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Fundamentals of Molecular Symmetry ***Exercises***

Week 5/11

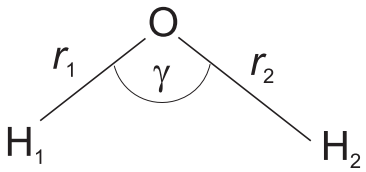
5.1 Consider the water molecule H_2O. Its vibrations are described by the following normal coordinates:

$$Q_1 \sim \frac{1}{\sqrt{2}}(r_1 + r_2 - 2r_e), \quad Q_2 \sim \gamma - \gamma_e, \quad Q_3 \sim \frac{1}{\sqrt{2}}(r_2 - r_1).$$

Here, r_1 and r_2 are the bond lengths and γ is the bond angle. The index e indicates the equilibrium values of the bond length and the bond angle. Expressed in terms of these coordinates, the zero-order vibrational wavefunction for the water molecule is given as:

$$\Psi_{\text{vib}} = \Psi_{v_1}(Q_1) \times \Psi_{v_2}(Q_2) \times \Psi_{v_3}(Q_3),$$

where the $\Psi_{v_i}(Q_i)$ functions are eigenfunctions for the associated one-dimensional harmonic oscillators. Determine the symmetry of Ψ_{vib} in the molecular symmetry group $\boldsymbol{C}_{2\text{v}}(\text{M})$.

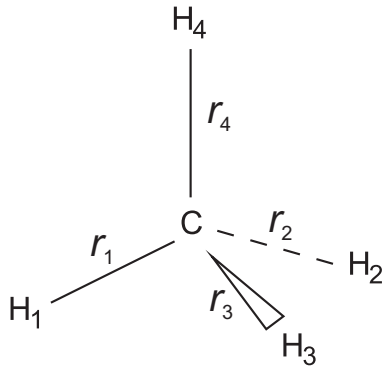


$\boldsymbol{C}_{2\text{v}}(\text{M})$	E	(12)	E^*	$(12)^*$
	1	1	1	1
$\boldsymbol{C}_{2\text{v}}$	E	C_2	σ_{ab}	σ_{bc}
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	−1	1
B_2	1	−1	1	−1

5.2 Consider the molecule methane CH_4. Its symmetry is normally described in terms of the so-called molecular symmetry group $\boldsymbol{T}_{\text{d}}(\text{M})$ which we will investigate more closely in Problem 6.1 below. The character table of $\boldsymbol{T}_{\text{d}}(\text{M})$, with one element of each class indicated, is given here:

$\boldsymbol{T}_{\mathrm{d}}(\mathrm{M})$	E	(123)	$(14)(23)$	$(1423)^*$	$(23)^*$
	1	8	3	6	6
T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
F_1	3	0	-1	1	-1
F_2	3	0	-1	-1	1

a) Determine the reducible representation of $\boldsymbol{T}_{\mathrm{d}}(\mathrm{M})$ generated by the four bond lengths r_1, r_2, r_3, r_4. It is sufficient to consider one element in each class since all elements in a given class have the same characters.



b) Decompose the representation obtained into a direct sum of irreducible representations.

When you need to consider a methane molecule in three dimensions, it is sometimes helpful to imagine it inscribed in a cube: