

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

Bang C. Huynh¹ Alex J. W. Thom¹

¹Department of Chemistry, University of Cambridge, United Kingdom

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

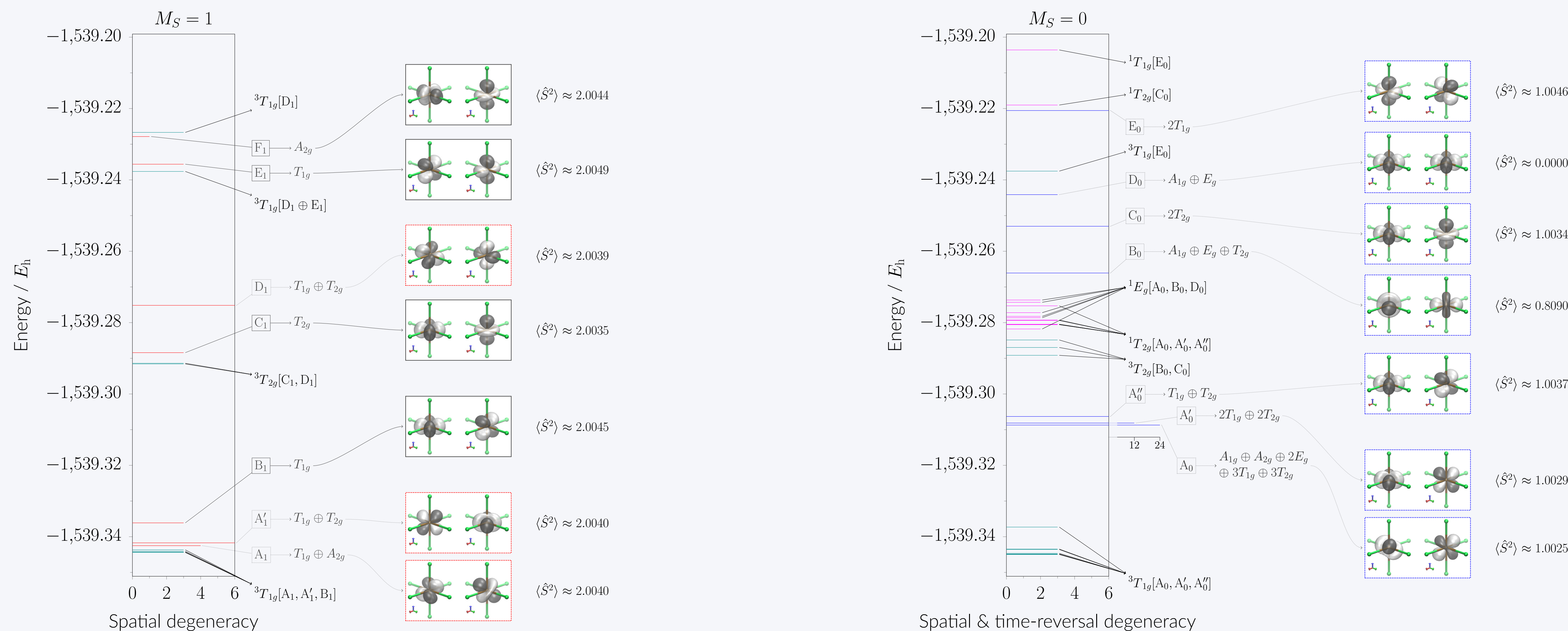


Figure 1. Energy and symmetry of low-lying UHF solutions and NOCI wavefunctions constructed from them in octahedral $[\text{VF}_6]^{3-}$.

$[\text{S}_{MS}]$: symmetry-conserved UHF set S with \hat{S}_z eigenvalue M_S . $[\text{S}_{MS}]$: 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**. Figure 2 gives such states for octahedral d^2 as an example.

