Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics


# Supplementary material for:
# Comparison of explicitly correlated local coupled-cluster methods with various choices of virtual orbitals

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In the tables I-III we present the detailed results of the calculations described in section 6.1 of the main text. Tables IV and V correspond to Tables 2 and 3 of the main text, but the PNOs and OSVs have been computed using approximate LMP2 amplitudes according to eq. (48), while the data in the main text are obtained with fully converged LMP2 amplitudes.

TABLE I. PNO-LCCSD correlation energies (in $E_h$) and fraction of correlation energy (in percent) relative to the corresponding canonical methods for various test molecules. See main text for computational details.

| | | LCCSD Correlation energy | | | | | Fraction relative to canonical methods | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $l_{\mathrm{PNO}}$ | Av. dom. size | LCCSD | LCCSD +ΔMP | LCCSD +ΔMP2F12 | LCCSD -F12a | LCCSD -F12b | LCCSD | LCCSD +ΔMP2 | LCCSD -F12a | LCCSD -F12b |
| vinylcyclopropane: | | | | | | | | | | |
| $3.2{\cdot}10^{-6}$ | 14 | -0.8653355 | -0.8859548 | -0.9716962 | -0.9557740 | -0.9376547 | 98.11 | 100.45 | 100.42 | 100.14 |
| $1.0{\cdot}10^{-6}$ | 21 | -0.8736978 | -0.8840093 | -0.9697508 | -0.9537089 | -0.9368977 | 99.06 | 100.22 | 100.20 | 100.06 |
| $3.2{\cdot}10^{-7}$ | 32 | -0.8781326 | -0.8828434 | -0.9685849 | -0.9526245 | -0.9364651 | 99.56 | 100.09 | 100.09 | 100.01 |
| $1.0{\cdot}10^{-7}$ | 44 | -0.8800573 | -0.8823152 | -0.9680567 | -0.9521908 | -0.9363867 | 99.78 | 100.03 | 100.04 | 100.00 |
| $3.2{\cdot}10^{-8}$ | 59 | -0.8810168 | -0.8820921 | -0.9678336 | -0.9518889 | -0.9362604 | 99.89 | 100.01 | 100.01 | 99.99 |
| $1.0{\cdot}10^{-8}$ | 79 | -0.8815147 | -0.8820303 | -0.9677717 | -0.9518172 | -0.9362752 | 99.94 | 100.00 | 100.00 | 99.99 |
| pyrazole: | | | | | | | | | | |
| $3.2 \cdot 10^{-6}$ | 17 | -0.8862780 | -0.9097589 | -1.0042504 | -0.9883459 | -0.9699624 | 97.85 | 100.44 | 100.43 | 100.16 |
| $1.0 \cdot 10^{-6}$ | 26 | -0.8961889 | -0.9074048 | -1.0018963 | -0.9859164 | -0.9689265 | 98.94 | 100.18 | 100.19 | 100.06 |
| $3.2 \cdot 10^{-7}$ | 38 | -0.9011715 | -0.9063783 | -1.0008698 | -0.9847304 | -0.9683370 | 99.49 | 100.06 | 100.07 | 100.00 |
| $1.0 \cdot 10^{-7}$ | 52 | -0.9034978 | -0.9059330 | -1.0004245 | -0.9842721 | -0.9682172 | 99.75 | 100.02 | 100.02 | 99.98 |
| $3.2 \cdot 10^{-7}$ | 38 | -0.9011715 | -0.9063783 | -1.0008698 | -0.9847304 | -0.9683370 | 99.49 | 100.06 | 100.07 | 100.00 |
| $1.0 \cdot 10^{-8}$ | 90 | -0.9051697 | -0.9057277 | -1.0002192 | -0.9840498 | -0.9682488 | 99.93 | 99.99 | 100.00 | 99.99 |
| neopentane: | | | | | | | | | | |
| $3.2 \cdot 10^{-6}$ | 12 | -0.9503813 | -0.9717784 | -1.0614097 | -1.0446536 | -1.0253121 | 98.21 | 100.43 | 100.44 | 100.18 |
| $1.0 \cdot 10^{-6}$ | 18 | -0.9582202 | -0.9699654 | -1.0595967 | -1.0424906 | -1.0243705 | 99.02 | 100.24 | 100.23 | 100.08 |
