.03]	0.23 [0.02]
SOGGA11X	x	-0.12 [0.57]	-0.18 [0.87]	-0.11 [0.63]	-0.14 [0.75]
TPSSH	x	0.14 [0.5]	0.16 [0.98]	0.15 [0.88]	0.15 [0.83]
WB97	x	0.25 [0.19]	-0.05 [0.01]	0.11 [0.11]	0.12 [0.07]
WB97X	x	-0.35 [0.51]	-0.33 [0.56]	-0.28 [0.58]	-0.35 [0.64]
WB97XD	x	0.07 [0.0]	-0.02 [0.0]	-0.03 [0.0]	0.04 [0.0]

4.2 ($H - E$)

Table S4. Comparison in ($H - E$) regressions across thermodynamic settings. m values with R^2 in brackets.

	Hybrid?	RRHO	Ribero	Grimme	Li
APFD	x	-0.02 [0.06]	-0.02 [0.06]	-0.02 [0.06]	-0.09 [0.59]
B3LYP	x	0.07 [0.9]	0.07 [0.9]	0.07 [0.9]	0.14 [0.59]
B3LYP+D3	x	0.04 [0.74]	0.04 [0.74]	0.04 [0.74]	0.05 [0.67]
B98	x	-0.06 [0.21]	-0.06 [0.21]	-0.06 [0.21]	-0.14 [0.39]
BMK	x	-0.04 [0.0]	-0.04 [0.0]	-0.04 [0.0]	0.08 [0.0]
CAM-B3LYP	x	0.0 [0.1]	0.0 [0.1]	0.0 [0.1]	-0.04 [0.77]
LC-WHPBE	x	0.01 [0.28]	0.01 [0.28]	0.01 [0.28]	0.03 [0.52]
M06	x	-0.34 [0.95]	-0.34 [0.95]	-0.34 [0.95]	-0.59 [0.95]
M062X	x	0.12 [0.41]	0.12 [0.41]	0.12 [0.41]	0.15 [0.51]
M06HF	x	-0.12 [0.07]	-0.12 [0.07]	-0.12 [0.07]	-0.06 [0.01]
M06L		-0.08 [0.14]	-0.08 [0.14]	-0.08 [0.14]	0.0 [0.0]
M11L		-0.28 [0.99]	-0.28 [0.99]	-0.28 [0.99]	-0.33 [0.92]
MN12L		0.01 [0.03]	0.01 [0.03]	0.01 [0.03]	0.07 [0.12]
MN15	x	0.13 [0.71]	0.13 [0.71]	0.13 [0.71]	0.29 [0.87]
O3LYP	x	0.02 [0.78]	0.02 [0.78]	0.02 [0.78]	0.04 [0.97]
PBE0	x	0.01 [0.63]	0.01 [0.63]	0.01 [0.63]	-0.0 [0.01]
SOGGA11		0.39 [0.23]	0.39 [0.23]	0.39 [0.23]	0.4 [0.66]
SOGGA11X	x	-0.07 [0.95]	-0.07 [0.95]	-0.07 [0.95]	-0.1 [0.98]
TPSSH	x	0.03 [0.62]	0.03 [0.62]	0.03 [0.62]	0.03 [0.64]
WB97	x	-0.11 [0.35]	-0.11 [0.35]	-0.11 [0.35]	-0.1 [0.16]
WB97X	x	-0.16 [0.78]	-0.16 [0.78]	-0.16 [0.78]	-0.23 [0.86]
WB97XD	x	0.07 [0.1]	0.07 [0.1]	0.07 [0.1]	0.14 [0.14]