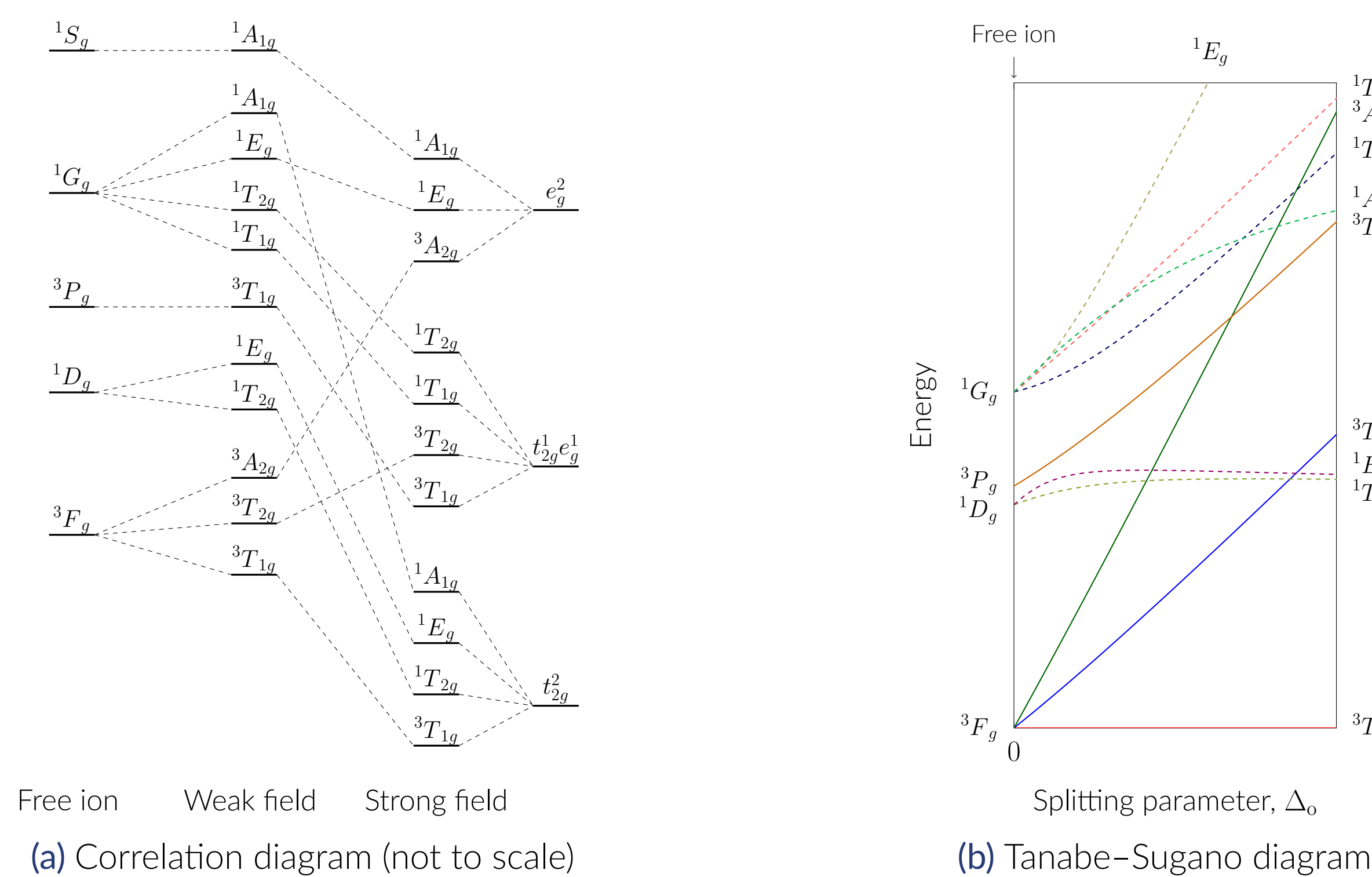


Figure 2. All electronic terms of a true d^2 system in an octahedral field.

The non-linear HF equations for these complexes therefore admit **multiple low-lying solutions** that are **degenerate** or **nearly degenerate**.

We have located these solutions using **SCF metadynamics** and investigated their **symmetry properties** in a model octahedral d^2 system, $[\text{VF}_6]^{3-}$ (Figure 1).

