Supporting Information: Projection-based Density Matrix Renormalization Group in Density Functional Theory Embedding

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Propionitrile (CH₃CH₂CN) C-N bond stretching

Table S1: Equilibrium geometry of CH₃CH₂CN, XYZ in Å.

|       |      |      |       |
|-------|------|------|-------|
| C     | -2.38207 | -0.46087 | 0.01893 |
| N     | -3.18147 | -0.80786 | 0.76930 |
| H     | -0.03176 | 0.93909  | 0.54131 |
| C     | 0.02231  | 0.17867  | -0.25262 |
| H     | 0.75941  | 0.50795  | -1.00054 |
| H     | 0.38038  | -0.75999 | 0.19640 |
| C     | -1.34723 | -0.01758 | -0.92251 |
| H     | -1.69162 | 0.92161  | -1.38724 |
| H     | -1.28110 | -0.76419 | -1.73200 |

Figure S1: Comparison of DMRG-in-DFT dissociation energy curves with different DFT functionals (B3LYP, PBE0, PBE) corresponding to the triple C-N bond stretching in CH₃CH₂CN. All calculations employ the cc-pVDZ basis set.
Table S2: Absolute energies of CH$_3$CH$_2$CN for a given C-N bond length (in Å). All calculations were performed in the cc-pVDZ basis, energies are listed in a.u., and FC denotes the frozen-core approximation. DMRG(FC) calculations were performed with the DBSS procedure and TRE=$10^{-5}$.

| $r_{C-N}$ | B3LYP   | CCSD    | CCSD-in-B3LYP | DMRG(FC) |
|----------|---------|---------|---------------|----------|
| 0.85     | -171.618382 | -171.106586 | -171.337520  | -171.11161047  |
| 1.00     | -171.891004  | -171.492235 | -171.723038  | -171.50086928  |
| 1.15     | -172.075359  | -171.584162 | -171.814725  | -171.59716505  |
| 1.30     | -172.043567  | -171.556873 | -171.786935  | -171.57557639  |
| 1.45     | -171.971320  | -171.487757 | -171.717006  | -171.51378665  |
| 1.60     | -171.891661  | -171.411147 | -171.639154  | -171.44582726  |
| 1.75     | -171.818215  | -171.344743 | -171.567481  | -171.38558935  |
| 1.90     | -171.755710  | -171.288331 | -171.506139  | -171.33720854  |
| 2.05     | -171.705096  | -171.239879 | -171.454591  | -171.30076817  |
| 2.20     | -171.665708  | -171.199782 | -171.411130  | -171.27519061  |
| 2.35     | -171.636018  | -171.168898 | -171.374676  | -171.25875127  |
| 2.50     | -171.614037  | -171.148550 | -171.344320  | -171.24910098  |

| $r_{C-N}$ | DMRG-in-B3LYP | DMRG-in-PBE | DMRG-in-PBE0 | DMRG(FC) |
|----------|----------------|-------------|--------------|----------|
| 0.85     | -171.341987   | -171.21918  | -171.24037   | -171.11161047  |
| 1.00     | -171.730008   | -171.60788  | -171.62800   | -171.50086928  |
| 1.15     | -171.825192   | -171.70209  | -171.72315   | -171.59716505  |
| 1.30     | -171.802364   | -171.67906  | -171.70089   | -171.57557639  |
| 1.45     | -171.738241   | -171.61693  | -171.63709   | -171.51378665  |
| 1.60     | -171.668690   | -171.54621  | -171.56718   | -171.44582726  |
| 1.75     | -171.605607   | -171.48355  | -171.50454   | -171.38558935  |
| 1.90     | -171.553929   | -171.43037  | -171.45251   | -171.33720854  |
| 2.05     | -171.513078   | -171.39197  | -171.41332   | -171.30076817  |
| 2.20     | -171.481714   | -171.36223  | -171.38363   | -171.27519061  |
| 2.35     | -171.458972   | -171.34112  | -171.36242   | -171.25875127  |
| 2.50     | -171.442953   | -171.32648  | -171.34336   | -171.24910098  |

[Fe(CN)$_5$(NO)]$^{2-}$ complex conformational isomerization

Geometries

Source: SI of Daniel, C.; Gourlaouen, C. Structural and Optical Properties of Metal-Nitrosyl Complexes. Molecules 2019, 24, 3638.
Table S3: Geometry of the standard isomer of [Fe(CN)$_5$(NO)]$^{2-}$ complex, XYZ in Å.

|    | XYZ in Å               |
|----|------------------------|
| Fe | 0.00149500  -0.00106700 -0.09336900 |
| C  | -0.03222200  0.02103400  1.86410100 |
| C  | -1.75416100  0.85771400  0.02002800 |
| C  | 0.85659200   1.75411800  0.05268600 |
| C  | 1.75258100   -0.85664900 0.09511900 |
| C  | -0.85785400  -1.75326800 0.06284700 |
| N  | -0.05222500  0.03386700  3.03384600 |
| N  | 2.80100800   -1.36744800 0.19103400 |
| N  | -1.37158600  -2.80173800 0.14115000 |
| N  | 1.36881800   2.80371400  0.12573200 |
| N  | -2.80414500  1.37165900  0.07265600 |
| N  | 0.02861100   -0.01928200 -1.73124100 |
| O  | 0.04726700   -0.03192100 -2.87166600 |

Table S4: Geometry of the flat isomer of [Fe(CN)$_5$(NO)]$^{2-}$ complex, XYZ in Å.