| $3.2 \cdot 10^{-7}$ | 28 | -0.9634076 | -0.9686560 | -1.0582873 | -1.0411037 | -1.0236945 | 99.56 | 100.10 | 100.09 | 100.02 |
| $1.0 \cdot 10^{-7}$ | 39 | -0.9655509 | -0.9680923 | -1.0577235 | -1.0406702 | -1.0236770 | 99.78 | 100.04 | 100.05 | 100.02 |
| $3.2 \cdot 10^{-8}$ | 54 | -0.9665876 | -0.9678317 | -1.0574630 | -1.0402879 | -1.0234823 | 99.89 | 100.02 | 100.02 | 100.00 |
| $1.0 \cdot 10^{-8}$ | 74 | -0.9671300 | -0.9677289 | -1.0573602 | -1.0402020 | -1.0234830 | 99.94 | 100.01 | 100.01 | 100.00 |
| vinylacetate: | | | | | | | | | | |
| $3.2 \cdot 10^{-6}$ | 12 | -1.1355687 | -1.1630167 | -1.2892523 | -1.2676744 | -1.2444679 | 97.96 | 100.33 | 100.26 | 100.05 |
| $1.0 \cdot 10^{-6}$ | 17 | -1.1475204 | -1.1606599 | -1.2868955 | -1.2655401 | -1.2439329 | 98.99 | 100.13 | 100.09 | 100.01 |
| $3.2 \cdot 10^{-7}$ | 26 | -1.1534622 | -1.1595349 | -1.2857705 | -1.2645286 | -1.2434532 | 99.50 | 100.03 | 100.01 | 99.97 |
| $1.0 \cdot 10^{-7}$ | 36 | -1.1562874 | -1.1591471 | -1.2853827 | -1.2642965 | -1.2435193 | 99.75 | 99.99 | 99.99 | 99.97 |
| $3.2 \cdot 10^{-8}$ | 48 | -1.1576647 | -1.1590511 | -1.2852866 | -1.2641574 | -1.2435197 | 99.87 | 99.99 | 99.98 | 99.97 |
| $1.0 \cdot 10^{-8}$ | 65 | -1.1583903 | -1.1590480 | -1.2852835 | -1.2641906 | -1.2436080 | 99.93 | 99.99 | 99.99 | 99.98 |
| 2-hydroxypyridine: | | | | | | | | | | |
| $3.2 \cdot 10^{-6}$ | 14 | -1.2187833 | -1.2529258 | -1.3858727 | -1.3632434 | -1.3380931 | 97.70 | 100.43 | 100.39 | 100.14 |
| $1.0 \cdot 10^{-6}$ | 21 | -1.2328760 | -1.2497855 | -1.3827324 | -1.3604439 | -1.3370666 | 98.83 | 100.18 | 100.18 | 100.07 |
| $3.2 \cdot 10^{-7}$ | 30 | -1.2404057 | -1.2483004 | -1.3812473 | -1.3588742 | -1.3362394 | 99.43 | 100.06 | 100.06 | 100.01 |
| $1.0 \cdot 10^{-7}$ | 43 | -1.2438066 | -1.2476085 | -1.3805554 | -1.3581597 | -1.3359154 | 99.70 | 100.01 | 100.01 | 99.98 |
| $3.2 \cdot 10^{-8}$ | 59 | -1.2456006 | -1.2474319 | -1.3803788 | -1.3579572 | -1.3358991 | 99.85 | 99.99 | 100.00 | 99.98 |
| $1.0 \cdot 10^{-8}$ | 79 | -1.2465362 | -1.2474277 | -1.3803746 | -1.3579471 | -1.3359950 | 99.92 | 99.99 | 100.00 | 99.99 |
| cyclooctatetraene: | | | | | | | | | | |
| $3.2 \cdot 10^{-6}$ | 12 | -1.2909907 | -1.3253650 | -1.4554483 | -1.4310329 | -1.4041468 | 97.83 | 100.44 | 100.36 | 100.09 |
| $1.0 \cdot 10^{-6}$ | 19 | -1.3048292 | -1.3224385 | -1.4525218 | -1.4287884 | -1.4035891 | 98.88 | 100.21 | 100.20 | 100.05 |
| $3.2 \cdot 10^{-7}$ | 28 | -1.3120813 | -1.3206346 | -1.4507179 | -1.4270404 | -1.4028197 | 99.43 | 100.08 | 100.08 | 99.99 |
| $1.0 \cdot 10^{-7}$ | 40 | -1.3158189 | -1.3199744 | -1.4500576 | -1.4264143 | -1.4027848 | 99.71 | 100.03 | 100.03 | 99.99 |
| $3.2 \cdot 10^{-8}$ | 56 | -1.3176766 | -1.3196902 | -1.4497735 | -1.4260738 | -1.4027454 | 99.85 | 100.01 | 100.01 | 99.99 |
| $1.0 \cdot 10^{-8}$ | 77 | -1.3185653 | -1.3195531 | -1.4496363 | -1.4259336 | -1.4027286 | 99.92 | 100.00 | 100.00 | 99.99 |

