# Supplementary Materials: Localized Polycentric Orbital Basis Set for Quantum Monte Carlo Calculations Derived from the Decomposition of Kohn-Sham Optimized Orbitals

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**Table S1.** Nuclear geometry (Å) of methane dimer configurations a, b and c considered in this work.

| **(a)** **Atom** | **x** | **y** | **z** |
|---|---|---|---|
| C | 0.000000 | 1.950001 | 0.000000 |
| H | 0.000000 | 3.038320 | 0.000000 |
| H | 1.026071 | 1.587222 | 0.000000 |
| H | −0.513036 | 1.587222 | 0.888604 |
| H | −0.513036 | 1.587222 | -0.888604 |
| C | 0.000000 | −1.949999 | 0.000000 |
| H | 0.888546 | −1.321558 | 0.000000 |
| H | −0.888546 | −1.321558 | 0.000000 |
| H | 0.000000 | −2.578440 | 0.888546 |
| H | 0.000000 | −2.578440 | -0.888546 |
| **(b)** **Atom** | **x** | **y** | **z** |
| C | 0.000000 | −1.999999 | 0.000000 |
| H | 0.000000 | −0.911680 | 0.000000 |
| H | 1.026071 | −2.362778 | 0.000000 |
| H | −0.513036 | −2.362778 | 0.888604 |
| H | −0.513036 | −2.362778 | −0.888604 |
| C | 0.000000 | 2.000001 | 0.000000 |
| H | 0.888546 | 1.371560 | 0.000000 |
| H | −0.888546 | 1.371560 | 0.000000 |
| H | 0.000000 | 2.628442 | 0.888546 |
| H | 0.000000 | 2.628442 | −0.888546 |
| **(c)** **Atom** | **x** | **y** | **z** |
| C | 0.000000 | 0.000000 | −2.174998 |
| H | 0.000000 | 0.000000 | −1.086679 |
| H | 0.000000 | 1.026071 | −2.537777 |
| H | 0.888604 | −0.513035 | −2.537777 |
| H | −0.888604 | −0.513035 | −2.537777 |
| C | 0.000000 | 0.000000 | 2.175002 |
| H | 0.000000 | 0.000000 | 3.263321 |
| H | 0.000000 | 1.026071 | 1.812223 |
| H | 0.888604 | −0.513035 | 1.812223 |
| H | −0.888604 | −0.513035 | 1.812223 |

**Table S2.** Nuclear geometry (Å) of methane dimer configurations d, e and f considered in this work.

| **(d)** | | | |
|---|---|---|---|
| **Atom** | **x** | **y** | **z** |
| C | 0.000000 | 0.000000 | 2.450000 |
| H | 0.000000 | 0.000000 | 1.361681 |
| H | 0.000000 | 1.026071 | 2.812779 |
| H | −0.888604 | -0.513035 | 2.812779 |
| H | 0.888604 | −0.513035 | 2.812779 |
| C | 0.000000 | 0.000000 | −2.450000 |
| H | 0.000000 | 0.000000 | −1.361681 |
| H | 0.000000 | 1.026071 | −2.812779 |
| H | −0.888604 | −0.513035 | −2.812779 |
| H | 0.888604 | −0.513035 | -2.812779 |
| **(e)** | | | |
| **Atom** | **x** | **y** | **z** |
| C | 0.000000 | 0.000000 | 1.950000 |
| H | 0.000000 | 0.000000 | 3.038319 |
| H | 0.000000 | 1.026071 | 1.587221 |
| H | 0.888604 | −0.513035 | 1.587221 |
| H | −0.888604 | −0.513035 | 1.587221 |
| C | 0.000000 | 0.000000 | −1.950000 |
| H | 0.000000 | 0.000000 | −3.038319 |
| H | 0.000000 | 1.026071 | −1.587221 |
| H | 0.888604 | −0.513035 | −1.587221 |
| H | −0.888604 | −0.513035 | −1.587221 |
| **(f)** | | | |
| **Atom** | **x** | **y** | **z** |
| C | 0.000000 | 0.000000 | 1.870623 |
| H | 0.000000 | 0.000000 | 2.958943 |
| H | 0.000000 | 1.026071 | 1.507844 |
| H | 0.888603 | −0.513035 | 1.507844 |
| H | −0.888603 | −0.513035 | 1.507844 |
| C | 0.000000 | 0.000000 | −1.870623 |
| H | 0.000000 | 0.000000 | −2.958943 |
| H | 0.000000 | −1.026071 | −1.507844 |
| H | −0.888603 | 0.513035 | −1.507844 |
| H | 0.888603 | 0.513035 | −1.507844 |

**Table S3.** Nuclear geometry (Å) of methane dimer configurations g and h considered in this work.

| **(g)** | | | |
|---|---|---|---|
| **Atom** | **x** | **y** | **z** |
| C | 0.000000 | 0.000000 | 1.950000 |
| H | 0.000000 | 0.888546 | 1.321559 |
| H | 0.000000 | −0.888546 | 1.321559 |
| H | −0.888546 | 0.000000 | 2.578441 |
| H | 0.888546 | 0.000000 | 2.578441 |
| C | 0.000000 | 0.000000 | −1.950000 |
| H | 0.000000 | 0.888546 | −2.578441 |
| H | 0.000000 | −0.888546 | −2.578441 |
| H | −0.888546 | 0.000000 | −1.321559 |
| H | 0.888546 | 0.000000 | −1.321559 |

