SUPPORTING INFORMATION

Gauge Effects in Local Hybrid Functionals Evaluated for Weak Interactions and the GMTKN30 Test Set

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Table S1. List of semi-empirical parameters used in the local hybrids validated in this work$^a$

| Method     | Parameters |
|------------|------------|
| $Lh$-LSDA, $t$-LMF | $b = 0.48$ |
| $Lh$-LSDA, $s$-LMF | $b_s = 0.22$ |
| $Lh$-LSDA, $ct$-LMF | $b = 0.534$ |
| $Lh$-LSDA, $\zeta$-$t$-LMF | $b = 0.446$, $d = 0.0531$ |
| $Lh$-LSDA, $\zeta$-$s$-LMF | $b = 0.197$, $d = 0.0423$ |
| $Lh$-LSDA-SIF-SRc | $b = 0.709$ |
|            | $\mu = 0.8$, $\lambda = 1.0$ |
| $Lh$-LSDA-SIR-SRc | $b = 0.646$ |
|            | $\mu = 0.8$, $\lambda = 0.646$ |
| $Lh$-BLYP-CG | $b = 0.488$, $nlx = 0.206$, $nlc = 0.497$ |
|            | CG: $\eta = 0.5$, $c = -0.000894$ |
| $Lh$-PBE-CG | $b = 0.50$, $nlx = 0.507$, $nlc = 0.451$ |
|            | CG: $\eta = 0.12$, $c = -0.00238$ |

$^a$ nlx and nlc are the coefficients of GGA corrections to exchange and correlation [eq. (14) in main text], respectively. $b_s$ is the prefactor of the $s$-LMF [eq. (8)], $b$ that of the $t$-LMF [eqs. (5,6,9)], $c$ is the prefactor of the calibration function [eq. (14)], $d$ controls the spin polarization contribution to the $\zeta$-$t$-LMF [eq. (9)], $\mu$ is the range-separation parameter for correlation eq. (11) and $\lambda$ is the prefactor of the short-range correlation SIE correction [eq. (11)].
Table S2. MAE/MSE values for a selection of functionals (in kcal/mol) for eight subsets of the GMTKN30 database concerning “basic properties” (atomization energies, reaction barriers, ionization potentials, electron and proton affinities, etc.), with and without DFT-D3 corrections.

|                | MB08-165   | W4-08      | G21IP      | G21EA      | PA         | SIE11      | BHPERI     | BH76       |