TABLE II. OSV-LCCSD correlation energies (in $E_h$) and fraction of correlation energy (in percent) relative to the corresponding canonical methods for various test molecules. See main text for computational details.

| | | LCCSD Correlation energy | | | | | Fraction relative to canonical methods | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $l_{\mathrm{OSV}}$ | Av. dom. size | LCCSD | LCCSD +ΔMP | LCCSD +ΔMP2F12 | LCCSD -F12a | LCCSD -F12b | LCCSD | LCCSD +ΔMP2 | LCCSD -F12a | LCCSD -F12b |
| vinylcyclopropane: | | | | | | | | | | |
| $3.2 \cdot 10^{-4}$ | 40 | -0.8572795 | -0.8897582 | -0.9754997 | -0.9505702 | -0.9322966 | 97.19 | 100.88 | 99.87 | 99.57 |
| $1.0 \cdot 10^{-4}$ | 58 | -0.8728592 | -0.8847640 | -0.9705055 | -0.9510672 | -0.9344843 | 98.96 | 100.31 | 99.92 | 99.80 |
| $3.2 \cdot 10^{-5}$ | 80 | -0.8781915 | -0.8830388 | -0.9687802 | -0.9510553 | -0.9351470 | 99.57 | 100.11 | 99.92 | 99.87 |
| $1.0 \cdot 10^{-5}$ | 103 | -0.8803597 | -0.8823216 | -0.9680631 | -0.9513013 | -0.9356573 | 99.81 | 100.03 | 99.95 | 99.93 |
| $3.2 \cdot 10^{-6}$ | 126 | -0.8812556 | -0.8820584 | -0.9677999 | -0.9515077 | -0.9359699 | 99.91 | 100.00 | 99.97 | 99.96 |
| pyrazole: | | | | | | | | | | |
| $3.2 \cdot 10^{-4}$ | 42 | -0.8800531 | -0.9134562 | -1.0079477 | -0.9835456 | -0.9651661 | 97.16 | 100.85 | 99.95 | 99.67 |
| $1.0 \cdot 10^{-4}$ | 62 | -0.8960842 | -0.9083984 | -1.0028899 | -0.9831030 | -0.9663319 | 98.93 | 100.29 | 99.90 | 99.79 |
| $3.2 \cdot 10^{-5}$ | 87 | -0.9021531 | -0.9064633 | -1.0009548 | -0.9834789 | -0.9673544 | 99.60 | 100.07 | 99.94 | 99.89 |
| $1.0 \cdot 10^{-5}$ | 111 | -0.9041377 | -0.9058853 | -1.0003768 | -0.9835684 | -0.9676971 | 99.82 | 100.01 | 99.95 | 99.93 |
| $3.2 \cdot 10^{-6}$ | 137 | -0.9050651 | -0.9056678 | -1.0001593 | -0.9837666 | -0.9679873 | 99.92 | 99.99 | 99.97 | 99.96 |
| neopentane: | | | | | | | | | | |
| $3.2 \cdot 10^{-4}$ | 39 | -0.9385478 | -0.9765432 | -1.0661745 | -1.0372467 | -1.0176047 | 96.99 | 100.92 | 99.72 | 99.42 |
| $1.0 \cdot 10^{-4}$ | 55 | -0.9562379 | -0.9711872 | -1.0608185 | -1.0392183 | -1.0212102 | 98.82 | 100.36 | 99.91 | 99.78 |
| $3.2 \cdot 10^{-5}$ | 76 | -0.9627533 | -0.9690403 | -1.0586716 | -1.0390354 | -1.0219243 | 99.49 | 100.14 | 99.90 | 99.85 |
