The Extended Molecular Symmetry Group $G_{36}(EM)$ and the Theoretical Spectroscopy of Ethane
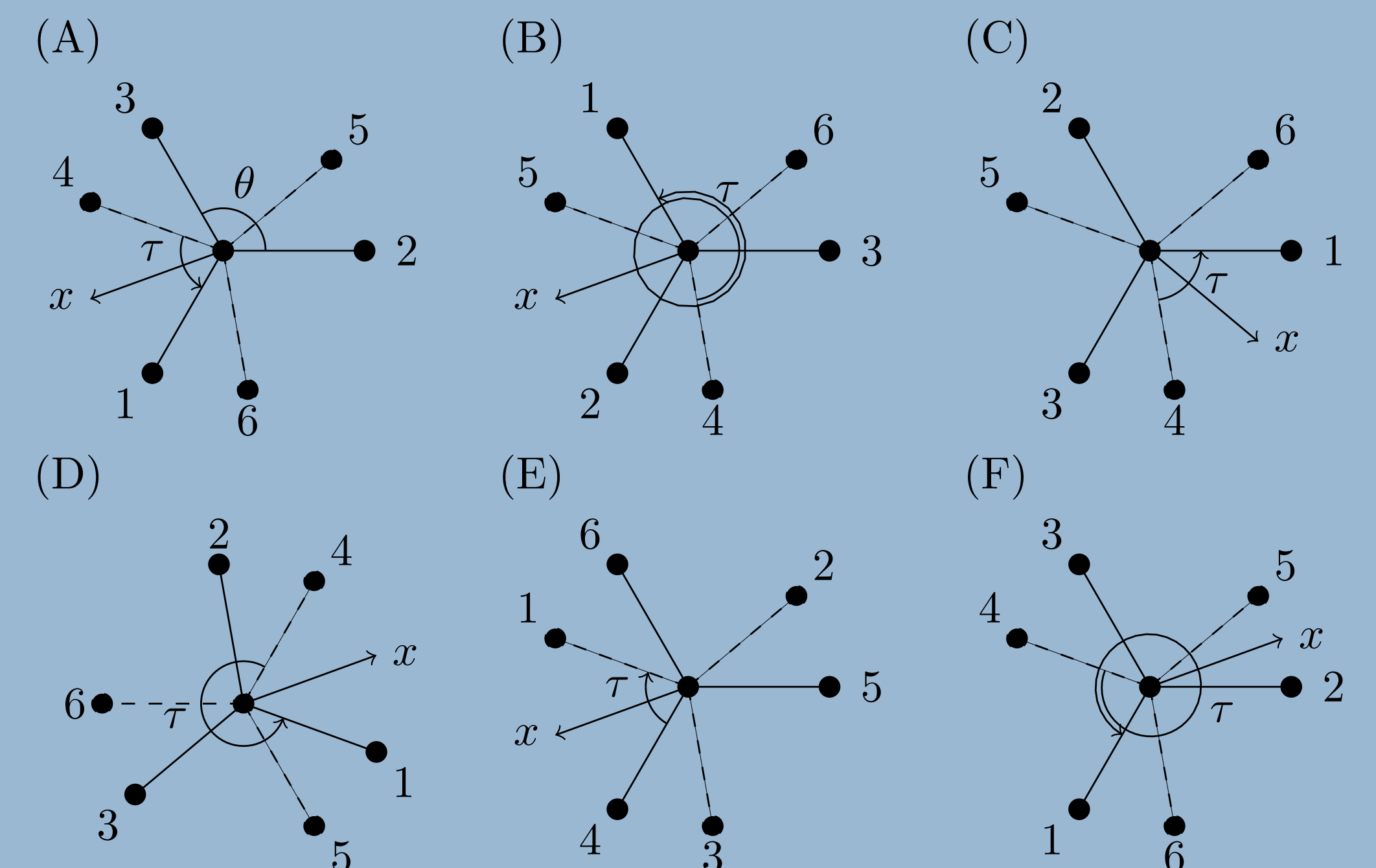