

Exploiting Multiple Symmetry-Broken SCF Solutions to Describe Ground and Excited States of Transition–Metal Complexes

Low-Lying UHF Solutions and NOCI Wavefunctions of Model Octahedral $[\text{VF}_6]^{3-}$

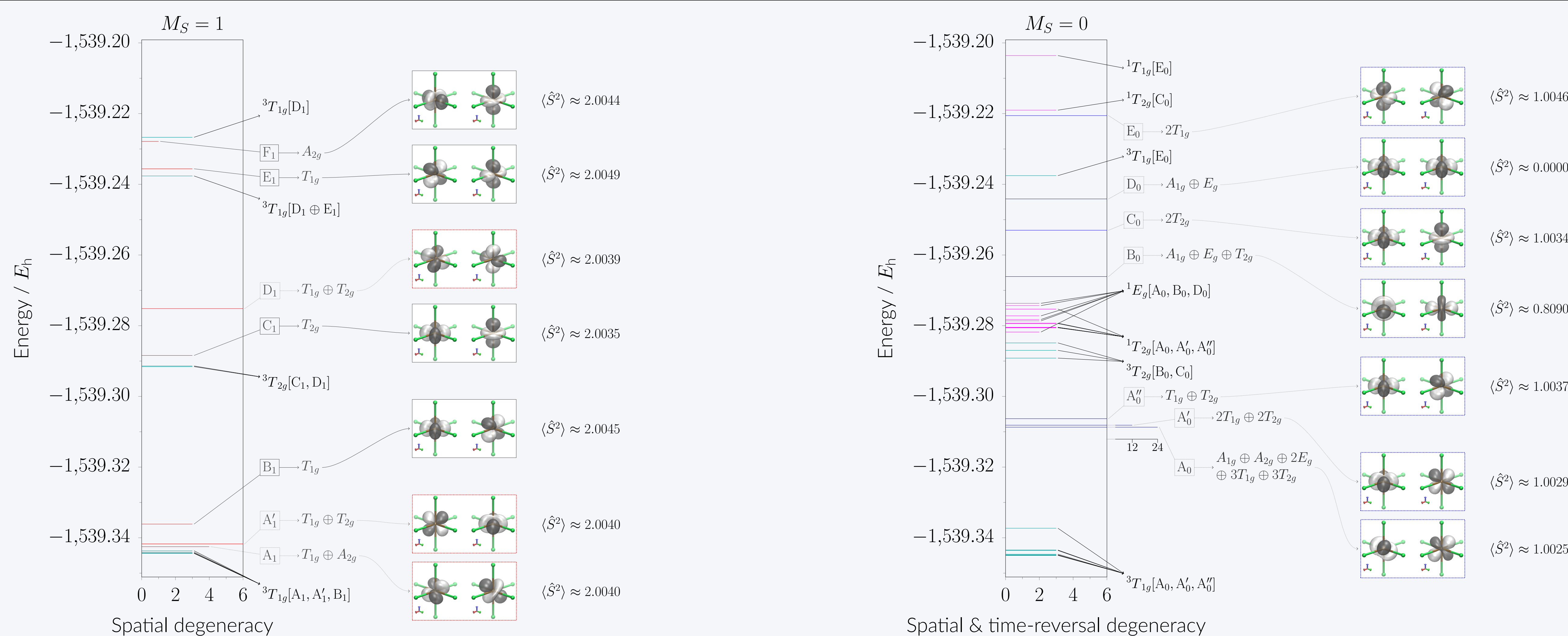


Figure 1. Energy and symmetry of low-lying UHF solutions and NOCI wavefunctions constructed from them in octahedral $[\text{VF}_6]^{3-}$.

\mathcal{S}_{M_S} : symmetry-conserved UHF set S with \hat{S}_z eigenvalue M_S . \mathcal{S}_{M_S} : spatial or spin symmetry-broken UHF set S with \hat{S}_z eigenvalue M_S .

$\Gamma[A \oplus B \oplus C]$: a specific NOCI set of symmetry Γ constructed from all of A , B , and C . $\Gamma[A, B, C]$: multiple NOCI sets of symmetry Γ constructed from all non-trivial combinations of A , B , and C .

Introduction

Transition-metal complexes are strongly correlated as they have many low-energy electronic states that exhibit high degrees of degeneracy by virtue of d electrons. Figure 2 gives such states for octahedral d^2 as an example.