| $1.0 \cdot 10^{-5}$ | 98 | -0.9654689 | -0.9681941 | -1.0578253 | -1.0395326 | -1.0226952 | 99.77 | 100.05 | 99.94 | 99.92 |
| $3.2 \cdot 10^{-6}$ | 121 | -0.9666002 | -0.9678294 | -1.0574607 | -1.0397432 | -1.0230246 | 99.89 | 100.02 | 99.96 | 99.95 |
| vinylacetate: | | | | | | | | | | |
| $3.2 \cdot 10^{-4}$ | 40 | -1.1303606 | -1.1659137 | -1.2921492 | -1.2623654 | -1.2389413 | 97.51 | 100.58 | 99.84 | 99.60 |
| $1.0 \cdot 10^{-4}$ | 57 | -1.1478677 | -1.1613543 | -1.2875898 | -1.2625234 | -1.2409771 | 99.02 | 100.18 | 99.85 | 99.77 |
| $3.2 \cdot 10^{-5}$ | 77 | -1.1543152 | -1.1596525 | -1.2858881 | -1.2629747 | -1.2421054 | 99.58 | 100.04 | 99.89 | 99.86 |
| $1.0 \cdot 10^{-5}$ | 97 | -1.1569093 | -1.1591145 | -1.2853500 | -1.2634439 | -1.2428003 | 99.80 | 99.99 | 99.93 | 99.91 |
| $3.2 \cdot 10^{-6}$ | 117 | -1.1580574 | -1.1590279 | -1.2852635 | -1.2638184 | -1.2432504 | 99.90 | 99.98 | 99.96 | 99.95 |
| 2-hydroxypyridine: | | | | | | | | | | |
| $3.2 \cdot 10^{-4}$ | 42 | -1.2105331 | -1.2580909 | -1.3910378 | -1.3563721 | -1.3311058 | 97.03 | 100.85 | 99.88 | 99.62 |
| $1.0 \cdot 10^{-4}$ | 63 | -1.2332555 | -1.2511541 | -1.3841010 | -1.3561393 | -1.3330272 | 98.86 | 100.29 | 99.86 | 99.76 |
| $3.2 \cdot 10^{-5}$ | 88 | -1.2415763 | -1.2485975 | -1.3815444 | -1.3567500 | -1.3344168 | 99.52 | 100.09 | 99.91 | 99.87 |
| $1.0 \cdot 10^{-5}$ | 113 | -1.2447395 | -1.2477036 | -1.3806505 | -1.3570533 | -1.3350276 | 99.78 | 100.01 | 99.93 | 99.91 |
| $3.2 \cdot 10^{-6}$ | 137 | -1.2461703 | -1.2474410 | -1.3803879 | -1.3574136 | -1.3354871 | 99.89 | 99.99 | 99.96 | 99.95 |
| cyclooctatetraene: | | | | | | | | | | |
| $3.2 \cdot 10^{-4}$ | 42 | -1.2793261 | -1.3324440 | -1.4625273 | -1.4229178 | -1.3956219 | 96.95 | 100.97 | 99.79 | 99.48 |
| $1.0 \cdot 10^{-4}$ | 62 | -1.3033693 | -1.3244769 | -1.4545602 | -1.4233358 | -1.3986128 | 98.77 | 100.37 | 99.82 | 99.69 |
| $3.2 \cdot 10^{-5}$ | 87 | -1.3129552 | -1.3212191 | -1.4513024 | -1.4243137 | -1.4005948 | 99.50 | 100.12 | 99.88 | 99.83 |
| $1.0 \cdot 10^{-5}$ | 113 | -1.3164932 | -1.3201680 | -1.4502512 | -1.4249366 | -1.4016125 | 99.76 | 100.04 | 99.93 | 99.91 |
| $3.2 \cdot 10^{-6}$ | 140 | -1.3180545 | -1.3197029 | -1.4497862 | -1.4253042 | -1.4021339 | 99.88 | 100.01 | 99.95 | 99.94 |