Symmetry Breaking in HF

Degenerate eigenfunctions of the spinless Hamiltonian *must* transform as a single irreducible representation (irrep) of the underlying point group \mathcal{B} , the spin rotation group $\text{SU}(2)$, or the time reversal group \mathcal{T} .

HF wavefunctions do not have to obey this due to their approximate nature. Thus, consider a set of degenerate HF solutions $S = \{\psi^w \mid w = 1, 2, \dots\}$ 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 **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**.

Restoring Symmetry: Non-Orthogonal CI (NOCI)

For a complete 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**

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

conserve symmetry and can be used to approximate corresponding electronic terms.

UHF vs. NOCI: Jahn-Teller Distortion

Consider the $T_{1g} \otimes e_g$ Jahn-Teller distortion in octahedral $[\text{VF}_6]^{3-}$. Figure 3 shows that:

- the UHF A_1 and A'_1 solutions fail to exhibit the expected energy minima;
- the ${}^3T_{1g}[A_1 \oplus A'_1]$ **NOCI wavefunctions** do **show the expected stabilisation** and give the **correct degeneracy splitting** upon symmetry descent.

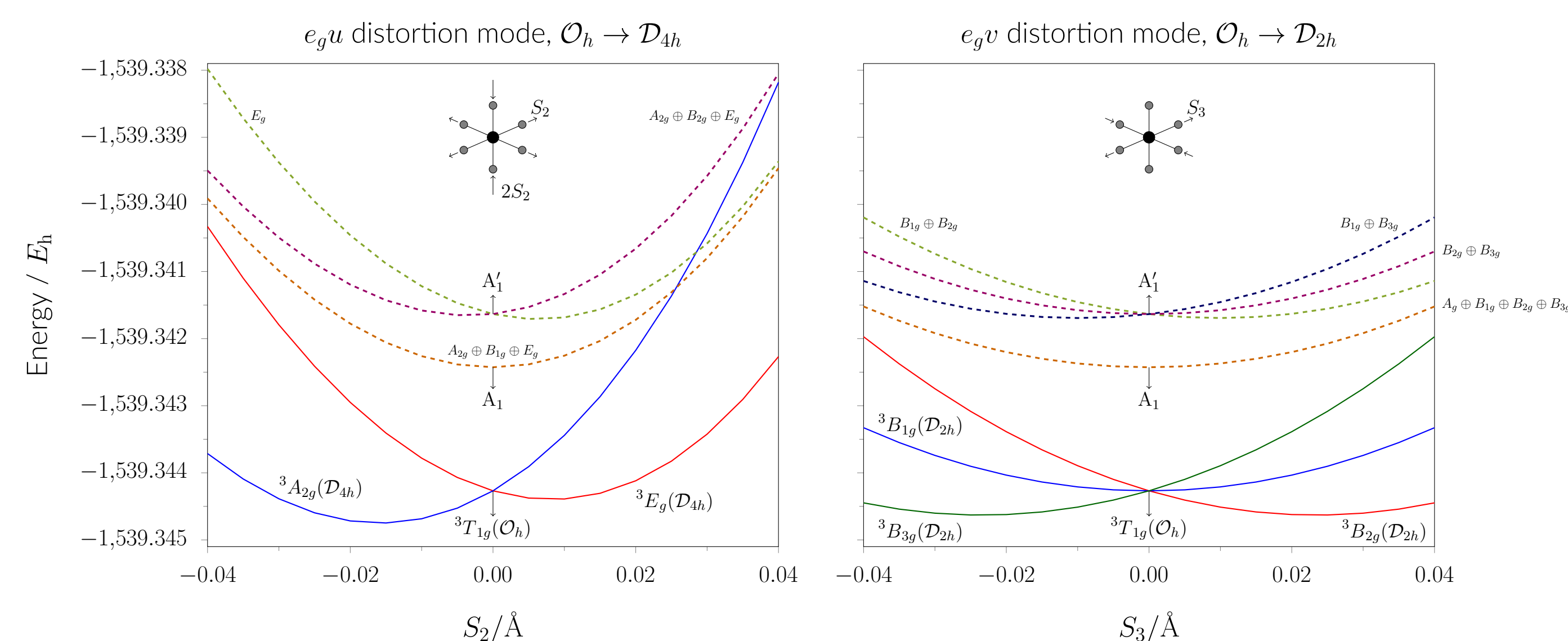


Figure 3. State energy in the $T_{1g} \otimes e_g$ Jahn-Teller distortion of octahedral $[\text{VF}_6]^{3-}$.

