

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

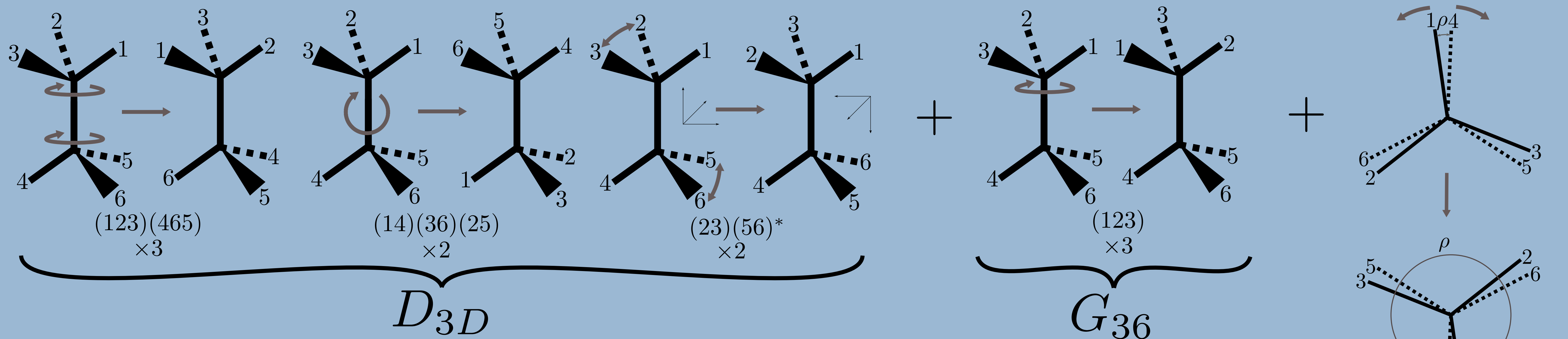
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The $G_{36}(EM)$ Extended Molecular Symmetry Group



With a large set of basis functions, the calculation of the matrix elements of the system Hamiltonian can become unwieldy. Making use of symmetries of the system can provide significant simplification by guaranteeing many elements of the matrix are zero. The ExoMol project has taken advantage of this in the generation of line lists for several molecules. In the following, we shall describe this procedure for our latest and largest molecule, (both in terms of the number of atoms and the size of the symmetry group) ethane (C_2H_6).

This begins with the observation that the Hamiltonian of the system commutes with a permutation of identical nuclei and an inversion of the atomic coordinates. Restricting ourselves to only 'feasible' elements (ones obtainable by rotation of the molecule) defines the molecular symmetry group. For ethane with torsion, this is the G_{36} group. One can understand the origin of all elements by combining a rotation about the C-C axis—first diagram column, $\times 3$ indicating the number of elements (including the identity) and (123) being an example—with a rotation perpendicular to this axis and a feasible inversion-type coordinate—12 elements in total. A single CH_3 rotation gives 3 more elements

to combine with, hence the full group is G_{36} . In practical calculations, the rotational, torsional, vibrational coordinates are separated. This leads to an ambiguity in the torsional angle ρ on the far right diagram. This can be appreciated intuitively by noticing that an increase in 2π of this angle, where each CH_3 group moves in an opposite direction, does not bring the molecule back to its starting point. The angle must therefore be 4π periodic with an element E' added to the group which increases it by 2π .

Because the Hamiltonian commutes with the group elements, wavefunctions transform to linear combinations of wavefunctions with the same energy, and the group operation can be represented by a matrix which transforms a vector of wavefunctions. It is elementary in group theory that by performing unitary transformations on the wavefunction set, we can 'reduce' these matrices to being block diagonal where each block is only one of a finite set of 'irreducible' representations. Crucially, Hamiltonian matrix elements between basis functions transforming irreducibly are only non-zero if both the representation and the component number is the same.

$G_{36}(EM)$ Representations

To be able to utilize the symmetry group, we require explicit matrices for every operation and representation. This is not as yet available in the literature, particularly in the 4 dimensional G representation, and is element that this study will provide. A few examples are shown below the table.