TABLE III. PAO-LCCSD correlation energies (in $E_h$) and fraction of correlation energy (in percent) relative to the corresponding canonical methods for various test molecules. See main text for computational details. `EXT=0` and `EXT=1` mean standard and extended domains, respectively.

| | | LCCSD Correlation energy | | | | | Fraction relative to canonical methods | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Av. dom. | | LCCSD | LCCSD | LCCSD | LCCSD | | LCCSD | LCCSD | LCCSD |
| EXT | size | LCCSD | +ΔMP | +ΔMP2F12 | -F12a | -F12b | LCCSD | +ΔMP2 | -F12a | -F12b |
| vinylcyclopropane: | | | | | | | | | | |
| 0 | 122 | -0.8715222 | -0.8834722 | -0.9692136 | -0.9520043 | -0.9354318 | 98.81 | 100.16 | 100.02 | 99.90 |
| 1 | 242 | -0.8807000 | -0.8822389 | -0.9679803 | -0.9518835 | -0.9362616 | 99.85 | 100.02 | 100.01 | 99.99 |
| pyrazole: | | | | | | | | | | |
| 0 | 148 | -0.8981592 | -0.9066990 | -1.0011905 | -0.9842614 | -0.9677813 | 99.16 | 100.10 | 100.02 | 99.94 |
| 1 | 245 | -0.9048975 | -0.9058896 | -1.0003811 | -0.9840962 | -0.9682829 | 99.90 | 100.01 | 100.00 | 99.99 |
| neopentane: | | | | | | | | | | |
| 0 | 116 | -0.9548656 | -0.9693512 | -1.0589825 | -1.0402329 | -1.0222713 | 98.68 | 100.17 | 100.01 | 99.88 |
| 1 | 237 | -0.9652763 | -0.9680287 | -1.0576600 | -1.0401976 | -1.0232831 | 99.75 | 100.04 | 100.01 | 99.98 |
| vinylacetate: | | | | | | | | | | |
| 0 | 130 | -1.1493838 | -1.1601452 | -1.2863808 | -1.2643533 | -1.2429066 | 99.15 | 100.08 | 100.00 | 99.92 |
| 1 | 241 | -1.1576671 | -1.1593584 | -1.2855939 | -1.2643738 | -1.2436985 | 99.87 | 100.01 | 100.00 | 99.99 |
| 2-hydroxypyridine: | | | | | | | | | | |
| 0 | 154 | -1.2352373 | -1.2489259 | -1.3818728 | -1.3580715 | -1.3350916 | 99.01 | 100.11 | 100.00 | 99.92 |
| 1 | 286 | -1.2455548 | -1.2477120 | -1.3806589 | -1.3580464 | -1.3359910 | 99.84 | 100.01 | 100.00 | 99.99 |
| cyclooctatetraene: | | | | | | | | | | |
| 0 | 165 | -1.3053178 | -1.3214753 | -1.4515586 | -1.4262007 | -1.4016349 | 98.92 | 100.14 | 100.02 | 99.91 |
| 1 | 314 | -1.3171319 | -1.3199304 | -1.4500137 | -1.4260434 | -1.4026930 | 99.81 | 100.02 | 100.01 | 99.98 |

TABLE IV. Statistical errors of reaction energies (in kJ/mol) for 52 reactions of closed-shell molecules relative to the corresponding canonical results with the same basis set (VTZ-F12). In the PNO and OSV cases the domains have been determined from the natural occupation numbers (see text) using thresholds $l_{\mathrm{PNO}}$ and $l_{\mathrm{OSV}}$, respectively. Approximate LMP2 amplitudes according to eq. (48) of the main text have been used to determine the PNOs and OSVs.

