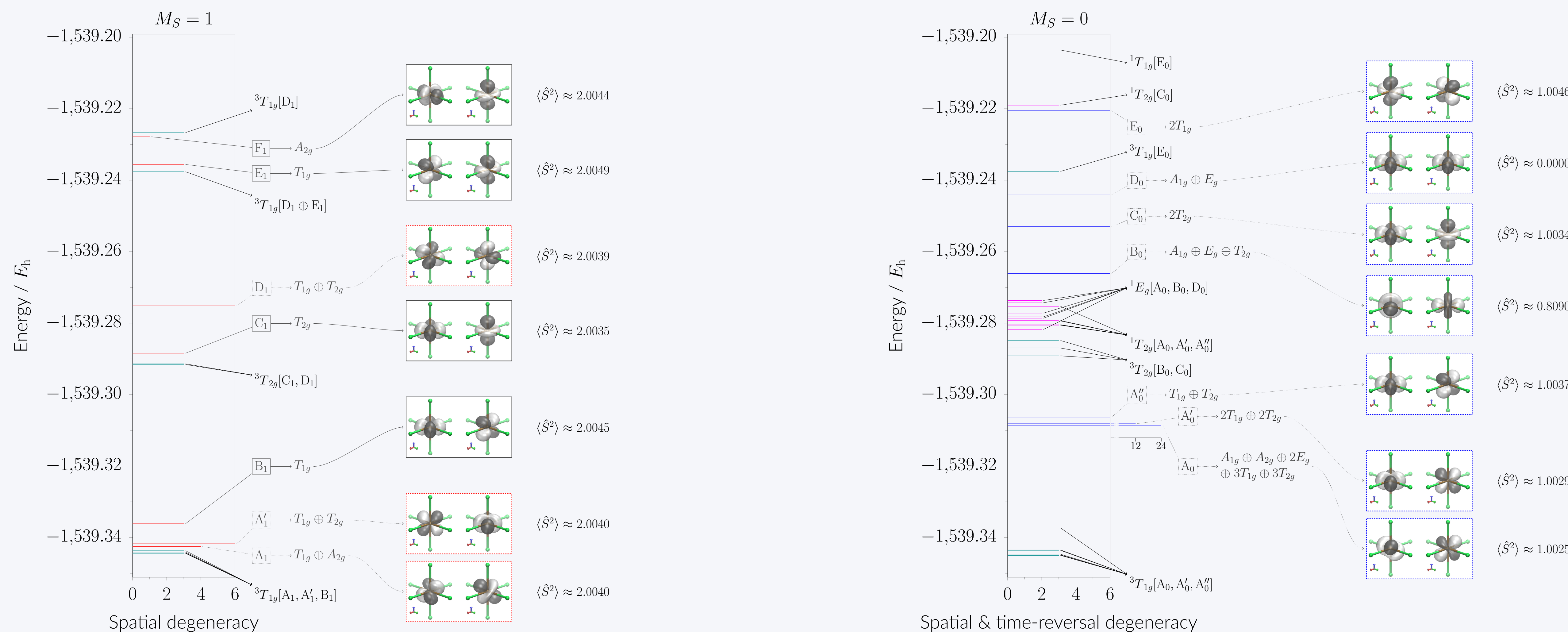


# Exploiting Multiple Symmetry-Broken SCF Solutions to Describe Ground and Excited States of Transition-Metal Complexes

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



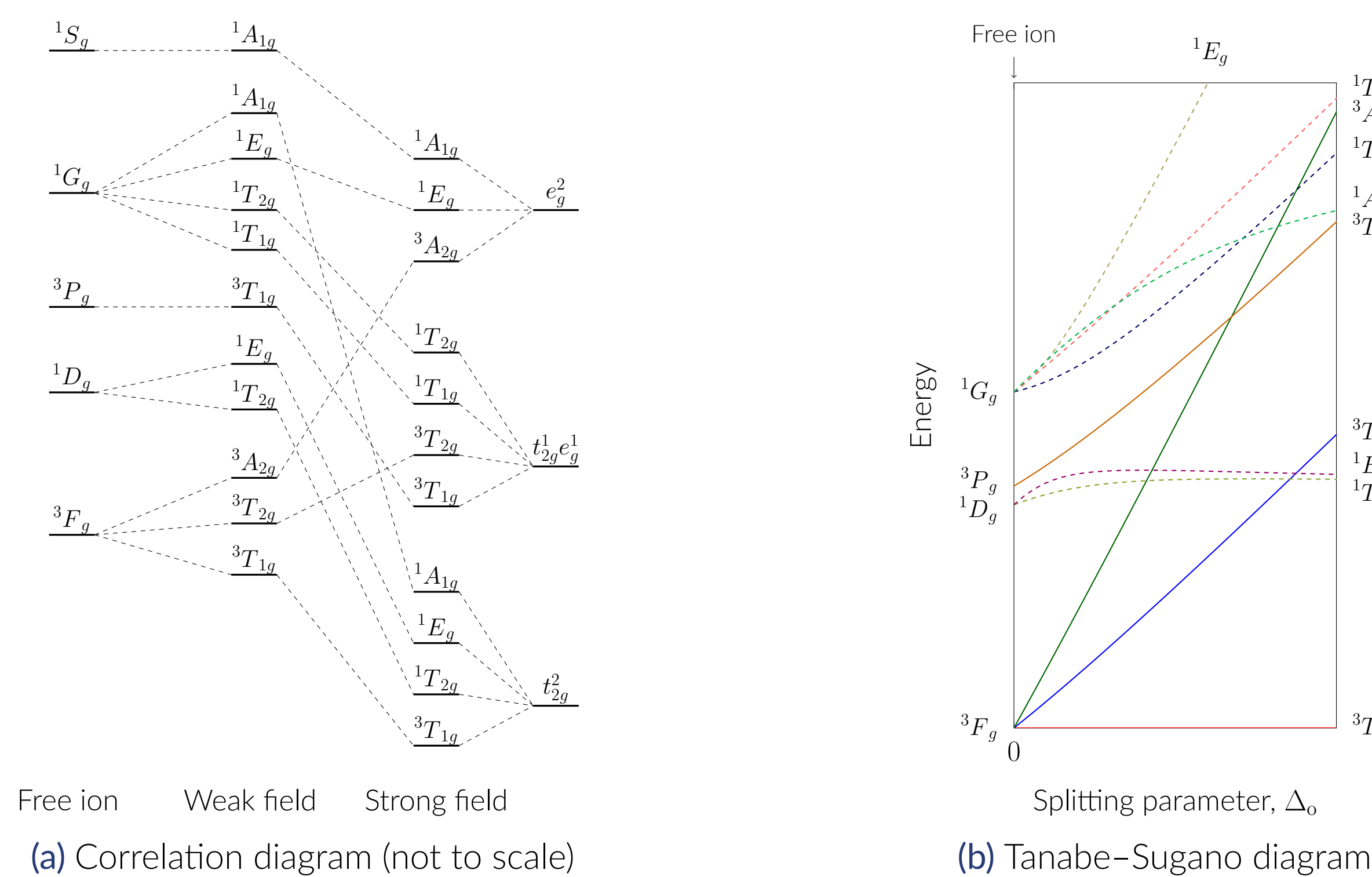
**Figure 1.** Energy and symmetry of low-lying UHF solutions and NOCI wavefunctions constructed from them in octahedral  $[\text{VF}_6]^{3-}$ .

$[\text{S}_{MS}]$ : 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  $\Gamma$  constructed from all of  $A$ ,  $B$ , and  $C$ .  $\Gamma[A, B, C]$ : multiple NOCI sets of symmetry  $\Gamma$  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**