|----------------|------------|------------|------------|------------|------------|------------|------------|------------|
| **global and double hybrids** |            |            |            |            |            |            |            |            |
| B3LYP +D3      | 8.14/-6.79 | 3.94/-2.35 | 3.55/-0.09 | 1.92 / 0.48 | 2.23 / 1.90 | 7.63 / 6.17 | 5.80 / 5.36 | 4.67/-4.57 |
|                | 6.38/-3.97 | 3.86/-2.14 | 3.55/-0.10 | 1.93 / 0.48 | 2.38 / 2.06 | 8.70 / 7.32 | 2.78 / 2.18 | 5.21/-5.14 |
| PBE0 +D3      | 8.65/-0.42 | 3.70/-1.88 | 3.68 / 0.03 | 2.61 /-0.46 | 2.66 / 2.66 | 7.13 / 6.38 | 2.37 / 1.07 | 4.11/-3.86 |
|                | 8.66 / 1.30| 3.67/-1.76 | 3.69 / 0.02 | 2.61 /-0.46 | 2.76 / 2.76 | 7.79 / 7.06 | 2.58 /-2.12 | 4.43/-4.20 |
| PW6B95 +D3    | 4.78/-0.77 | 2.38/-0.87 | 2.78 / 0.99 | 1.24 / 0.06 | 2.45 / 2.30 | 7.02 / 6.21 | 3.53 / 2.98 | 3.21/-3.14 |
|                | 4.69 / 0.53| 2.37/-0.77 | 2.78 / 0.99 | 1.25 / 0.06 | 2.52 / 2.37 | 7.54 / 6.76 | 2.34 / 1.55 | 3.47/-3.40 |
| DSD-BLYP +D3  | 4.15/-3.90 | 2.49/-1.70 | 2.06/-0.92 | 1.98/-1.52 | 1.19 / 1.01 | 3.01 / 0.71 | 1.91 / 1.16 | 1.18 / 0.00 |
|                | 3.38 /-2.89| 2.45/-1.61 | 2.06/-0.92 | 1.98/-1.51 | 1.24 / 1.06 | 3.10 / 1.15 | 1.19 / 0.04 | 1.21/-0.21 |
| **Local hybrids** |            |            |            |            |            |            |            |            |
| Lh-LSDA, t-LMF +D3 | 8.79/-4.31 | 3.46/-1.50 | 4.57 / 3.64 | 4.11 / 4.11 | 1.48 / 0.12 | 6.39 / 4.75 | 5.90 / 5.48 | 2.55/-2.00 |
|                | 7.31/-0.68 | 3.49/-1.17 | 4.58 / 3.63 | 4.12 / 4.11 | 1.55 / 0.38 | 7.69 / 6.27 | 1.92 / 0.99 | 3.19/-2.85 |
| Lh-LSDA, s-LMF +D3 | 9.34/-7.89 | 4.13/-1.19 | 4.00 / 2.25 | 3.39 / 3.38 | 1.72 / 0.90 | 6.75 / 4.95 | 6.20 / 5.34 | 3.39/-3.01 |
|                | 6.64/-2.12 | 4.29/-0.48 | 3.99 / 2.24 | 3.41 / 3.40 | 1.89 / 1.44 | 8.82 / 7.30 | 2.14/-1.88 | 4.76/-4.51 |
Table S2 continued…..

