# Supporting Information for "State-Targeted Energy Projection: A Simple and Robust Approach to Orbital Relaxation of Non-Aufbau Self-Consistent Field Solutions"

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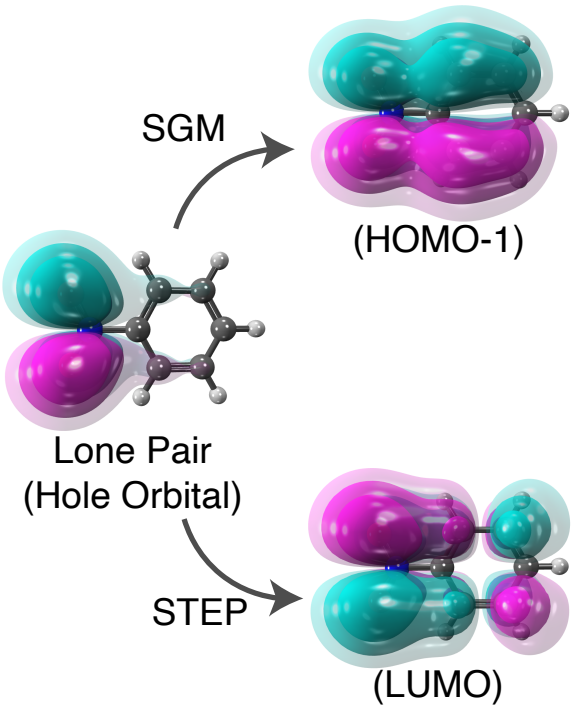


Figure S1: Left: the $n_\pi$ MO in nitrobenzene as the hole in the ground state initial guess for $n_\pi \rightarrow \pi^*$ excitation. Right: the same orbital with corresponding MO index after optimization using SGM (top) and STEP (bottom). Using SGM, the $n_\pi$ MO becomes part of the occupied space (HOMO $-$ 1) following optimization, whereas with STEP this orbital remains unoccupied, showing up as the LUMO.

Table S1: Excitation Energies (in eV) for $H_2CO$, aug-cc-pVTZ Basis Set.

| Transition | STEP | | | | | | CIS | CIS(D) | TBE[a] | Expt.[b] |
|---|---|---|---|---|---|---|---|---|---|---|
| | $\omega$B97X-V | B97M-V | B3LYP | BLYP | HF | MP2[c] | | | | |
| $n \rightarrow \pi^*$ ($^1A_2$) | 3.53 | 3.47 | 3.41 | 3.43 | 2.58 | 4.20 | 4.53 | 4.03 | 3.97 | 4.07 |
| $n \rightarrow$ 3s ($^1B_2$) | 7.19 | 6.96 | 6.92 | 6.77 | 6.01 | 7.69 | 8.62 | 6.44 | 7.30 | 7.11 |
| $n \rightarrow$ 3p ($^1B_2$) | 8.11 | 7.91 | 7.74 | 7.56 | 6.92 | 8.69 | 9.37 | 7.26 | 8.14 | 7.97 |
| $n \rightarrow$ 3p ($^1A_1$) | 8.17 | 7.91 | 7.77 | 7.61 | 6.98 | 8.69 | 9.76 | 7.48 | 8.27 | 8.14 |
| $n \rightarrow$ 3p ($^1A_2$) | 8.64 | 8.57 | 8.30 | 8.11 | 6.98 | 8.58 | 9.50 | 7.99 | 8.50 | 8.37 |
| $n \rightarrow \pi^*$ ($^3A_2$) | 3.36 | 3.25 | 3.26 | 3.29 | 2.47 | 3.97 | 3.71 | 3.54 | 3.58 | 3.50 |
| $\pi \rightarrow \pi^*$ ($^3A_1$) | 6.00 | 5.86 | 5.91 | 6.18 | 4.26 | 6.36 | 4.79 | 6.17 | 6.07 | 5.86 |
| $n \rightarrow$ 3s ($^3B_2$) | 7.14 | 6.81 | 6.86 | 6.69 | 6.00 | 7.64 | 8.30 | 6.46 | 7.14 | 6.83 |
| $n \rightarrow$ 3p ($^3B_2$) | 8.06 | 7.75 | 7.68 | 7.48 | 6.92 | 8.49 | 9.07 | 7.27 | 7.96 | 7.79 |
| $n \rightarrow$ 3p ($^3A_1$) | 8.13 | 7.79 | 7.72 | 7.50 | 6.93 | 8.65 | 9.72 | 7.65 | 8.15 | 7.96 |
| $n \rightarrow$ 3d ($^3B_1$) | 8.66 | 8.57 | 8.32 | 8.12 | 7.59 | 9.15 | 9.31 | 7.33 | 8.42 | 8.16 |
| MAD(TBE) | 0.13 | 0.28 | 0.33 | 0.45 | 1.26 | 0.43 | 1.07 | 0.56 | — | — |
| Max(TBE) | 0.44 | 0.50 | 0.56 | 0.71 | 1.81 | 0.73 | 1.57 | 1.09 | — | — |
| MAD(Expt.) | 0.24 | 0.19 | 0.21 | 0.33 | 1.10 | 0.59 | 1.19 | 0.44 | — | — |
| Max(Expt.) | 0.54 | 0.60 | 0.66 | 0.64 | 1.60 | 0.99 | 1.76 | 0.83 | — | — |

[a] Theoretical best estimates, from Ref. 1.