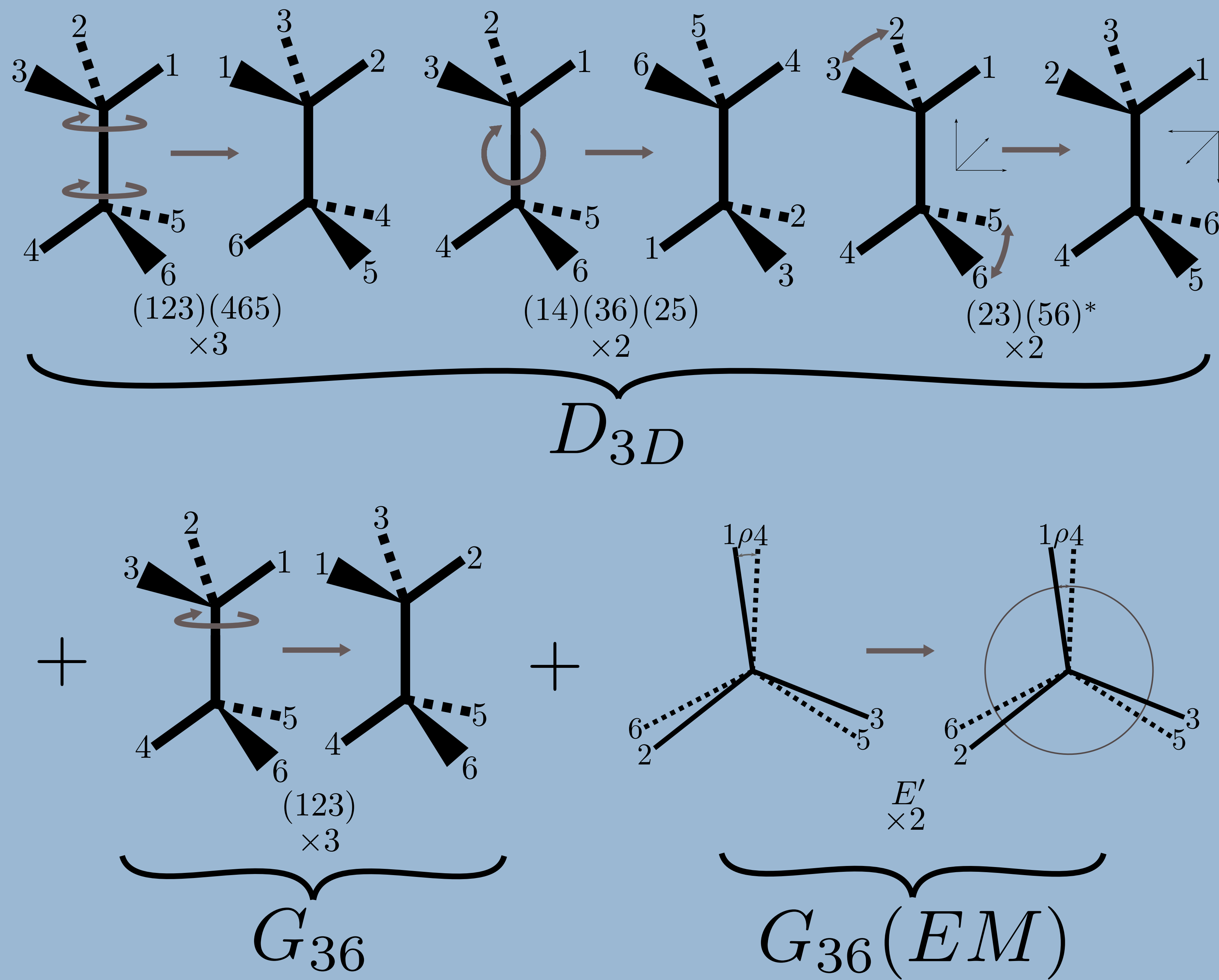
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The $G_{36}(EM)$ Extended Molecular Symmetry Group