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

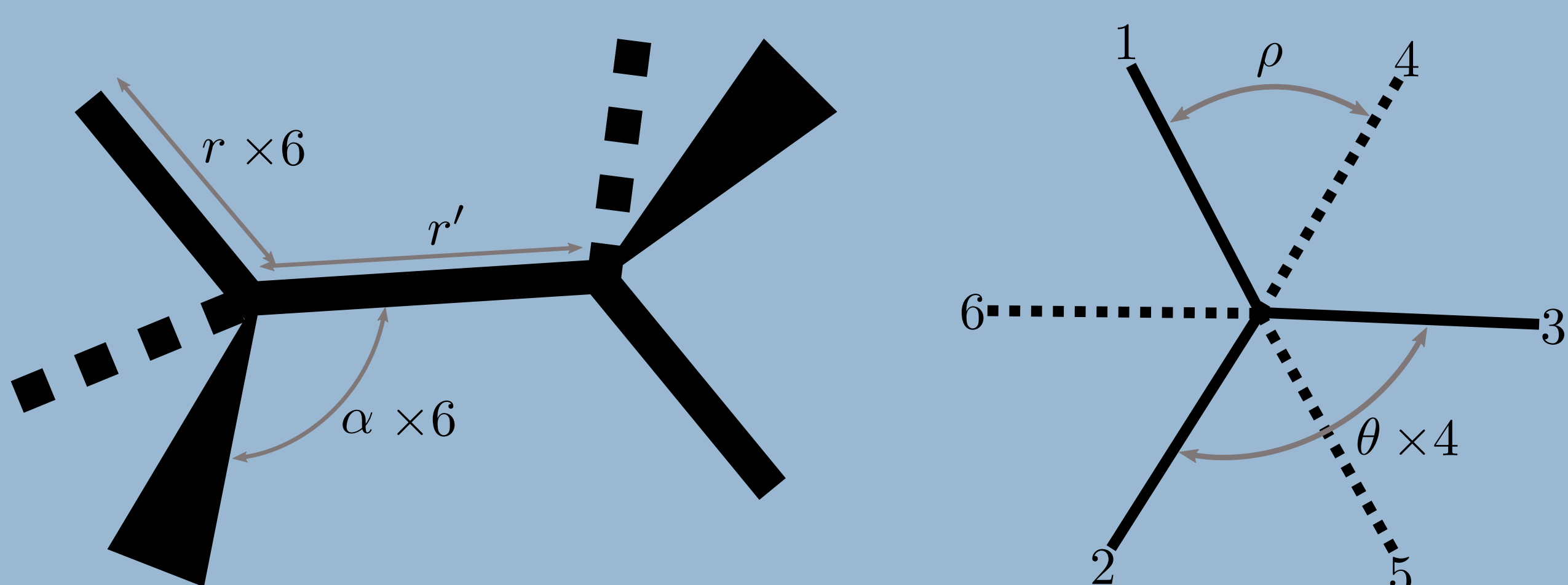
$$M_{G_s}[(14)(25)(36)(ab)] = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \quad M_{E_{1s}}[(123)] = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$$

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. In the case of ethane, there are 5 classes: 1 C-C bond, 6 C-H bonds, 6 C-C-H angles, 4 independent H-C-H dihedral angles, and the torsion angle ρ . Reduced Hamiltonians are created for each class by integrating out the other coordinates with the group state, described by

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

where Q^i is the coordinate set for a given class and p, q, \dots, r are the other coordinates. This reduced Hamiltonian is then solved with an appropriate basis set providing the eigenfunctions. These are then 'symmetrised' which transforms them so that they transform irreducibly. The symmetrised functions from each class are combined into a function of all the variables and once again symmetrised so that the matrix of the full Hamiltonian using these functions as a basis set is block diagonal.