[b] Experimental data from Ref. 2.

[c] Frozen core.

Table S2: Spin-Purified Singlet Excitation Energies (in eV) for $H_2CO$.

| Transition | STEP-Based ΔSCF[a] | | | | | TBE[b] | Expt.[c] |
|---|---|---|---|---|---|---|---|
| | ωB97X-V | B97M-V | B3LYP | BLYP | HF | | |
| $n \rightarrow \pi^*$ ($^1A_2$) | 3.69 | 3.70 | 3.56 | 3.58 | 2.68 | 3.97 | 4.07 |
| $n \rightarrow 3s$ ($^1B_2$) | 7.24 | 7.11 | 6.98 | 6.84 | 6.03 | 7.30 | 7.11 |
| $n \rightarrow 3p$ ($^1B_2$) | 8.17 | 8.06 | 7.80 | 7.64 | 6.93 | 8.14 | 7.97 |
| $n \rightarrow 3p$ ($^1A_1$) | 8.21 | 8.02 | 7.81 | 7.72 | 7.03 | 8.27 | 8.14 |
| $n \rightarrow 3p$ ($^1A_2$) | 8.63 | 8.56 | 8.29 | 8.10 | 6.37 | 8.50 | 8.37 |
| ΔMAD(TBE) | −0.05 | −0.13 | −0.06 | −0.08 | +0.09 | — | — |
| ΔMAD(Expt.) | −0.01 | −0.09 | −0.06 | −0.08 | +0.09 | — | — |

[a] aug-cc-pVTZ basis set.

[b] Theoretical best estimates, from Ref. 1.

[c] Experimental data from Ref. 2.

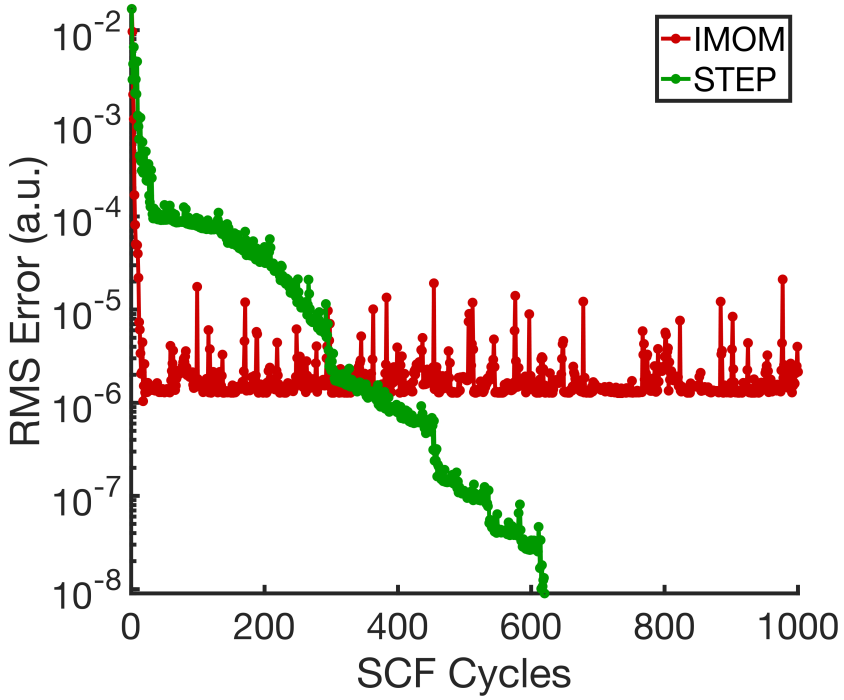


Figure S2: Convergence of the RMS error with respect to SCF cycles for IMOM and STEP algorithms for the core-ionized $[O(1s)]^{-1}$ state of $N_2O$ (UHF/cc-pCVTZ).

## References

[1] Loos, P.-F.; Scemama, A.; Blondel, A.; Garniron, Y.; Caffarel, M.; Jacquemin, D. A mountaineering strategy to excited states: Highly accurate reference energies and benchmarks. *J. Chem. Theory Comput.* **2018,** *14,* 4360–4379.

[2] Robin, M. R. *Higher Excited States of Polyatomic Molecules;* volume III Academic Press: New York, 1985.