$(123)(465)$
$\times 3$

$(14)(36)(25)$
$\times 2$

$(23)(56)^*$
$\times 2$

D_{3D}

$+$

(123)
$\times 3$

G_{36}

$+$

E'
$\times 2$

$G_{36}(EM)$

(A) (B) (C)
(D) (E) (F)

The left shows how the $G_{36}(EM)$ group is constructed with representative members from first D_{3D}, then G_{36}, and then $G_{36}(EM)$. The right shows the effects of the six generating operations, from which we construct all operations, on the torsion angle. We determine the effects of the generators on the coordinates to symmetrise the basis set. The aim is to put the Hamiltonian matrix into the form

$$\left\langle \Psi_{\mu,n_s}^{J,\Gamma_s} \left| \hat{H}_{\mathrm{rv}} \right| \Psi_{\mu',n_t}^{J,\Gamma_t} \right\rangle = H_{\mu,\mu'} \, \delta_{t,s} \, \delta_{n_s,n_t} \quad (1)$$

where the indices μ, μ' label the basis functions, Γ_s and Γ_t denote irreducible representations of the symmetry group, and $n_s(n_t)$ labels the components of the irrep $\Gamma_s(\Gamma_t)$.
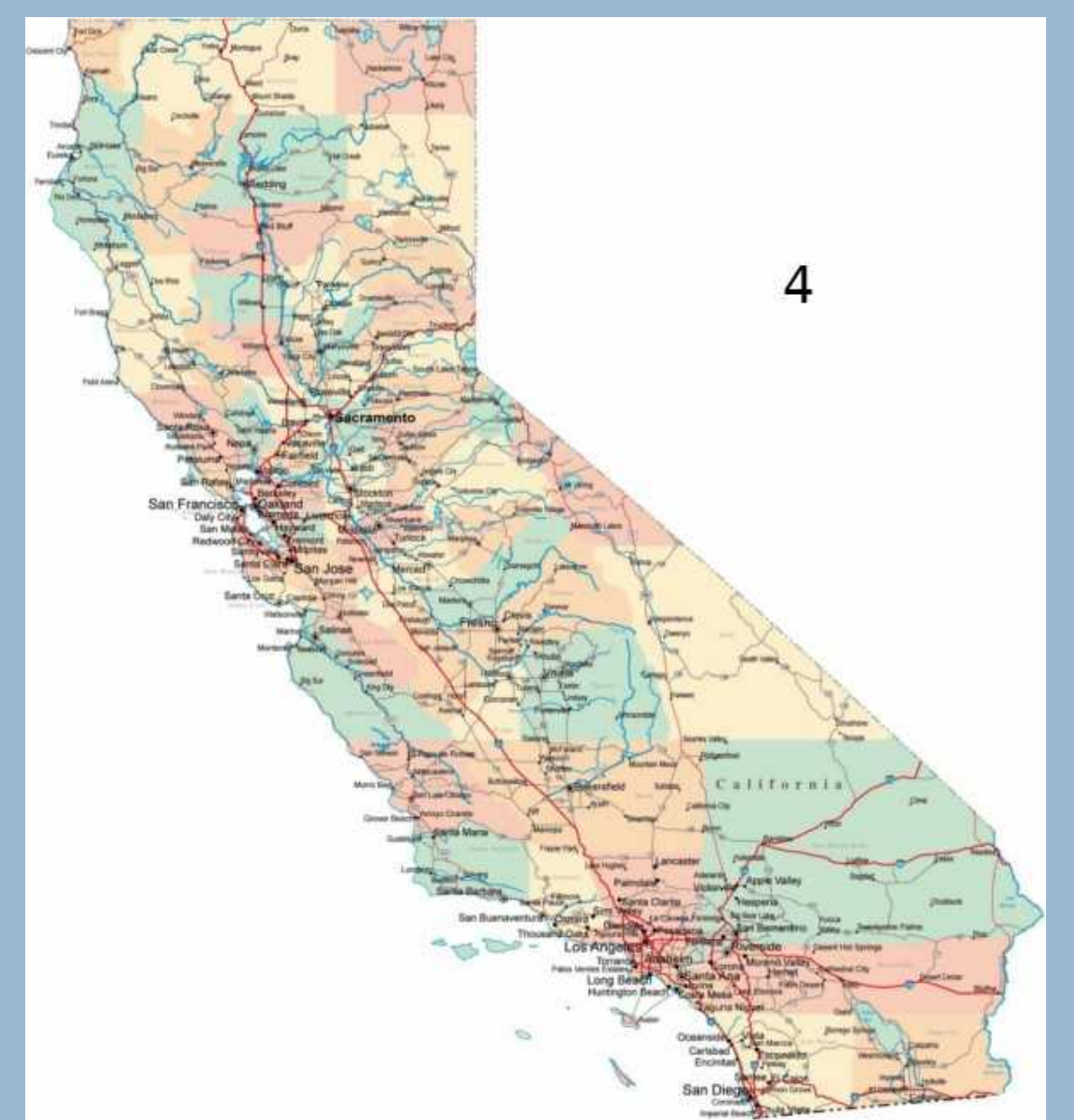
$G_{36}(EM)$ Representations

To be able to utilize the symmetry group, we require explicit matrices for every operation and representation. A few examples shown below.