|                | MB08-165 | W4-08  | G21IP  | G21EA  | PA     | SIE11  | BHPERI  | BH76  |
|----------------|----------|--------|--------|--------|--------|--------|---------|-------|
| **local hybrids** |          |        |        |        |        |        |         |       |
| \(L_h\)-LSDA, *ct*-LMF +D3 | 10.77 /-6.32 | 2.98 / 0.54 | 5.11 / 4.76 | 4.89 / 4.89 | 1.59 / 0.67 | 5.78 / 3.79 | 7.48 / 7.31 | 1.69 /-0.68 |
|                         | 8.70 /-1.99  | 3.12 / 0.90 | 5.11 / 4.75  | 4.89 / 4.89  | 1.66 / 0.92  | 7.72 / 5.64  | 2.75 / 2.50  | 2.15 /-1.58 |
| \(L_h\)-LSDA, *\(\zeta\)-t*-LMF +D3 | 7.68 /-2.95 | 2.74 /-1.03 | 4.47 / 3.49  | 4.14 / 4.14  | 1.53 /-0.24 | 6.94 / 5.45  | 4.98 / 4.33  | 2.95 /-2.62 |
|                         | 6.74 / 0.08  | 2.73 /-0.78 | 4.47 / 3.48  | 4.14 / 4.14  | 1.51 /-0.04 | 8.02 / 6.70  | 1.84 / 0.64  | 3.53 /-3.28 |
| \(L_h\)-LSDA, *\(\zeta\)-s*-LMF +D3 | 8.43 /-6.30 | 3.18 /-0.51 | 3.94 / 2.09  | 3.47 / 3.41  | 1.62 / 0.51 | 7.35 / 5.62  | 5.27 / 4.12  | 3.85 /-3.63 |
|                         | 6.61 /-1.48  | 3.36 /-0.01 | 3.94 / 2.08  | 3.48 / 3.42  | 1.69 / 0.90 | 9.10 / 7.63  | 2.08 /-1.88  | 4.92 /-4.81 |
| \(L_h\)-LSDA-SIF-SRc +D3 | 9.48 /-5.85  | 3.69 /-1.51 | 3.41 / 1.65  | 2.56 / 2.39  | 1.71/-0.90 | 4.58 / 1.66  | 7.53 / 7.25  | 1.79 / 1.43 |
|                         | 6.63 / 1.30  | 4.04 /-0.13 | 3.37 / 1.67  | 2.60 / 2.45  | 1.69 / 0.17 | 6.90 / 4.73  | 2.77 /-2.07  | 1.98 /-0.84 |
| \(L_h\)-LSDA-SIR-SRc +D3 | 9.73 /-5.91  | 3.13 /-0.65 | 3.81 / 2.74  | 3.40 / 3.39  | 1.59/-0.36 | 4.98 / 2.42  | 6.92 / 6.69  | 1.55 / 0.67 |
|                         | 6.53 / 0.82  | 3.68 / 0.65 | 3.79 / 2.75  | 3.45 / 3.44  | 1.67 / 0.65 | 7.30 / 5.28  | 2.59 /-2.11  | 2.25 /-1.47 |
| \(L_h\)-BLYP-CG +D3 | 6.89 /-2.49  | 2.69 /-1.98 | 3.35 /-0.26  | 1.95 / 1.00  | 2.02 /-1.16 | 6.87 / 5.39  | 3.03 / 2.33  | 3.22 /-2.94 |
|                         | 6.17 / 0.18  | 2.60 /-1.78 | 3.36 /-0.26  | 1.96 / 1.00  | 2.01 /-0.99 | 7.80 / 6.45  | 1.15 /-0.85  | 3.72 /-3.49 |
| \(L_h\)-PBE-CG +D3 | 5.98 /-0.50  | 3.42 /-2.85 | 4.46 / 3.46  | 3.84 / 3.75  | 1.40 / 0.71 | 6.98 / 5.98  | 1.33 / 0.44  | 3.16 /-2.83 |
|                         | 5.83 / 1.23  | 3.35 /-2.73 | 4.47 / 3.46  | 3.84 / 3.75  | 1.44 / 0.80 | 7.60 / 6.65  | 1.60 /-1.57  | 3.46 /-3.17 |
Table S3. MAE/MSE values for a selection of functionals (in kcal/mol) for twelve subsets of the GMTKN30 database concerning “reaction energies”, with and without DFT-D3 corrections.

