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## Low-Lying UHF Solutions and NOCI Wavefunctions of Model Octahedral $[VF_6]^{3-}$
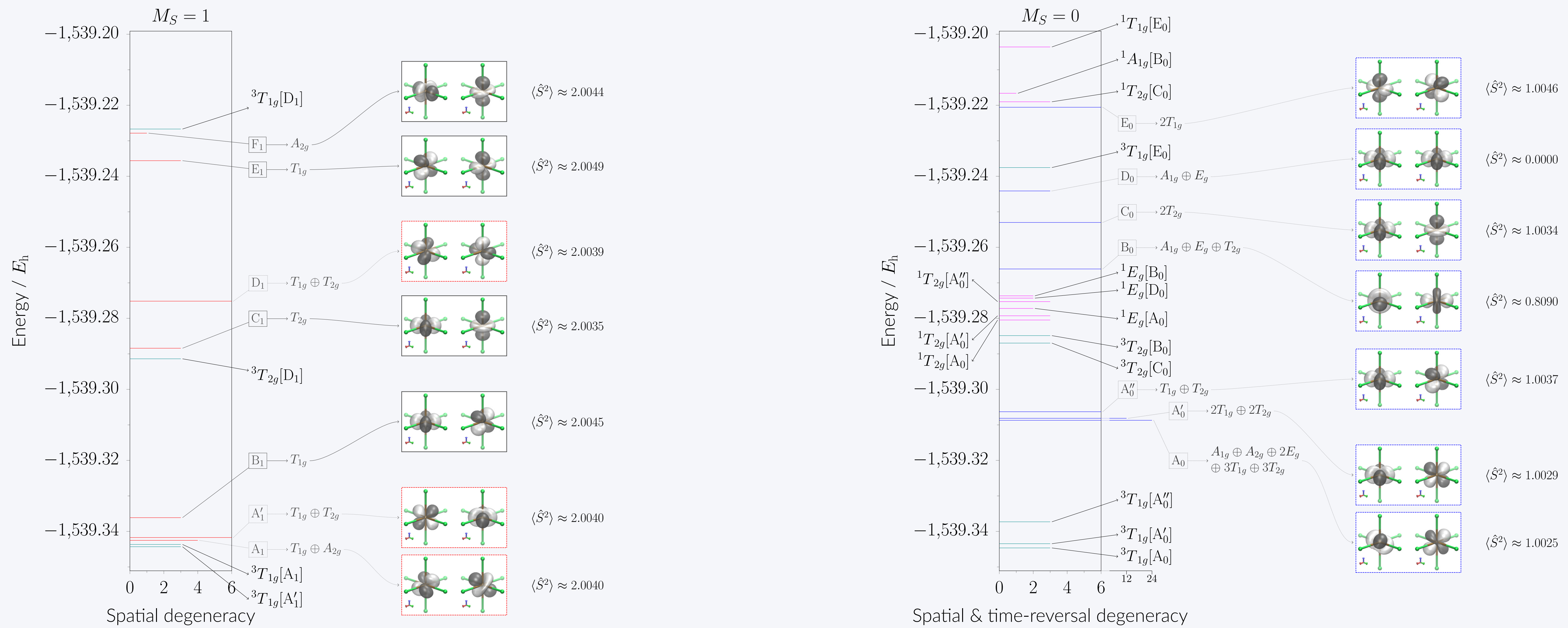
Figure 1. Energy and symmetry of low-lying UHF solutions and NOCI wavefunctions constructed from them in octahedral $[VF_6]^{3-}$.
$\boxed{S_{M_S}}$: symmetry-conserved UHF set S with $\hat{S}_z$ eigenvalue M_S. $\boxed{S_{M_S}}$: spatial or spin symmetry-broken UHF set S with $\hat{S}_z$ eigenvalue M_S.
$\Gamma[S_{M_S}]$: a specific NOCI set of symmetry Γ constructed from the UHF set S with $\hat{S}_z$ eigenvalue M_S.

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.