**Table S3.** *Cont.*

| (h) Atom | x | y | z |
|---|---|---|---|
| C | 0.000000 | 0.000000 | 2.000000 |
| H | 0.000000 | 0.888546 | 1.371559 |
| H | 0.000000 | −0.888546 | 1.371559 |
| H | −0.888546 | 0.000000 | 2.628441 |
| H | 0.888546 | 0.000000 | 2.628441 |
| C | 0.000000 | 0.000000 | −2.000000 |
| H | 0.000000 | 0.888546 | −1.371559 |
| H | 0.000000 | −0.888546 | −1.371559 |
| H | −0.888546 | 0.000000 | −2.628441 |
| H | 0.888546 | 0.000000 | −2.628441 |

**Table S4.** Carbon atomic Gaussian basis set used for the QMC calculations on methane dimer.

| Type | Exponent | Coefficient |
|---|---|---|
| s | | |
| 1 | 0.051344 | 0.013991 |
| 2 | 0.102619 | 0.169852 |
| 3 | 0.205100 | 0.397529 |
| 4 | 0.409924 | 0.380369 |
| 5 | 0.819297 | 0.180113 |
| 6 | 1.63749 | −0.033512 |
| 7 | 3.272791 | −0.121499 |
| 8 | 6.541187 | 0.015176 |
| 9 | 13.073594 | −0.000705 |
| s | | |
| 1 | 0.921552 | 1.000000 |
| s | | |
| 1 | 0.132800 | 1.000000 |
| s | | |
| 1 | 0.02 | 1.000000 |
| p | | |
| 1 | 0.029281 | 0.001787 |
| 2 | 0.058547 | 0.050426 |
| 3 | 0.117063 | 0.191634 |
| 4 | 0.234064 | 0.302667 |
| 5 | 0.468003 | 0.289868 |
| 6 | 0.935757 | 0.210979 |
| 7 | 1.871016 | 0.112024 |
| 8 | 3.741035 | 0.054425 |
| 9 | 7.480076 | 0.021931 |
| p | | |
| 1 | 0.042257 | 1.000000 |
| p | | |
| 1 | 0.126772 | 1.000000 |
| p | | |
| 1 | 0.376742 | 1.000000 |
| d | | |
| 1 | 0.329486 | 1.000000 |
| d | | |
| 1 | 1.141611 | 1.000000 |
| f | | |
| 1 | 0.773485 | 1.000000 |

**Table S5.** Hydrogen atomic Gaussian basis set used for the QMC calculations on methane dimer.

| Type | Exponent | Coefficient |
|---|---|---|
| s | | |
| 1 | 8.70088777 | 0.01416863 |
| 2 | 1.95552046 | 0.05917887 |
| 3 | 0.55904363 | 0.17101570 |
| s | | |
| 1 | 0.16492543 | 1.0000000 |
| s | | |
| 1 | 0.065 | 1.0000000 |
| s | | |
| 1 | 0.02 | 1.0000000 |
| p | | |
| 1 | 1.4070000 | 1.0000000 |
| p | | |
| 1 | 0.3880000 | 1.0000000 |
| p | | |
| 1 | 0.1020000 | 1.0000000 |
| d | | |
| 1 | 0.88381786 | 1.0000000 |

**Table S6.** QMC/J-LGVB0 energies (Hartree) of methane dimer configurations considered in this work. The table includes monomer data for comparison. $\tau$ is the DMC time step in a.u.

| Configuration | VMC | DMC ($\tau = 0.05$) | DMC ($\tau = 0.01$) |
|---|---|---|---|
| a | −16.15428(8) | −16.19048(5) | −16.18968(4) |
| b | −16.15420(8) | −16.19033(5) | −16.18936(4) |
| c | −16.15445(8) | −16.19045(5) | −16.18960(4) |
| d | −16.15431(8) | −16.19004(5) | −16.18931(4) |
| e | −16.15451(8) | −16.19066(5) | −16.18969(4) |
| f | −16.15441(8) | −16.19072(5) | −16.18986(4) |
| g | −16.15441(8) | −16.19046(5) | −16.18961(4) |
| h | −16.15417(8) | −16.19041(5) | −16.18935(4) |
| monomer | −8.07696(5) | −8.09485(2) | −8.09441(2) |

**Table S7.** QMC/J-LGVB1 energies (Hartree) of methane dimer configurations considered in this work. The table includes monomer data for comparison. $\tau$ is the DMC time step in a.u.