|    | XYZ in Å               |
|----|------------------------|
| Fe | -0.00016900  0.02806300 -0.12906000 |
| C  | 0.00035300   -0.17615400 1.76755000 |
| C  | -1.38040600  1.40923600  0.04432800 |
| C  | 1.37930400   1.41018200  0.04440300 |
| C  | 1.48359600   -1.27200700 -0.02254300 |
| C  | -1.48287100  -1.27288100 -0.02213100 |
| N  | 0.00074600   -0.27164900 2.93388700 |
| N  | 2.36724000   -2.03798600 0.03986000 |
| N  | -2.36594400  -2.03946500 0.04094100 |
| N  | 2.19600000   2.24404000  0.13982500 |
| N  | -2.19754400  2.24305200  0.13952600 |
| N  | 0.00022500   -0.74637000 -1.85226200 |
| O  | -0.00006700  0.36702500  -2.20081400 |
Table S5: Geometry of the reverse isomer of $[\text{Fe(CN)}_5(\text{NO})]^2-$ complex, XYZ in Å.

|   | X   | Y   | Z   |
|---|-----|-----|-----|
| Fe| -0.00060500 | 0.00018400 | -0.05436100 |
| C | 0.03567000  | -0.02895700 | 1.86383700  |
| C | -1.53095900 | 1.21983800  | 0.09791900  |
| C | 1.22394800  | 1.53034400  | 0.04912800  |
| C | 1.53359200  | -1.22166100 | 0.00102400  |
| C | -1.21846800 | -1.53465800 | 0.04870100  |
| N | 0.05817700  | -0.04746800 | 3.03450200  |
| N | 2.44981100  | -1.95160100 | 0.02040000  |
| N | -1.94702900 | -2.45095200 | 0.09594500  |
| N | 1.95614400  | 2.44363500  | 0.09789000  |
| N | -2.44506900 | 1.94860300  | 0.17478400  |
| O | -0.03787600 | 0.03041200  | -1.80130200 |
| N | -0.06403000 | 0.05242500  | -2.92921600 |
Energies

Table S6: Absolute energies (in a.u.) of standard, flat, and reverse isomers of [Fe(CN)\(_5\)(NO)]\(^{2-}\) complex in 6-31G basis.

|             | standard        | flat            | reverse         |
|-------------|-----------------|-----------------|-----------------|
| B3LYP       | -1857.204433    | -1857.139493    | -1857.134402    |
| CCSD\(^{a}\) | -1854.298712    | -1854.235608    | -1854.224112    |
| CCSD\(^{b}\) | -1854.344365    | -1854.275324    | -1854.278839    |
| CASSCF(14,15)| -1852.95065     | -1852.890706    | -1852.905416    |
| NEVPT2(14,15)| -1854.268748    | -1854.184329    | -1854.219546    |
| AC0(14,15)  | -1854.294758    | -1854.208607    | -1854.251568    |
| AC(14,15)   | -1854.089513    | -1854.008786    | -1854.047418    |
| DMRG-SCF(16,16)| -1852.997355    | -1852.930239    | -1852.953831    |
| AC0(16,16)  | -1854.304948    | -1854.224917    | -1854.251228    |
| AC(16,16)   | -1854.107123    | -1854.028369    | -1854.05652     |
| icMRCISD(4,4)| -1853.756956    | -1853.680976    | -1853.703916    |
| CCSD-in-B3LYP | -1856.113810    | -1856.067165    | -1856.045671    |
| CCSD-in-HF  | -1853.102533    | -1853.052473    | -1853.024501    |
| DMRG-in-B3LYP | -1856.159181    | -1856.088551    | -1856.116160    |
| DMRG-in-PBE0 | -1855.606274    | -1855.536965    | -1855.559453    |
| DMRG-in-HF  | -1853.146749    | -1853.072713    | -1853.093745    |

\(^{a}\)CCSD performed in\( \text{Orca}\) preceeded by HF with DIIS convergence acceleration.

\(^{b}\)CCSD performed in\( \text{Q-Chem}\) preceeded by HF with GDM convergence acceleration.

Natural orbitals of [Fe(CN)\(_5\)(NO)]\(^{2-}\) complex

![Natural orbitals of Fe-NO complex](image)

(1) \(n_{\text{ occup }} = 1.8235\)  (2) \(n_{\text{ occup }} = 1.8231\)  (3) \(n_{\text{ occup }} = 0.1765\)  (4) \(n_{\text{ occup }} = 0.1765\)

Figure S2: Fe-NO complex, standard, CASSCF(4,4)
Figure S3: Fe-NO complex, flat, CASSCF(4, 4)

(1) $n_{\text{occup}} = 1.9024$
(2) $n_{\text{occup}} = 1.6449$
(3) $n_{\text{occup}} = 0.3550$
(4) $n_{\text{occup}} = 0.0977$

Figure S4: Fe-NO complex, reverse, CASSCF(4, 4)

(1) $n_{\text{occup}} = 1.6793$
(2) $n_{\text{occup}} = 1.6679$
(3) $n_{\text{occup}} = 0.3321$
(4) $n_{\text{occup}} = 0.3207$
Figure S5: Fe-NO complex, standard, CASSCF(14, 15)
Figure S6: Fe-NO complex, flat, CASSCF(14, 15)
Figure S7: Fe-NO complex, reverse, CASSCF(14, 15)
Figure S8: Fe-NO complex, standard, DMRG-SCF(16, 16)
Figure S9: Fe-NO complex, flat, DMRG-SCF(16, 16)
Figure S10: Fe-NO complex, reverse, DMRG-SCF(16, 16)