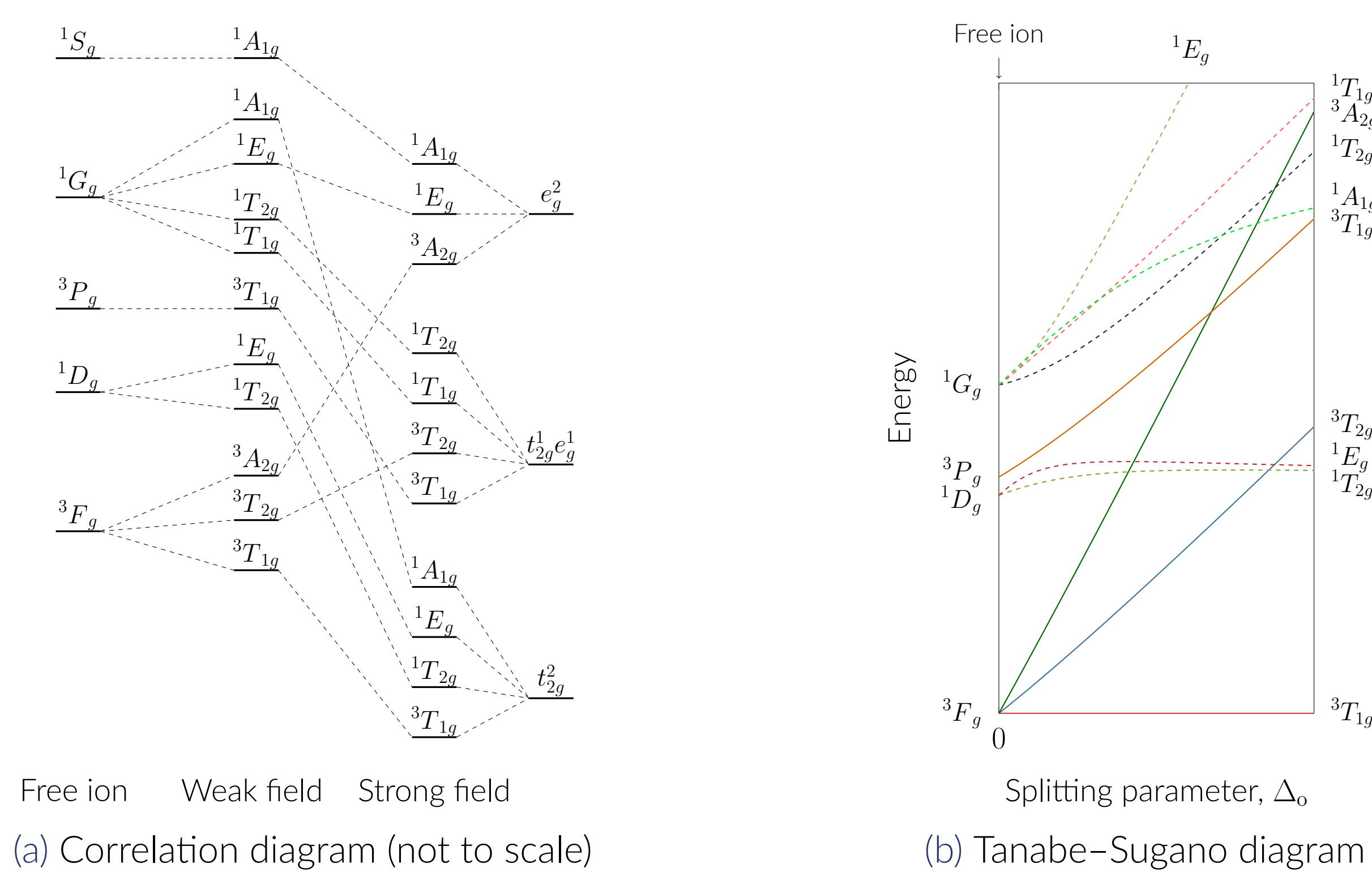


Figure 2. All electronic terms of a true d^2 system in an octahedral field.

The non-linear HF equations for these complexes are therefore expected to admit multiple low-lying and degenerate or nearly degenerate solutions that are physically significant.

We have located these solutions using SCF metadynamics¹ and investigated their symmetry properties in a model octahedral $[\text{VF}_6]^{3-}$ system (Figure 1).

Symmetry Breaking in HF

Each degenerate set of exact solutions to the spinless electronic Schrödinger equation *must* transform as a single irreducible representation (irrep) of the underlying point group \mathcal{B} , the spin rotation group $\text{SU}(2)$, and the time reversal group \mathcal{T} .

The approximated nature of HF does not guarantee this, however. Specifically, UHF wavefunctions are not necessarily eigenfunctions of \hat{S}^2 nor do they and their degenerate partners have to transform as a single irreducible representation of \mathcal{B} .

Thus, consider a degenerate set $S = \{\Psi^w \mid w = 1, 2, \dots\}$ and a particular group \mathcal{G} :

- if S spans a single irrep in \mathcal{G} , then S is **symmetry-conserved** in \mathcal{G} ;
- if S spans a representation that can be reduced to multiple irreps in \mathcal{G} , then S is **symmetry-broken** in \mathcal{G} .

HF solutions break symmetry to become lower in energy and possibly recover some electron correlation. Restoring symmetry of symmetry-broken HF solutions allows us to form physically meaningful wavefunctions while incorporating said correlation.