5 Hirshfeld Charge Analysis

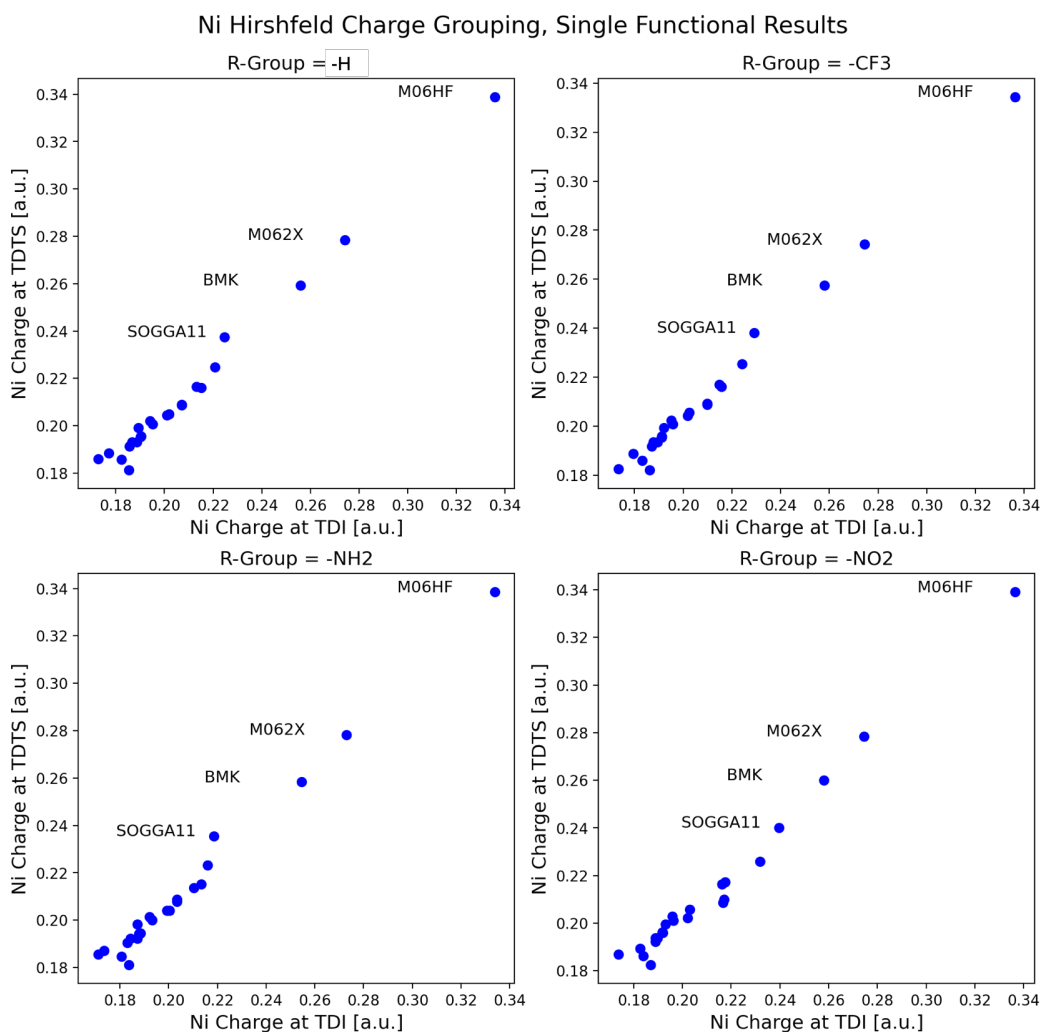


Figure S2. Four sets of plots showing the Hirshfeld charge on Ni in the TDS and TDI given by all 22 functionals across the Hammett series of R = -NH₂, -H, -CF₃, and -NO₂. Functionals with high charge localization are shown in text.

We investigated the extent of Hirshfeld charge localization^{S24–S26} in the geometries of all 22 functionals (Figure S2). As is to be expected,^{S27} there is significantly more charge localization on the Ni using hybrid functionals (e.g., M06-HF, M06-2X, and BMK). However, this charge localization does not correlate meaningfully to any trend in the predicted catalytic activity, and there is little difference between the charge localized on Ni in the transition state and the TDI, as well as between the different R groups. Thus, we posit that different functionals give signifi-

cantly different descriptions of the density with little correlation to the small energy differences in the catalytic activity.

6 Table of Quasiharmonic Settings

Table S5. Thermochemical settings used for the calculation of enthalpies and free energies in GoodVibes.

Name	Setting
RRHO	-t 373.15 -v 1 -f 0
Ribero	-qs truhlar -t 373.15 -v 1
Grimme	-qs grimme -t 373.15 -v 1
Li	-qs grimme -qh -t 373.15 -v 1

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