|                | BH76RC  | RSE43   | O3ADD6 | G2RC   | AL2X   | NBPRC  | ISO34  | ISOL22 | DC9    | DARC   | ALK6   | BSR36  |
|----------------|---------|---------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| **global and double hybrids** |         |         |        |        |        |        |        |        |        |        |        |        |        |
| **B3LYP** | 2.32/-0.24 | 2.37/-2.37 | 1.99/-0.88 | 2.64/0.46 | 8.46/-8.46 | 4.78/3.99 | 2.28/-0.23 | 9.08/-5.53 | 15.10/6.92 | 15.28/15.28 | 9.23/-9.14 | 11.32/-11.32 | 6.00/-6.00 |
| +D3 | 2.25/-0.28 | 1.97/-1.97 | 2.75/-2.75 | 2.76/0.21 | 4.28/-4.28 | 3.02/1.67 | 1.86/-0.09 | 6.96/-4.39 | 11.92/4.68 | 10.11/10.11 | 4.82/-4.63 |         |        |
| **PBE0** | 2.52/-0.01 | 2.00/-2.00 | 4.81/-4.59 | 6.47/-3.52 | 2.68/-1.80 | 2.61/0.19 | 1.81/-0.22 | 4.15/-1.87 | 10.41/1.89 | 3.52/-0.00 | 2.42/-0.81 | 8.24/-8.24 |        |
| +D3 | 2.55/-0.03 | 1.76/-1.76 | 5.71/-5.71 | 6.77/-3.67 | 1.89/0.75 | 3.27/-1.21 | 1.61/-0.14 | 2.94/-1.18 | 9.36/0.45 | 3.32/-3.19 | 3.50/3.33 | 4.73/-4.73 |        |
| **PW6B95** | 1.53/0.12 | 2.63/-2.63 | 3.52/-3.47 | 3.21/-1.15 | 2.33/-1.59 | 2.07/0.74 | 1.36/-0.50 | 5.52/-3.50 | 8.42/3.23 | 5.84/5.76 | 2.79/2.51 | 6.63/-6.63 |        |
| +D3 | 1.56/0.10 | 2.44/-2.44 | 4.31/-4.31 | 3.36/-1.26 | 1.25/0.36 | 1.80/-0.36 | 1.20/-0.44 | 4.57/-2.96 | 6.96/2.22 | 3.61/3.41 | 4.73/4.73 | 4.06/-4.06 |        |
| **DSD-BLYP** | 0.99/-0.12 | 0.95/-0.23 | 2.03/-0.24 | 1.85/-0.98 | 2.30/-2.12 | 1.32/1.12 | 1.06/-0.39 | 3.85/-2.08 | 4.04/1.58 | 3.96/-3.96 | 2.36/-1.73 | 2.93/-2.93 |        |
| +D3 | 1.01/-0.14 | 0.85/-0.08 | 2.38/-0.42 | 1.89/-1.07 | 0.95/-0.63 | 0.83/-0.27 | 0.96/-0.43 | 3.08/-1.66 | 3.04/-0.83 | 2.23/2.16 | 1.22/0.06 | 1.10/-1.10 |        |
| **local hybrids** |         |         |        |        |        |        |        |        |        |        |        |        |        |
| **Lh-LSDA, t-LMF** | 2.96/-0.93 | 1.92/-1.92 | 1.64/0.08 | 2.60/0.42 | 8.13/-8.13 | 5.56/4.54 | 1.73/-0.60 | 6.97/-4.51 | 8.68/6.48 | 11.18/11.18 | 7.43/-7.43 | 6.41/-6.38 | 0.48/-0.15 |
| +D3 | 2.78/-0.99 | 1.34/-1.32 | 2.45/-2.43 | 2.79/0.00 | 3.14/-3.14 | 2.28/1.40 | 1.33/-0.40 | 4.27/-2.87 | 5.20/3.59 | 4.14/4.14 | 3.42/3.16 |        |        |
| **Lh-LSDA, s-LMF** | 3.01/-0.86 | 2.22/-2.22 | 1.82/-1.09 | 2.81/-0.09 | 9.89/-9.89 | 5.35/4.91 | 1.92/-0.56 | 6.78/-4.52 | 9.32/-7.09 | 10.09/10.09 | 9.14/-9.14 | 10.33/-10.33 |        |
| +D3 | 2.84/-0.93 | 1.32/-1.32 | 3.19/-3.05 | 3.64/-0.91 | 2.97/-2.97 | 0.98/0.01 | 1.40/-0.32 | 2.91/-1.56 | 5.59/2.44 | 1.79/-0.92 | 3.71/-1.64 | 2.06/-2.06 |        |
| **Lh-LSDA, ct-LMF** | 2.31/-0.63 | 2.26/-2.26 | 1.49/-1.39 | 3.07/-1.23 | 9.72/-9.72 | 7.23/-5.79 | 1.85/-0.67 | 7.50/-5.11 | 9.19/7.23 | 13.65/13.65 | 8.98/-8.98 | 7.05/-7.01 |        |
| +D3 | 2.11/-0.69 | 1.65/-1.62 | 1.52/-1.43 | 2.84/0.84 | 3.40/-3.40 | 3.53/2.21 | 1.41/-0.48 | 4.56/-3.34 | 4.52/4.08 | 6.04/6.04 | 4.64/-1.28 | 0.99/0.50 |        |
Table S3 continued..

