

Supporting information

Mn₂ dimers encapsulated in silicon cages: a complex challenge to MC-SCF theory

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Functional dependence of Mn-Mn bond lengths in Mn₂Si₁₀, Mn₂Si₁₂ and [Mn₂Si₁₃]⁺

In order to explore the functional dependence of geometry, and in particular the Mn-Mn bond length, we have re-optimised the geometries using hybrid functionals (B3LYP, PBE0), a metaGGA (SCAN) and a metahybrid (TPSSH).

Table S1 Optimized Mn-Mn bond lengths (in Angstrom) in Mn₂Si₁₀, Mn₂Si₁₂ and [Mn₂Si₁₃]⁺ using the PBE, SCAN, B3LYP, PBE0 and TPSSH functionals.

| | PBE | SCAN | B3LYP | PBE0 | TPSSH |
|--|------|------|-------|------|-------|
| Mn ₂ Si ₁₀ | 2.36 | 2.38 | 2.44 | 2.42 | 2.37 |
| Mn ₂ Si ₁₂ | 2.26 | 2.28 | 2.40 | 2.41 | 2.27 |
| [Mn ₂ Si ₁₃] ⁺ | 2.35 | 2.36 | 2.44 | 2.42 | 2.36 |

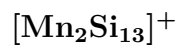
Cartesian coordinates used in RAS/GAS calculations on $\text{Mn}_2\text{Si}_{10}$, $\text{Mn}_2\text{Si}_{12}$ and $[\text{Mn}_2\text{Si}_{13}]^+$ (optimized with the PBE functional)

$\text{Mn}_2\text{Si}_{10}$

| | | | |
|----|-------------|-------------|-------------|
| Mn | 0.11795933 | -0.11381712 | -0.00000000 |
| Mn | 2.46729237 | 0.13738000 | -0.00000000 |
| Si | -1.07737015 | 0.58436286 | 2.03365367 |
| Si | 1.06641812 | 1.55021925 | 1.37903040 |
| Si | -0.99480515 | -1.79119004 | 1.26655830 |
| Si | -1.07737015 | 0.58436286 | -2.03365367 |
| Si | -0.99480515 | -1.79119004 | -1.26655830 |
| Si | 1.40583470 | -1.42508757 | 1.43245794 |
| Si | -1.00444419 | 2.10847172 | -0.00000000 |
| Si | 1.06641812 | 1.55021925 | -1.37903040 |
| Si | 1.40583470 | -1.42508757 | -1.43245794 |
| Si | -2.38096254 | 0.03135638 | -0.00000000 |

$\text{Mn}_2\text{Si}_{12}$

| | | | |
|----|-------------|-------------|-------------|
| Mn | 0.00000000 | 0.00000000 | -0.40922965 |
| Mn | 0.00000000 | 0.00000000 | 1.84690040 |
| Si | 2.10442167 | -1.21498842 | -1.37422324 |
| Si | 2.10442167 | 1.21498842 | -1.37422324 |
| Si | 0.00000000 | -2.42997684 | -1.37422324 |
| Si | 0.00000000 | 2.42997684 | -1.37422324 |
| Si | -2.10442167 | -1.21498842 | -1.37422324 |
| Si | -2.10442167 | 1.21498842 | -1.37422324 |
| Si | 2.41883792 | 0.00000000 | 0.87072311 |
| Si | 1.20941896 | 2.09477509 | 0.87072311 |
| Si | 1.20941896 | -2.09477509 | 0.87072311 |
| Si | -1.20941896 | 2.09477509 | 0.87072311 |
| Si | -1.20941896 | -2.09477509 | 0.87072311 |
| Si | -2.41883792 | 0.00000000 | 0.87072311 |



| | | | |
|----|--------------|--------------|--------------|
| Mn | 0.000000000 | 0.000000000 | 0.380000000 |
| Mn | 0.000000000 | 0.000000000 | -1.972152290 |
| Si | 2.048763690 | -1.182854270 | -0.823965660 |
| Si | 2.048763690 | 1.182854270 | -0.823965660 |
| Si | 0.000000000 | -2.365708530 | -0.823965660 |
| Si | 0.000000000 | 2.365708530 | -0.823965660 |
| Si | -2.048763690 | -1.182854270 | -0.823965660 |
| Si | -2.048763690 | 1.182854270 | -0.823965660 |
| Si | 2.446465770 | 0.000000000 | 1.344989400 |
| Si | 1.223232880 | 2.118701500 | 1.344989400 |
| Si | 1.223232880 | -2.118701500 | 1.344989400 |
| Si | -1.223232880 | 2.118701500 | 1.344989400 |
| Si | -1.223232880 | -2.118701500 | 1.344989400 |
| Si | -2.446465770 | 0.000000000 | 1.344989400 |
| Si | 0.000000000 | 0.000000000 | 2.651539260 |