| Configuration | VMC | DMC ($\tau = 0.05$) | DMC ($\tau = 0.01$) |
|---|---|---|---|
| a | −16.16627(7) | −16.19160(4) | −16.19034(4) |
| b | −16.16600(7) | −16.19146(4) | −16.19009(4) |
| c | −16.16630(7) | −16.19160(4) | −16.19028(4) |
| d | −16.16616(7) | −16.19128(4) | −16.19012(4) |
| e | −16.16616(7) | −16.19174(4) | −16.19041(4) |
| f | −16.16651(7) | −16.19185(4) | −16.19053(4) |
| g | −16.16624(7) | −16.19169(4) | −16.19040(4) |
| h | −16.16591(7) | −16.19151(4) | −16.19023(4) |
| monomer | −8.08298(5) | −8.09546(2) | −8.09486(2) |

**Table S8.** QMC/J-LGVB2 energies (Hartree) of methane dimer configurations considered in this work. The table includes monomer data for comparison. $\tau$ is the DMC time step in a.u.

| Configuration | VMC | DMC ($\tau = 0.05$) |
|---|---|---|
| a | −16.16900(7) | −16.19281(5) |
| b | −16.16877(7) | −16.19255(5) |
| c | −16.16903(7) | −16.19275(5) |
| d | −16.16891(7) | −16.19255(5) |
| e | −16.16907(7) | −16.19283(5) |
| f | −16.16920(7) | −16.19303(5) |
| g | −16.16910(7) | −16.19291(5) |
| h | −16.16864(7) | −16.19275(5) |
| monomer | −8.08439(5) | −8.09603(3) |

**Table S9.** VMC interaction energy (kcal/mol) for the methane dimer configurations considered in this work for the three levels of calculation J-LGVB0-2. The two columns MP2 and MP2+BSSE represent, respectively, the all electron MP2/aug-cc-pvTZ uncorrected and counterpoise corrected values (the interval of interest).

| Configuration | MP2 | MP2 + BSSE | J-LGVB0 | J-LGVB1 | J-LGVB2 |
|---|---|---|---|---|---|
| a | −0.50 | −0.38 | −0.23(8) | −0.19(8) | −0.14(8) |
| b | −0.30 | −0.14 | −0.18(8) | −0.03(8) | 0.01(8) |
| c | −0.44 | −0.33 | −0.33(8) | −0.21(8) | −0.16(8) |
| d | −0.25 | −0.15 | −0.24(8) | −0.13(8) | −0.08(8) |
| e | −0.51 | −0.39 | −0.37(8) | −0.13(8) | −0.18(8) |
| f | −0.59 | −0.45 | −0.31(8) | −0.35(8) | −0.26(8) |
| g | −0.46 | −0.34 | −0.31(8) | −0.18(8) | −0.20(8) |
| h | −0.36 | −0.24 | −0.16(8) | 0.03(8) | 0.09(8) |

**Table S10.** DMC (time step 0.05 a.u.) interaction energy (kcal/mol) for the methane dimer configurations considered in this work for the three levels of calculation J-LGVB0-2. The two columns MP2 and MP2+BSSE represent, respectively, the all electron MP2/aug-cc-pvTZ uncorrected and counterpoise corrected values (the interval of interest).

| Configuration | MP2 | MP2 + BSSE | J-LGVB0 | J-LGVB1 | J-LGVB2 |
|---|---|---|---|---|---|
| a | −0.50 | −0.38 | −0.49(4) | −0.43(4) | −0.47(5) |
| b | −0.30 | −0.14 | −0.40(4) | −0.34(4) | −0.31(5) |
| c | −0.44 | −0.33 | −0.47(4) | −0.43(4) | −0.43(5) |
| d | -0.25 | −0.15 | −0.21(4) | −0.23(4) | −0.31(5) |
| e | −0.51 | −0.39 | −0.60(4) | −0.51(4) | −0.48(5) |
| f | −0.59 | −0.45 | −0.64(4) | −0.58(4) | −0.61(5) |
| g | −0.46 | −0.34 | −0.48(4) | −0.48(4) | −0.53(5) |
| h | −0.36 | −0.24 | −0.45(4) | −0.37(4) | −0.43(5) |

**Table S11.** DMC (time step 0.01 a.u.) interaction energy (kcal/mol) for the methane dimer configurations considered in this work for the two levels of calculation J-LGVB0 and J-LGVB1. The two columns MP2 and MP2+BSSE represent, respectively, the all electron MP2/aug-cc-pvTZ uncorrected and counterpoise corrected values (the interval of interest).

| Configuration | MP2 | MP2 + BSSE | J-LGVB0 | J-LGVB1 |
|---|---|---|---|---|
| a | −0.50 | −0.38 | −0.54(4) | −0.39(4) |
| b | −0.30 | −0.14 | −0.34(4) | −0.23(4) |
| c | −0.44 | −0.33 | −0.49(4) | −0.35(4) |
| d | −0.25 | −0.15 | −0.31(4) | −0.25(4) |
| e | −0.51 | −0.39 | −0.55(4) | −0.43(4) |
| f | −0.59 | −0.45 | −0.65(4) | −0.51(4) |
| g | −0.46 | −0.34 | −0.50(4) | −0.43(4) |
| h | −0.36 | −0.24 | −0.33(4) | −0.32(4) |