|                  | BH76RC | RSE43 | O3ADD6 | G2RC | AL2X | NBPRC | ISO34 | ISOL22 | DC9 | DARC | ALK6 | BSR36 |
|------------------|--------|-------|--------|------|------|-------|-------|--------|-----|------|------|-------|
| **Local hybrids** |        |       |        |      |      |       |       |        |     |      |      |       |
| **Lh-LSDA, \(\zeta-t\)-LMF +D3** |        |       |        |      |      |       |       |        |     |      |      |       |
| 2.39/ -0.62      | 2.08/ -2.08 | 1.96/ -0.75 | 2.74/ -0.09 | 7.14/ -7.14 | 4.51/ -3.75 | 1.67/ -0.56 | 6.66/ -4.14 | 8.17/ -5.82 | 9.62/ 9.62 | 6.45/ -6.45 | 6.00/ -5.98 |
| 2.25/ -0.67      | 1.58/ -1.58 | 2.83/ -2.83 | 3.07/ -0.41 | 2.72/ -2.72 | 2.04/ -1.15 | 1.31/ -0.38 | 4.30/ -2.81 | 5.83/ 3.29 | 3.64/ 3.64 | 2.91/ -2.88 | 0.68/ -0.52 |
| **Lh-LSDA, \(\zeta-s\)-LMF +D3** |        |       |        |      |      |       |       |        |     |      |      |       |
| 2.35/ -0.45      | 2.46/ -2.46 | 2.18/ 0.29 | 3.37/ -0.51 | 8.81/ -8.81 | 4.48/ 4.09 | 1.92/ -0.53 | 6.50/ -3.87 | 9.20/ 6.46 | 8.77/ 8.61 | 8.14/ -8.14 | 9.56/ -9.56 |
| 2.27/ -0.51      | 1.68/ -1.68 | 3.19/ -3.07 | 4.05/ -1.10 | 2.56/ -2.56 | 0.98/ -0.06 | 1.42/ -0.30 | 3.14/ -1.66 | 6.44/ 2.69 | 1.82/ -0.55 | 3.53/ -2.05 | 1.85/ -1.85 |
| **Lh-LSDA-SIF-SRe +D3** |        |       |        |      |      |       |       |        |     |      |      |       |
| 2.21/ -1.03      | 2.28/ -2.28 | 2.94/ 2.58 | 2.85/ -0.68 | 11.13/ -11.13 | 8.23/ 7.01 | 2.28/ -3.33 | 6.31/ -4.09 | 8.80/ 8.61 | 11.42/ 11.42 | 10.45/ -10.45 | 5.81/ -5.63 |
| 1.82/ -1.16      | 1.38/ -1.28 | 4.07/ -3.46 | 3.83/ -2.31 | 3.47/ -2.96 | 2.27/ -0.81 | 1.88/ -0.15 | 2.39/ -0.28 | 7.35/ 1.02 | 4.11/ -4.11 | 4.02/ -0.10 | 3.14/ 3.14 |
| **Lh-LSDA-SIR-SRe +D3** |        |       |        |      |      |       |       |        |     |      |      |       |
| 2.23/ -0.88      | 2.29/ -2.29 | 2.42/ 2.16 | 2.54/ 0.00 | 10.61/ -10.61 | 7.85/ 6.56 | 2.01/ -0.44 | 6.70/ -4.45 | 7.89/ 7.29 | 12.22/ 12.22 | 9.91/ -9.91 | 6.23/ -6.10 |
| 1.81/ -1.00      | 1.40/ -1.33 | 3.97/ -3.51 | 3.09/ -1.54 | 3.38/ -3.09 | 1.97/ 0.74 | 1.58/ -0.01 | 2.39/ -0.86 | 6.82/ 1.28 | 2.39/ -2.39 | 3.58/ -0.23 | 1.95/ 1.95 |
| **Lh-BLYP-CG +D3** |        |       |        |      |      |       |       |        |     |      |      |       |
| 2.30/ -0.61      | 1.91/ -1.91 | 2.86/ -1.91 | 2.52/ -0.25 | 6.79/ -6.79 | 4.11/ 3.43 | 1.58/ -0.50 | 6.67/ -3.98 | 7.91/ 5.37 | 9.57/ 9.57 | 7.43/ -7.43 | 5.81/ -5.80 |
| 2.19/ -0.66      | 1.49/ -1.48 | 3.72/ -3.72 | 2.73/ -0.51 | 2.80/ -2.80 | 1.95/ 1.17 | 1.21/ -0.33 | 5.27/ -1.89 | 4.94/ 3.07 | 4.30/ -4.30 | 4.21/ -4.21 | 0.92/ -0.84 |
| **Lh-PBE-CG +D3** |        |       |        |      |      |       |       |        |     |      |      |       |
| 2.10/ -0.45      | 1.48/ -1.46 | 4.08/ -3.71 | 3.34/ -0.83 | 4.10/ -4.07 | 2.46/ 1.99 | 1.44/ -0.60 | 5.43/ -3.31 | 6.54/ 3.19 | 5.55/ 5.52 | 2.81/ -2.81 | 5.94/ -5.94 |
| 2.08/ -0.48      | 1.24/ -1.21 | 4.88/ -4.88 | 3.58/ -0.97 | 1.66/ -1.44 | 1.57/ 0.55 | 1.22/ -0.49 | 4.03/ -2.61 | 5.86/ 1.64 | 2.60/ 2.14 | 1.24/ -0.52 | 2.33/ -2.33 |
Table S4. MAE/MSE values for a selection of functionals (in kcal/mol) for ten subsets of the GMTKN30 database concerning energies of non-covalent interactions, with and without DFT-D3 corrections.

