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Group theory and symmetries in quantum mechanics
Summer semester 2015 - Exercise sheet 8
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Problem 23: Vibrations of the CO_2 molecule

The procedure of finding the molecular vibrations of linear molecules, such as CO_2, is somewhat different from what we discussed in the lecture. Assuming that the molecular axis is along the $\hat{z}$ direction, only two rotational degrees of freedom has to be removed, because rotations around $\hat{z}$ by an arbitraty angle Φ correspond to the identity operation (we consider atoms as homogeneous balls). In particular CO_2 is a molecule with $D_{\infty h}$ symmetry group, whose character table is given below.

			E	$2C_\Phi$	C_2'	i	$2iC_\Phi$	iC_2'
x^2+y^2, z^2		A_{1g}	1	1	1	1	1	1
		A_{1u}	1	1	1	-1	-1	-1
	R_z	A_{2g}	1	1	-1	1	1	-1
	z	A_{2u}	1	1	-1	-1	-1	1
(xy, yz)	(R_x, R_y)	E_{1g}	2	$2\cos\Phi$	0	2	$2\cos\Phi$	0
	(x, y)	E_{1u}	2	$2\cos\Phi$	0	-2	$-2\cos\Phi$	0
(x^2-y^2, xy)		E_{2g}	2	$2\cos 2\Phi$	0	2	$2\cos 2\Phi$	0
		E_{2u}	2	$2\cos 2\Phi$	0	-2	$-2\cos 2\Phi$	0
		$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$

Similarly to $\mathbb{R}(3)$, since there is an infinite number of symmetry operations, there is an infinite number of irreps.

(a) Find the characters of the atomic site representation $\Gamma^{a.s.}$!

(b) Find $\Gamma_{mol.vib.}$, the symmetries of the normal modes of the molecular vibrations! Which are infrared active and which are not?

Problem 24: Vibrations of the ammonia molecule NH_3

The hydrogen atoms in NH_3 are at the corners of an equilateral triangle and the nitrogen atom is either above or below the centre of this triangle.

(a) What is point group corresponding the symmetries of this molecule? Find $\Gamma^{a.s.}$ and $\Gamma_{mol.vib.}$!

(b) Which modes are infrared active? What is the polarization dependence of the normal mode excitation?

Problem 25: Selection rules and parity

Consider a paramagnetic ion with a single electron in its highest occupied orbital.

(a) Formulate the selection rule for the dipole transitions in terms of the change in the angular momentum quantum number l !

(b) Consider now this paramagnetic ion in an octahedral crystal field! We have seen that the $2l+1$-fold degenerate atomic levels will split due to the crystal field potential. Can one investigate this crystal field splitting using dipole transitions? Are there new allowed dipole transitions if we stress the crystal along the (110) direction ?