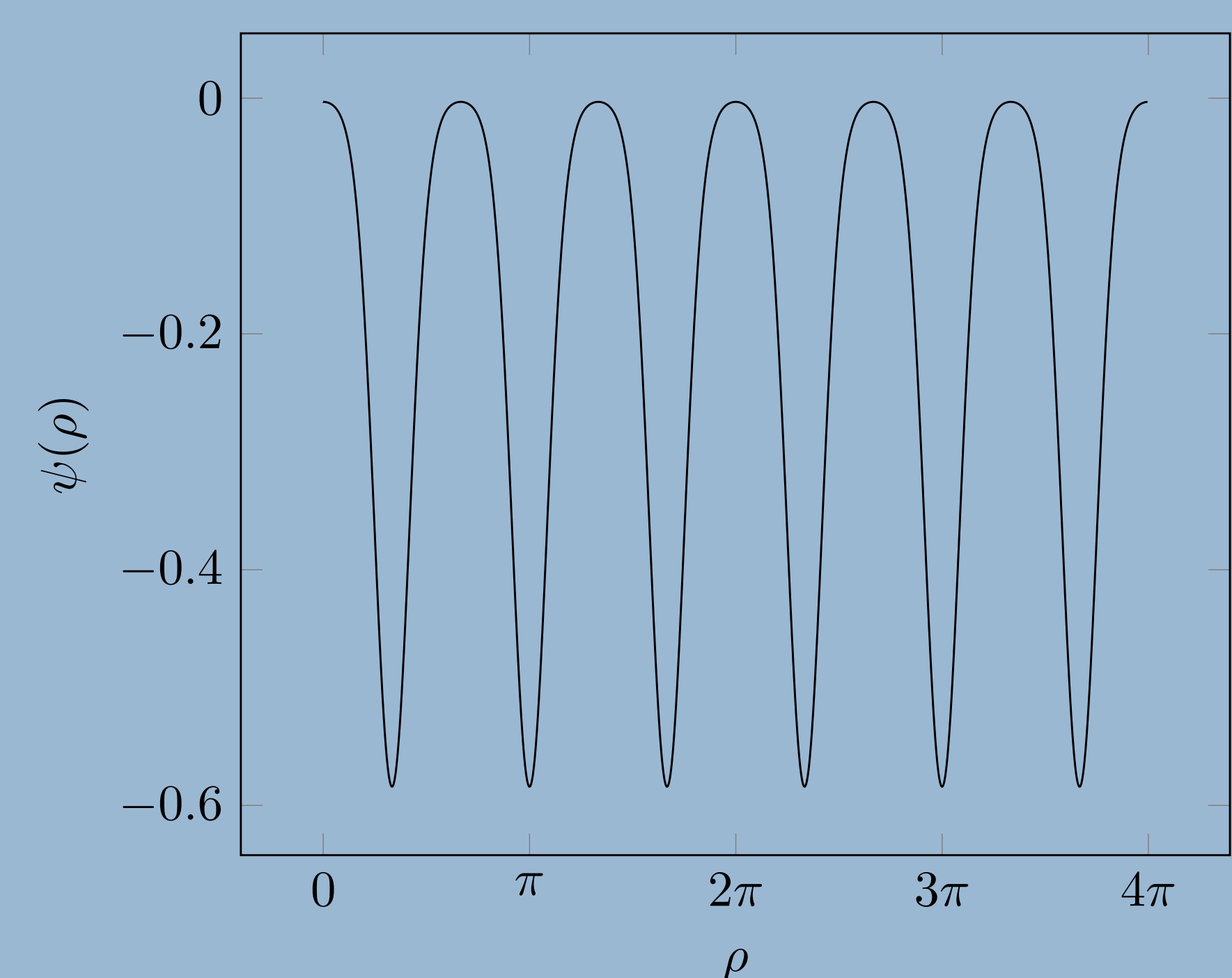


Torsional Wavefunctions

Below are examples symmetrised wavefunctions for the torsion coordinate ρ . The first is a ground state wavefunction which is totally symmetric under $G_{36}(EM)$, as expected. The negative 'peaks' have a periodicity of $2/3\pi$ starting at $\pi/3$ corresponding to the minima of the potential—the staggered position.

The second example shows a pair of E symmetrised wavefunctions. Under group operations, these are mixed. A salient feature of these wavefunctions is that they are odd under a 2π rotation, the E' operation of the extended molecular symmetry group. We label such states with d symmetry.

Ground state A representation torsion wavefunction



E representation torsion wavefunctions