(a) Correlation diagram (not to scale)   (b) Tanabe–Sugano diagram
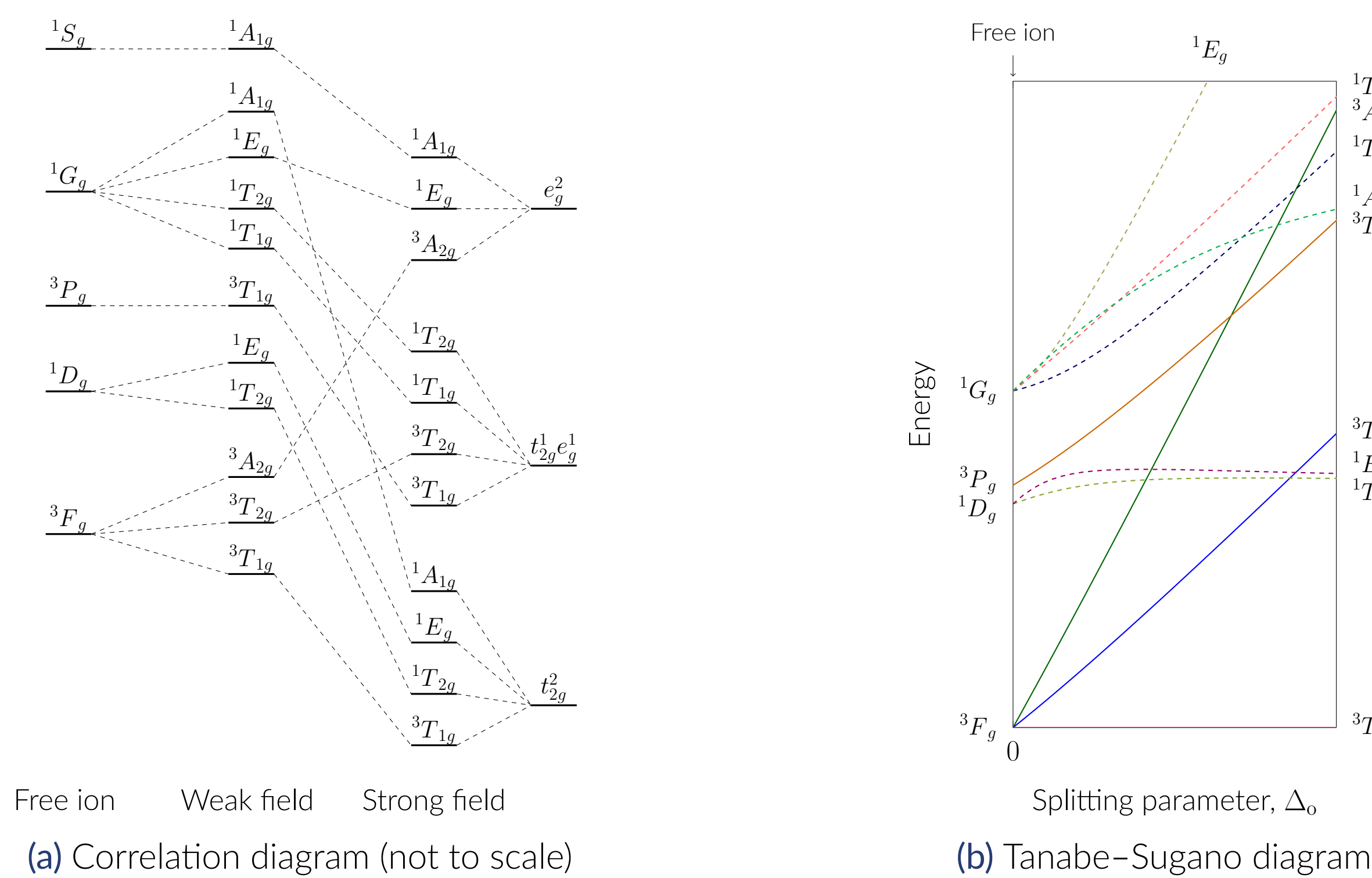
Figure 2. All electronic terms of a true d^2 system in an octahedral field.

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, $[VF_6]^{3-}$ (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 $SU(2)$, 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 $S = \{^w\Psi \mid w = 1, 2, \ldots\}$ 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 $S = \{^w\Psi \mid w = 1, 2, \ldots\}$, solving the generalised eigenvalue equation

$$\boldsymbol{HA} = \boldsymbol{SAE} \quad \text{where} \quad (\boldsymbol{H})_{wx} = \langle {}^w\Psi | \hat{\mathscr{H}} | {}^x\Psi \rangle \text{ and } (\boldsymbol{S})_{wx} = \langle {}^w\Psi | {}^x\Psi \rangle$$