Non-Orthogonal Configuration Interaction (NOCI)

For a symmetry-broken set $S = \{\Psi^w \mid w = 1, 2, \dots\}$, solving the generalised eigenvalue equation

$$\mathbf{H}\mathbf{A} = \mathbf{S}\mathbf{A}\mathbf{E} \quad \text{where} \quad (\mathbf{H})_{wx} = \langle \Psi^w | \hat{\mathcal{H}} | \Psi^x \rangle \quad \text{and} \quad (\mathbf{S})_{wx} = \langle \Psi^w | \Psi^x \rangle$$

gives coefficients A_{wm} such that the NOCI wavefunctions

$${}^m\Phi = \sum_w \Psi^w A_{wm}$$

can be segregated into symmetry-conserved sets. These can then be used to approximate actual electronic terms of the corresponding symmetry.

UHF vs. NOCI: Jahn–Teller Distortion

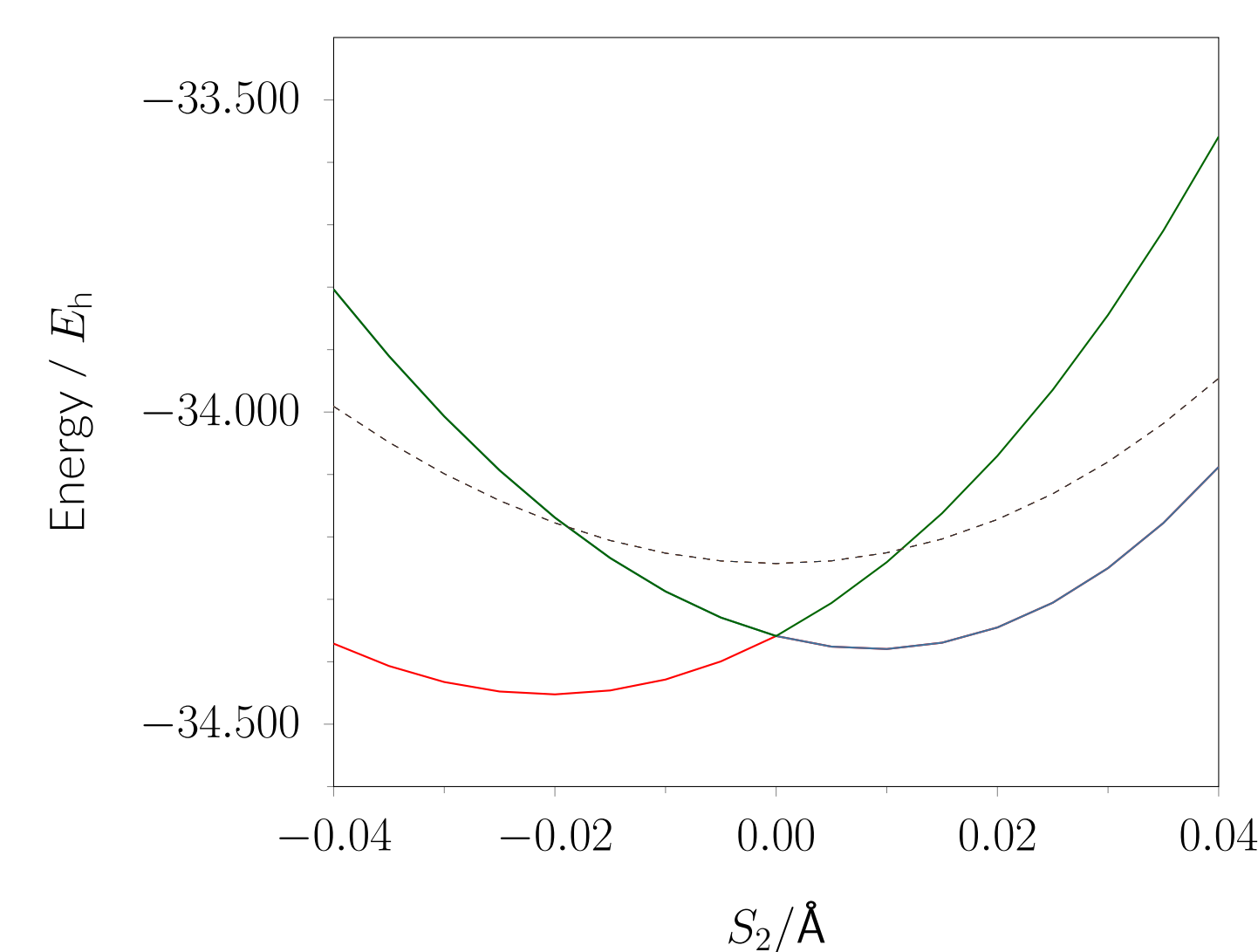


Figure 3. Correlation diagram (not to scale)

References

1. Thom, A. J. W. & Head-Gordon, M. *Physical Review Letters* **101**, 193001 (November 2008).