$$M_{E_{1s}}[(14)(25)(36)(ab)] = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad M_{G_s}[(456)] = \begin{pmatrix} \frac{1}{4} & -\frac{\sqrt{3}}{4} & -\frac{3}{4} & -\frac{\sqrt{3}}{4} \\ \frac{\sqrt{3}}{4} & \frac{1}{4} & \frac{\sqrt{3}}{4} & -\frac{3}{4} \\ -\frac{3}{4} & -\frac{\sqrt{3}}{4} & \frac{1}{4} & -\frac{\sqrt{3}}{4} \\ \frac{\sqrt{3}}{4} & -\frac{3}{4} & \frac{\sqrt{3}}{4} & \frac{1}{4} \end{pmatrix}$$

$$M_{G_s}[(14)(25)(36)(ab)] = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \qquad M_{E_{1s}}[(123)] = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$$

Coordinate Classes

To create symmetry adapted basis sets, we analyse the transformations of the internal molecular coordinates due to the group operations. In general, coordinates are naturally grouped into sets which transform into each other. Reduced Hamiltonians are the created for each class by integrating out the other coordinates with the group state, described by

$$H^i(\boldsymbol{Q}^i) = \langle 0_p | \langle 0_q | \dots \langle 0_r | H^{rv} | 0_r \rangle \dots \dots | 0_q \rangle | 0_p \rangle$$

where $\boldsymbol{Q}^i$ is the coordinate set for a given class and $p, q, \dots, r$ are the other coordinates. The reduced Hamiltonian eigenfunctions are 'symmetrised'. The symmetrised functions from each class are combined and once again symmetrised so that the matrix of the full Hamiltonian using these functions as a basis set is block diagonal.
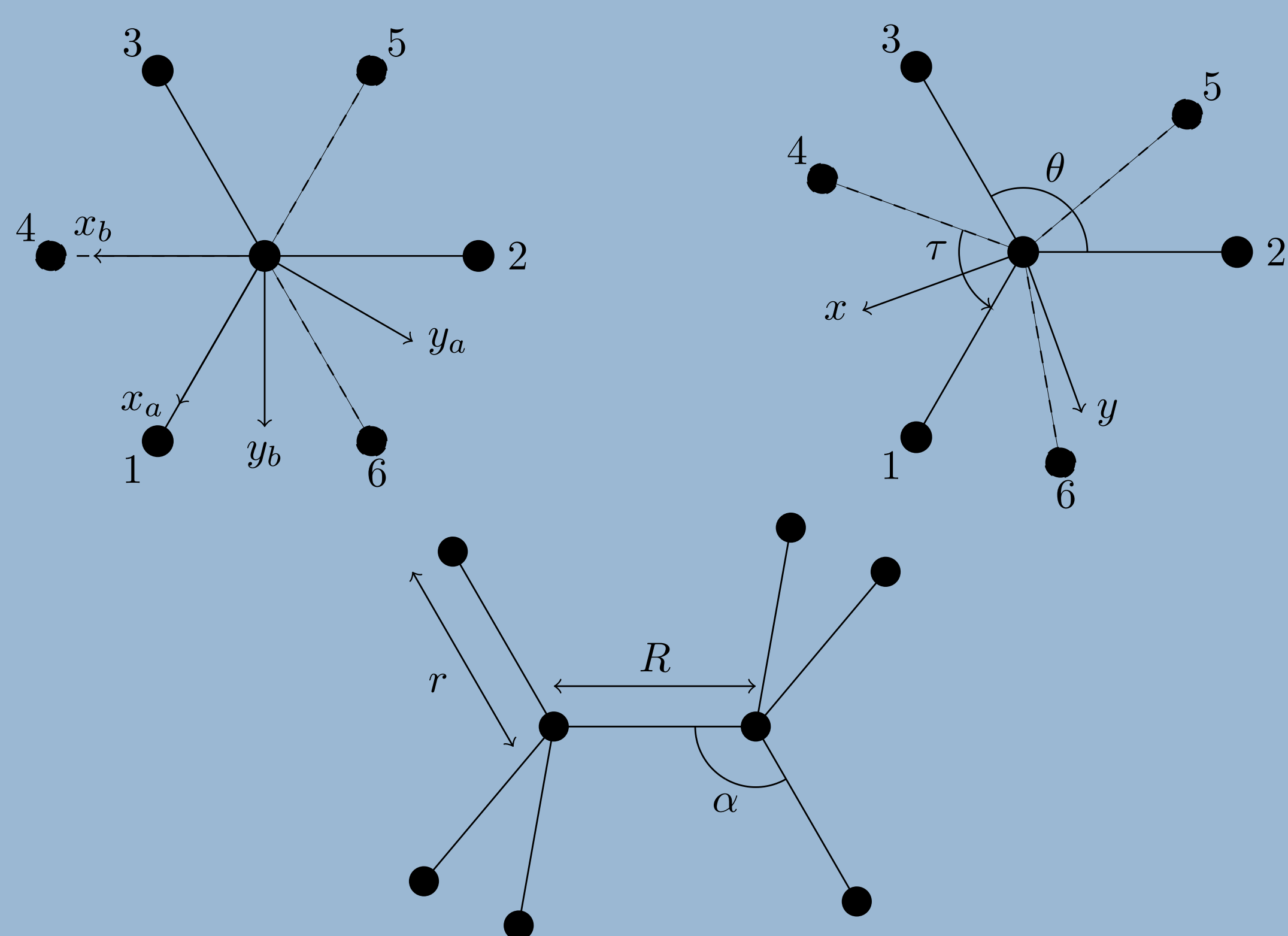
Torsional Wavefunctions