gives coefficients A_{wm} such that the **NOCI wavefunctions**

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

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 octaheral $[VF_6]^{3-}$. 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.
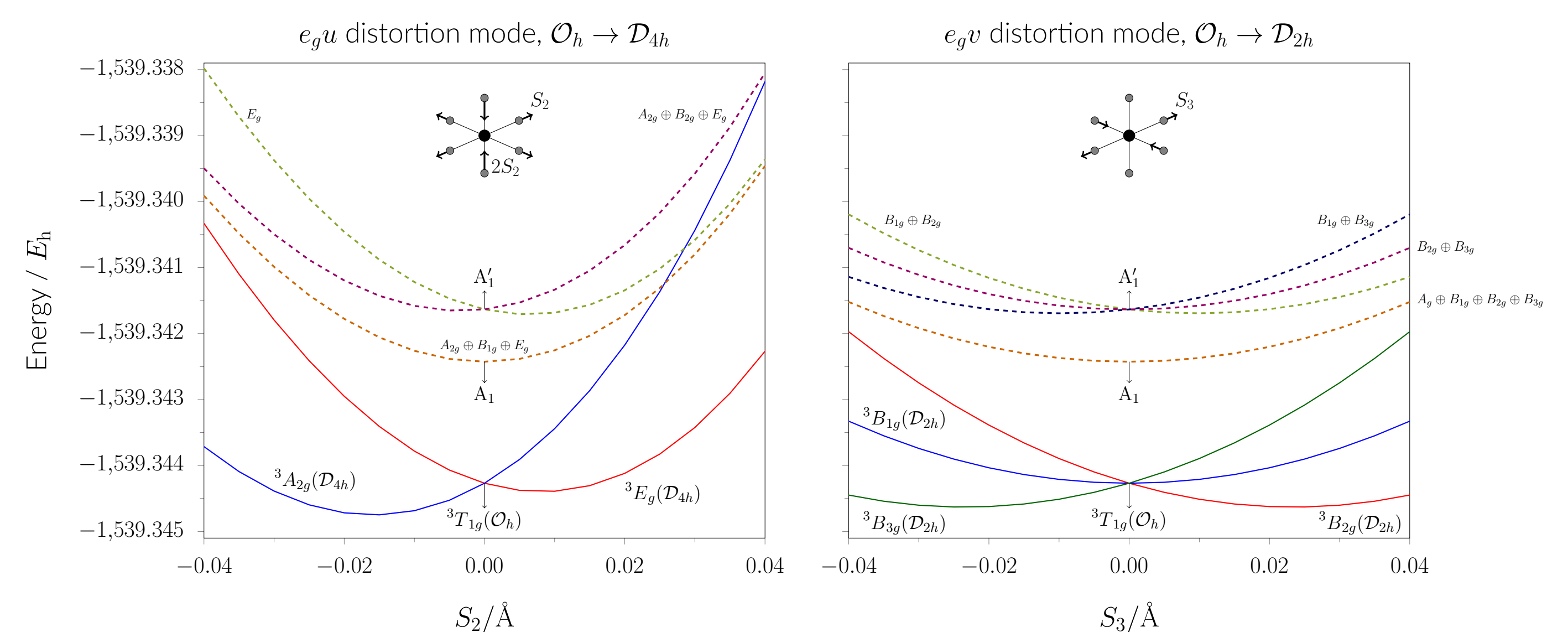
Figure 3. State energy in the $T_{1g} \otimes e_g$ Jahn–Teller distortion of octahedral $[VF_6]^{3-}$.
Dashed curves: symmetry-broken UHF A_1 or A_1' solutions. Solid curves: $^3T_{1g}[A_1 \oplus A_1']$ NOCI wavefunctions.

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.

(a) $S_2 = -0.04\,\text{Å}$ (b) $S_2 = 0$ (c) $S_2 = 0.04\,\text{Å}$
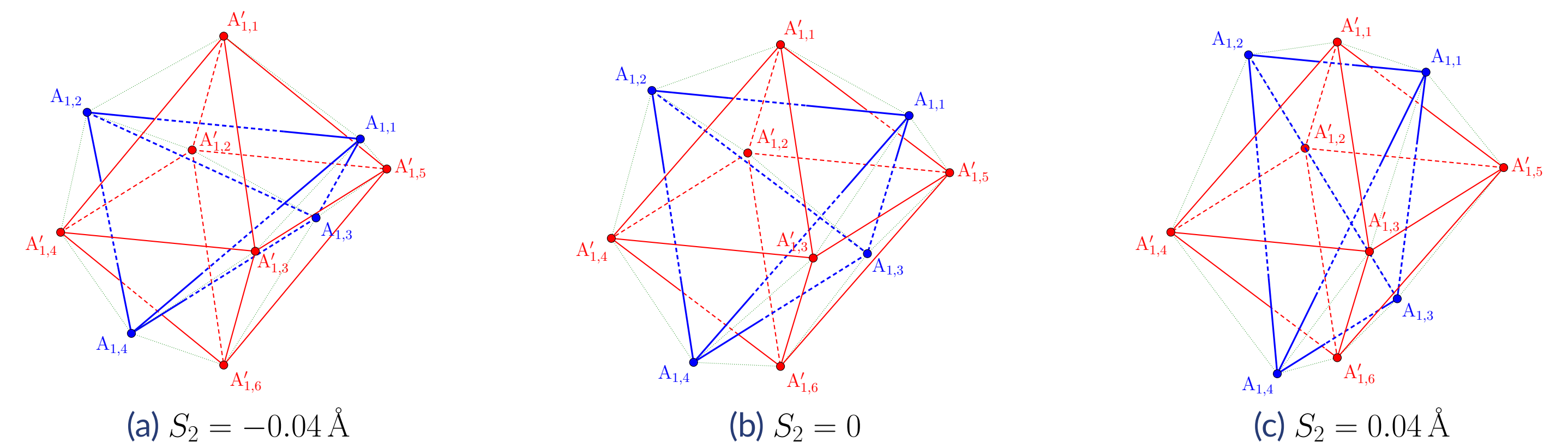
Figure 4. Three-dimensional projections of polytopes of A_1 and A_1' solutions along the e_gu distortion.

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

1. Thom, A. J. W. & Head-Gordon, M. *Physical Review Letters* **101**, 193001 (November 2008).
2. Thom, A. J. W. & Head-Gordon, M. *The Journal of Chemical Physics* **131**, 124113 (September 2009).
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