Dashed curves: symmetry-broken UHF A_1 or A'_1 solutions. Solid curves: ${}^3T_{1g}[A_1 \oplus A'_1]$ NOCI wavefunctions.

Solution Topology: Euclidean Realisation of State Distances

By realising the distance matrices between symmetry-broken HF solutions to give **polytopes** showing their **arrangements in Euclidean space** (Figure 4), we hope to gain insight into the nature of their symmetry breaking.

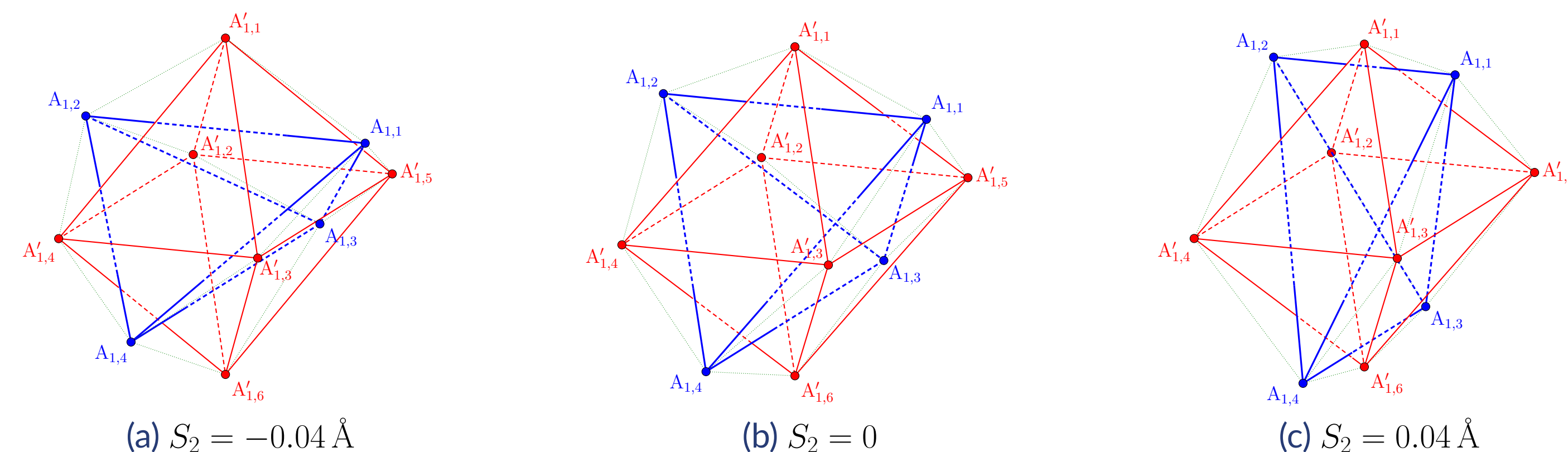


Figure 4. Three-dimensional projections of polytopes of A_1 and A'_1 solutions along the $e_g u$ distortion.

In a Nutshell

- There exist **many low-lying HF solutions** in transition-metal complexes.
- Some solutions **break symmetry**, spin or spatial or both.
- NOCI can **restore symmetry** to give **proper physical behaviours**, e.g., vibronic coupling.
- There are **clear patterns** in symmetry breaking that need further understanding.

References

- Thom, A. J. W. & Head-Gordon, M. *Physical Review Letters* **101**, 193001 (November 2008).
- Thom, A. J. W. & Head-Gordon, M. *The Journal of Chemical Physics* **131**, 124113 (September 2009).
- Huynh, B. C. & Thom, A. J. W. (Manuscript in preparation).