Below are examples symmetrised wavefunctions for the torsion coordinate ρ and the torsional potential energy with eigenenergies marked.

The torsional potential energy as a function of the torsion angle τ. The allowed energy values are marked by blue horizontal lines.

Ground state A representation torsion wavefunction
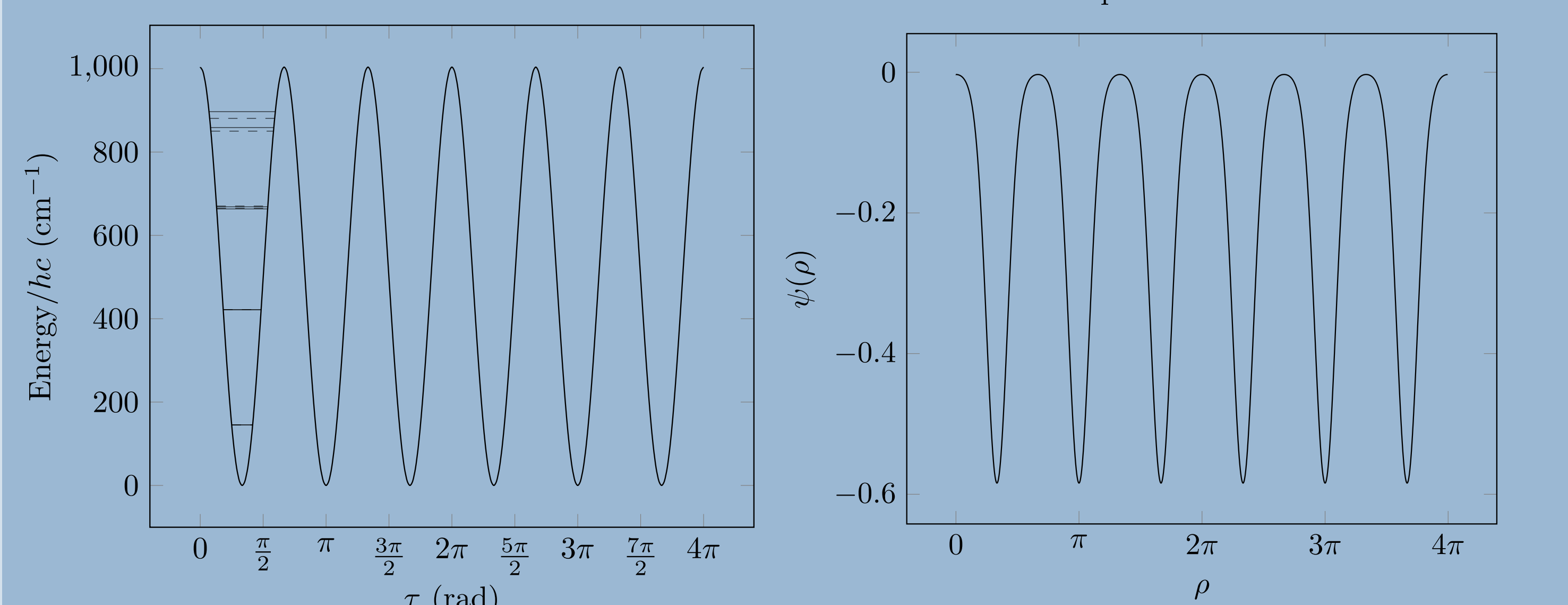
The degenerate first excited state torsional wavefunctions. Top display: Functions transforming irreducibly as E_{3d}, but not with the transformation properties of the matrices show on the right. Bottom display: The first excited degenerate wavefunctions in the desired way.