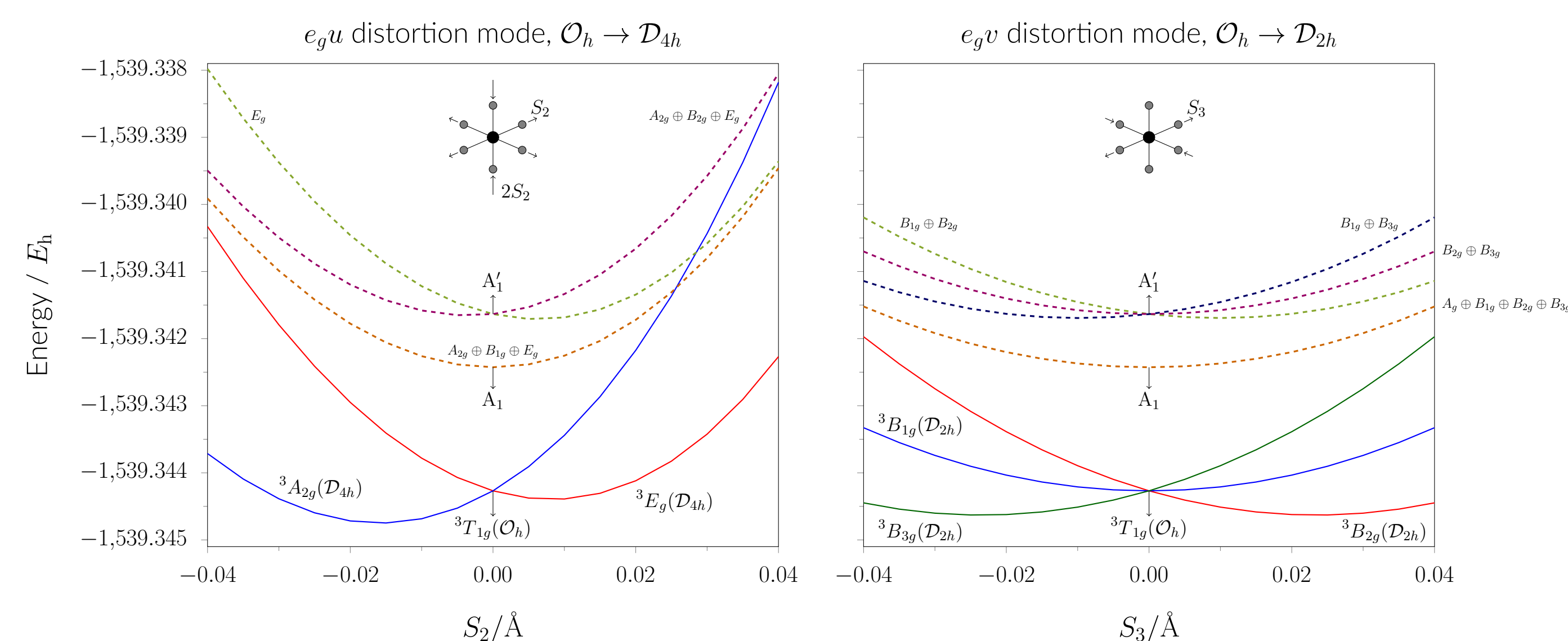
$$^m\Phi = \sum_w \psi^w A_{wm}$$

**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.

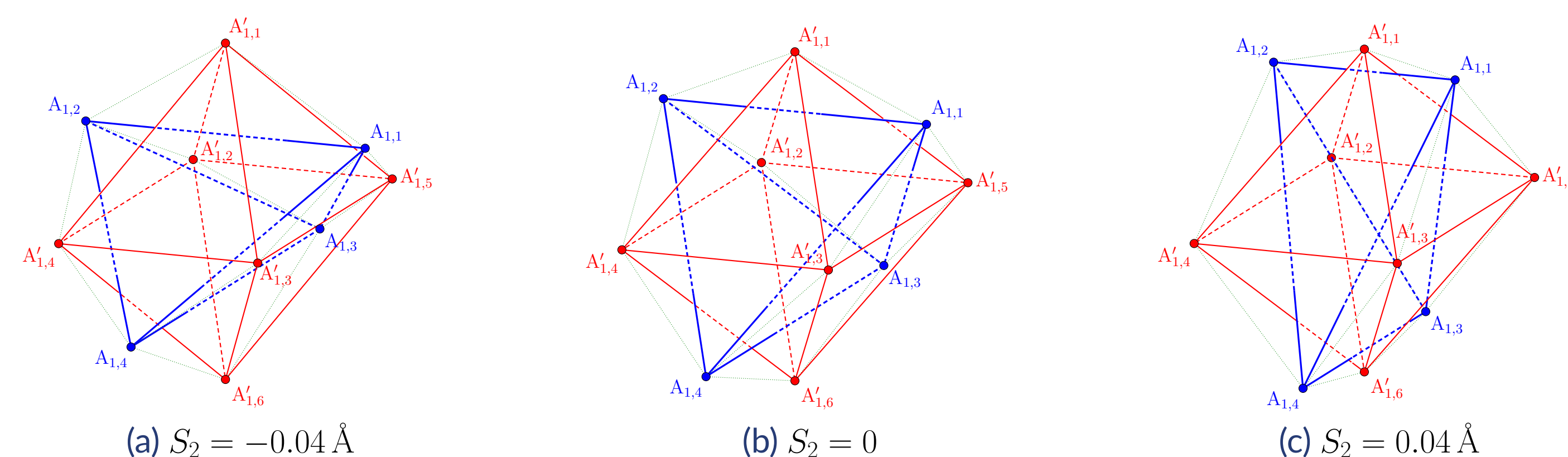


**Figure 3.** State energy in the  $T_{1g} \otimes e_g$  Jahn-Teller distortion of octahedral  $[\text{VF}_6]^{3-}$ .

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

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