|                | IDISP    | WATER27 | S22    | ADIM6   | RG6     | HEAVY2  | PCONF   | ACONF   | SCONF   | CYCONF   |
|----------------|----------|---------|--------|---------|---------|---------|---------|---------|---------|----------|
|                |          |         |        |         |         |         |         |         |         |          |
| Global hybrids |          |         |        |         |         |         |         |         |         |          |
| B3LYP +D3      | 17.46/ 3.75 | 6.50/ 6.20 | 3.79/ -3.79 | 5.02/ -5.02 | 0.80/ -0.80 | 1.37/ -1.37 | 3.98/ -3.98 | 0.96/ 0.96 | 0.98/ -0.70 | 0.46/ -0.38 |
|                | 4.26/ 4.12 | 0.36/ 0.17 | 0.43/ 0.43 | 0.07/ 0.01 | 0.16/ -0.05 | 0.34/ -0.26 | 0.14/ 0.14 | 0.52/ -0.52 | 0.24/ -0.14 |
| PBE0 +D3       | 10.59/ 0.78 | 2.80/ -0.76 | 2.38/ -2.34 | 3.41/ -3.41 | 0.43/ -0.43 | 0.66/ -0.66 | 3.33/ -3.33 | 0.64/ 0.64 | 0.47/ -0.39 | 0.58/ 0.36 |
|                | 3.48/ 0.70 | 0.57/ 0.29 | 0.36/ 0.36 | 0.03/ 0.03 | 0.17/ 0.11 | 0.89/ -0.89 | 0.10/ 0.10 | 0.32/ -0.30 | 0.55/ 0.49 |
| PW6B95 +D3     | 8.19/ 1.78 | 5.91/ -5.74 | 1.95/ -1.95 | 2.01/ -2.01 | 0.39/ -0.37 | 0.68/ -0.68 | 1.24/ -1.24 | 0.21/ 0.21 | 0.51/ -0.37 | 0.31/ 0.22 |
|                | 3.54/ 1.77 | 1.66/ -0.96 | 0.34/ -0.13 | 0.58/ 0.58 | 0.03/ 0.02 | 0.13/ -0.03 | 0.51/ 0.37 | 0.15/ -0.15 | 0.31/ -0.27 | 0.31/ 0.30 |
| DSD-BLYP +D3   | 5.05/ 0.40 | 2.54/ -2.19 | 1.04/ -1.04 | 1.89/ -1.89 | 0.32/ -0.32 | 0.42/ -0.42 | 1.17/ -1.17 | 0.32/ 0.32 | 0.53/ -0.32 | 0.15/ -0.15 |
|                | 1.37/ 0.36 | 1.50/ 1.22 | 0.28/ 0.27 | 0.13/ -0.13 | 0.07/ -0.01 | 0.11/ 0.09 | 0.16/ 0.03 | 0.06/ 0.06 | 0.25/ -0.23 | 0.09/ -0.08 |
| Local hybrids  |          |         |        |         |         |         |         |         |         |          |
| Lh-LSDA, t-LMF +D3 | 15.92/ 2.35 | 17.00/ -16.98 | 4.92/ -4.92 | 6.64/ -6.64 | 1.10/ -1.10 | 1.88/ -1.88 | 4.57/ -4.57 | 1.27/ 1.27 | 1.02/ -0.54 | 0.52/ -0.14 |
|                | 2.93/ 2.22 | 0.33/ -0.06 | 0.17/ -0.01 | 0.25/ -0.25 | 0.44/ -0.44 | 0.34/ -0.10 | 0.19/ 0.19 | 0.32/ -0.22 | 0.31/ 0.20 |
| Lh-LSDA, s-LMF  | 19.74/    | 22.79/ -22.76 | 6.27/ -6.27 | 8.76/ -8.76 | 1.30/ -1.30 | 2.24/ -2.24 | 6.31/ -6.31 | 1.61/ 1.61 | 1.34/ -0.71 | 0.70/ -0.06 |
| +D3     | 2.17  | 3.48/-3.00 | 0.31/-0.01 | 0.64/-0.64 | 0.24/-0.14 | 0.28/-0.13 | 0.82/-0.80 | 0.04/-0.03 | 0.82/ 0.13 | 0.55/ 0.53 |
|---------|-------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| Lh-LSDA, ct-LMF | 17.81/2.68 | 22.92/-22.92 | 5.69/-5.69 | 7.44/-7.44 | 1.24/-1.24 | 2.19/-2.19 | 4.83/-4.83 | 1.44/ 1.44 | 1.44/-0.75 | 0.56/-0.40 |
| +D3     | 3.47/ 2.35 | 8.89/-8.88  | 0.54/-0.31 | 0.46/-0.46 | 0.42/ 0.12 | 0.38/-0.05 | 0.43/ 0.28 | 0.29/ 0.29 | 0.36/-0.35 | 0.31/-0.06 |