| | LCCSD | | LCCSD+ΔMP2 | | LCCSD-F12a | | LCCSD-F12b | |
|---|---|---|---|---|---|---|---|---|
| Threshold | MAX | RMS | MAX | RMS | MAX | RMS | MAX | RMS |
| PNO ($l_{\mathrm{PNO}}$): | | | | | | | | |
| $3.2 \cdot 10^{-6}$ | 15.6 | 6.7 | 3.3 | 1.1 | 8.6 | 1.9 | 7.1 | 1.7 |
| $1.0 \cdot 10^{-6}$ | 15.0 | 4.4 | 2.4 | 0.9 | 5.1 | 1.3 | 5.1 | 1.4 |
| $3.2 \cdot 10^{-7}$ | 6.5 | 2.3 | 2.0 | 0.6 | 5.0 | 1.1 | 4.9 | 1.1 |
| $1.0 \cdot 10^{-7}$ | 4.8 | 1.3 | 1.4 | 0.5 | 2.8 | 0.7 | 2.7 | 0.7 |
| OSV ($l_{\mathrm{OSV}}$): | | | | | | | | |
| $1.0 \cdot 10^{-6}$ | 14.4 | 4.8 | 4.5 | 1.3 | 9.4 | 2.5 | 10.3 | 2.7 |
| $3.2 \cdot 10^{-7}$ | 6.9 | 2.3 | 2.1 | 0.7 | 3.9 | 1.2 | 4.1 | 1.2 |
| $1.0 \cdot 10^{-7}$ | 3.8 | 1.2 | 2.1 | 0.6 | 2.6 | 0.8 | 2.6 | 0.8 |
| $3.2 \cdot 10^{-8}$ | 2.4 | 0.8 | 2.1 | 0.5 | 2.1 | 0.5 | 2.1 | 0.6 |

TABLE V. Statistical errors of reaction energies (in kJ/mol) for 52 reactions of closed-shell molecules relative to extrapolated CCSD-F12b/C complete basis set estimates.[a] In the PNO and OSV cases the domains have been determined from the natural occupation numbers (see text) using thresholds $l_{\mathrm{PNO}}$ and $l_{\mathrm{OSV}}$, respectively. Approximate LMP2 amplitudes according to eq. (48) of the main text have been used to determine the PNOs and OSVs.

| | LCCSD | | LCCSD+ΔMP2 | | LCCSD-F12a | | LCCSD-F12b | | LCCSD+ΔLMP2F12 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Threshold | MAX | RMS | MAX | RMS | MAX | RMS | MAX | RMS | MAX | RMS |
| PNO ($l_{\mathrm{PNO}}$): | | | | | | | | | | |
| $3.2 \cdot 10^{-6}$ | 20.3 | 9.3 | 11.2 | 3.7 | 5.8 | 1.4 | 5.1 | 1.5 | 6.5 | 1.6 |
| $1.0 \cdot 10^{-6}$ | 14.1 | 6.4 | 11.9 | 3.8 | 2.3 | 0.8 | 4.1 | 1.0 | 2.6 | 0.8 |
| $3.2 \cdot 10^{-7}$ | 13.7 | 5.4 | 12.1 | 4.0 | 2.2 | 0.6 | 2.9 | 0.8 | 1.7 | 0.6 |
| $1.0 \cdot 10^{-7}$ | 12.7 | 4.6 | 11.8 | 4.1 | 2.1 | 0.5 | 2.0 | 0.5 | 2.2 | 0.7 |
| OSV ($l_{\mathrm{OSV}}$): | | | | | | | | | | |
| $1.0 \cdot 10^{-6}$ | 18.0 | 6.7 | 11.8 | 3.9 | 6.5 | 2.1 | 8.3 | 2.5 | 4.9 | 1.9 |
| $3.2 \cdot 10^{-7}$ | 13.1 | 5.5 | 11.8 | 4.0 | 3.8 | 1.2 | 3.8 | 1.3 | 3.7 | 1.1 |
| $1.0 \cdot 10^{-7}$ | 13.0 | 4.8 | 11.7 | 4.0 | 3.2 | 1.0 | 3.0 | 1.0 | 3.4 | 1.0 |
| $3.2 \cdot 10^{-8}$ | 12.2 | 4.5 | 11.5 | 4.1 | 2.2 | 0.7 | 2.0 | 0.7 | 2.5 | 0.8 |

[a] Reference values from Ref. 42 of main text.