Table S4 continued…

| IDISP   | WATER27 | S22 | ADIM6 | RG6 | HEAVY2/8 | PCONF | ACONF | SCONF | CYCONF |
|---------|---------|-----|-------|-----|----------|-------|-------|-------|--------|

Local hybrids

| Lh-LSDA, ζ-t-LMF | 14.73/2.14 | 13.31/-13.24 | 4.44/-4.44 | 6.13/-6.13 | 1.00/-1.00 | 1.68/-1.68 | 4.42/-4.42 | 1.16/1.16 | 0.75/-0.40 | 0.51/ 0.02 |
| +D3     | 3.19/ 2.18 | 2.25/-1.77   | 0.27/ 0.00 | 0.17/ 0.08 | 0.24/-0.24 | 0.43/ 0.43 | 0.41/-0.29 | 0.25/ 0.25 | 0.35/-0.22 | 0.46/ 0.33 |

| Lh-LSDA, ζ-s-LMF | 18.30/1.96 | 19.35/-19.26 | 5.83/-5.83 | 8.37/-8.37 | 1.26/-1.26 | 2.10/-2.10 | 6.12/-6.12 | 1.48/1.48 | 0.98/-0.52 | 0.75/ 0.14 |
| +D3     | 1.86/ 1.54 | 3.08/-2.38   | 0.29/-0.01 | 0.67/-0.67 | 0.24/-0.20 | 0.31/-0.22 | 0.86/-0.83 | 0.08/ 0.08 | 0.70/ 0.03 | 0.64/ 0.59 |

| Lh-LSDA-SIF-SRc | 19.39/1.38 | 32.11/-32.11 | 7.00/-7.00 | 9.23/-9.23 | 1.59/-1.59 | 2.89/-2.89 | 5.72/-5.72 | 1.77/1.77 | 1.85/-0.72 | 0.61/-0.42 |
| +D3     | 3.20/-0.13 | 5.75/-5.53   | 0.47/-0.09 | 0.76/-0.76 | 0.39/-0.37 | 0.53/-0.51 | 0.57/-0.47 | 0.13/-0.13 | 1.31/ 0.53 | 0.65/ 0.65 |

| Lh-LSDA-SIR-SRc | 19.50/1.91 | 28.85/-28.85 | 6.54/-6.54 | 8.59/-8.59 | 1.46/-1.46 | 2.67/-2.67 | 5.41/-5.41 | 1.65/1.65 | 1.73/-0.84 | 0.59/-0.41 |
| +D3     | 4.08/-3.84 | 0.44/-0.11   | 0.68/-0.68 | 0.37/-0.37 | 0.50/-0.49 | 0.60/-0.56 | 0.14/-     | 1.35/ 0.59 | 0.60/ 0.60 |
|        | +D3      | 2.41/ 1.76 |        |        |        |        | 0.14  |        |
|--------|----------|------------|--------|--------|--------|--------|-------|--------|
|\( Lh \)-BLYP-CG +D3 | 13.76/ 2.09 | 9.49/-3.99 | 3.99/-3.99 | 5.70/-5.70 | 0.95/-0.95 | 1.61/-1.61 | 4.15/-4.15 | 1.04/ 1.04 | 0.50/-0.27 | 0.43/ 0.03 |
|        | 8.54/ 8.26 | 1.62/ 0.97 | 0.28/ 0.10 | 0.20/ 0.13 | 0.25/-0.25 | 0.49/-0.49 | 0.43/-0.34 | 0.22/ 0.22 | 0.37/-0.17 | 0.45/ 0.32 |
|\( Lh \)-PBE-CG +D3 | 10.36/ 1.79 | 5.07/-4.69 | 2.71/-2.71 | 3.81/-3.81 | 0.56/-0.56 | 0.87/-0.87 | 3.17/-3.17 | 0.71/ 0.71 | 0.40/-0.31 | 0.39/ 0.10 |
|        | 2.93/ 1.81 | 2.79/ 2.58 | 0.25/ 0.12 | 0.36/ 0.36 | 0.12/-0.11 | 0.22/-0.12 | 0.56/-0.56 | 0.16/ 0.16 | 0.31/-0.27 | 0.38/ 0.26 |
Table S5. Deviations from S22 reference values (in kcal/mol) for two uncalibrated and two calibrated local hybrids, with and without D3 corrections.

|                          | ref. values<sup>a</sup> | $Lh$-LSDA-SIF-SRc +D3 | $Lh$-LSDA-SIR-SRc +D3 |
|--------------------------|--------------------------|------------------------|------------------------|
| **H-bonded complexes**   |                          |                        |                        |
| (NH$_3$)$_2$             | -3.17                    | 3.29                   | 2.99                   | 0.83 |
| (H$_2$O)$_2$             | -5.02                    | 2.79                   | 2.48                   | 0.40 |
| formic acid dimer        | -18.80                   | 5.33                   | -0.77                  | 4.82 | -0.87 |
| formamide dimer          | -16.12                   | 6.30                   | -0.16                  | 5.79 | -0.25 |
| uracil dimer             | -20.69                   | 7.22                   | -0.05                  | 6.72 | -0.07 |
| 2-pyridoxine-2-aminopyridine | -17.00               | 7.78                   | -0.11                  | 7.24 | -0.13 |
| adenine*thymine WC       | -16.74                   | 8.99                   | 0.72                   | 8.39 | 0.67 |
| **dispersion-dominated complexes** |                        |                        |                        |
| (CH$_4$)$_2$             | -0.53                    | 2.12                   | 0.82                   | 1.94 | 0.73 |
| (C$_2$H$_4$)$_2$         | -1.50                    | 4.38                   | 0.47                   | 4.05 | 0.42 |
| benzene*CH$_4$           | -1.45                    | 4.14                   | 0.60                   | 3.86 | 0.57 |
| PD benzene dimer         | -2.62                    | 9.46                   | 0.47                   | 8.90 | 0.55 |
| pyrazine dimer           | -4.20                    | 10.08                  | 0.21                   | 9.48 | 0.33 |
| stacked uracil dimer     | -9.74                    | 13.51                  | -0.76                  | 12.72 | -0.52 |
| stacked indole*benzene   | -4.59                    | 13.34                  | 0.25                   | 12.61 | 0.45 |
| stacked adenine*thymine  | -11.66                   | 19.00                  | -0.88                  | 17.95 | -0.50 |
| **mixed complexes**      |                          |                        |                        |
| ethene*ethine            | -1.51                    | 2.28                   | 0.51                   | 2.10 | 0.45 |
| benzene*H$_2$O           | -3.29                    | 3.65                   | -0.35                  | 3.37 | -0.36 |
| benzene*NH$_3$           | -2.32                    | 3.87                   | 0.08                   | 3.60 | 0.07 |
| benzene*HCN              | -4.55                    | 4.77                   | -0.58                  | 4.47 | -0.51 |
| T-shaped benzene dimer   | -2.71                    | 6.05                   | 0.16                   | 5.69 | 0.20 |
| T-shaped indole benzene  | -5.62                    | 7.86                   | -0.54                  | 7.43 | -0.44 |
| phenol dimer             | -7.09                    | 7.85                   | 0.31                   | 7.33 | 0.29 |

cont....
Table S5 continued…

|                              | ref. values<sup>a</sup> | \( Lh \)-BLYP-CG | \( Lh \)-PBE-CG |
|------------------------------|--------------------------|------------------|-----------------|
|                              |                          | +D3              | +D3             |
| **H-bonded complexes**       |                          |                  |                 |
| \((\text{NH}_3)_2\)          | -3.17                    | 1.43             | 0.52            |
| \((\text{H}_2\text{O})_2\)   | -5.02                    | 0.72             | -0.01           |
| formic acid dimer            | -18.80                   | 1.05             | -1.35           |
| formamide dimer              | -16.12                   | 2.32             | -0.31           |
| uracil dimer                 | -20.69                   | 3.04             | -0.29           |
| 2-pyridoxine-2-aminopyridine | -17.00                   | 3.55             | -0.40           |
| adenine*thymine WC           | -16.74                   | 4.45             | 0.12            |
| **dispersion-dominated complexes** |                        |                  |                 |
| \((\text{CH}_4)_2\)          | -0.53                    | 1.26             | -0.26           |
| \((\text{C}_2\text{H}_4)_2\) | -1.50                    | 2.53             | -0.11           |
| benzene*\text{CH}_4\        | -1.45                    | 2.53             | -0.18           |
| PD benzene dimer             | -2.62                    | 6.30             | -0.06           |
| pyrazine dimer               | -4.20                    | 6.60             | -0.02           |
| stacked uracil dimer         | -9.74                    | 8.73             | 0.76            |
| stacked indole*benzene       | -4.59                    | 9.02             | -0.16           |
| stacked adenine*thymine WC   | -11.66                   | 12.49            | 0.49            |
| **mixed complexes**          |                          |                  |                 |
| ethene*ethine                | -1.51                    | 1.22             | -0.12           |
| benzene*\text{H}_2\text{O}\  | -3.29                    | 1.96             | 0.42            |
| benzene*\text{NH}_3\        | -2.32                    | 2.29             | 0.13            |
| benzene*\text{HCN}\        | -4.55                    | 2.79             | -0.04           |
| T-shaped benzene dimer       | -2.71                    | 3.91             | -0.21           |
| T-shaped indole benzene      | -5.62                    | 5.13             | -0.18           |
| phenol dimer                 | -7.09                    | 4.44             | -0.03           |

<sup>a</sup> Relative energies were calculated as \( \text{E(dimer)} - \Sigma \text{E(monomers)} \).