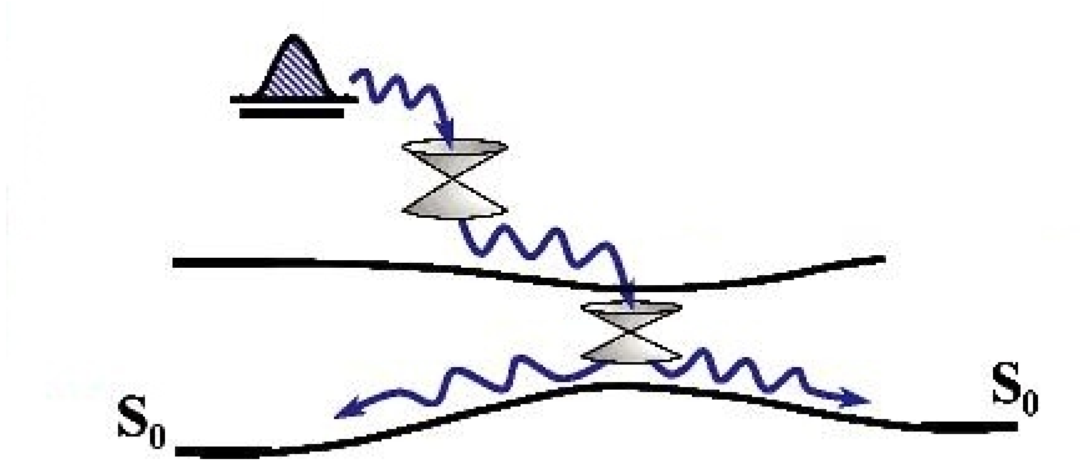
Theoretical Photochemistry WiSe 2016/17

Lecture 12



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http://www.theochem.uni-frankfurt.de/teaching/ ⟶ Theoretical Photochemistry

Topics

1. Photophysical Processes
2. The Born-Oppenheimer approximation
3. Wavepackets
4. Beyond Born-Oppenheimer – non-adiabatic transitions
5. The Franck-Condon picture of electronic transitions
6. Interaction with light: allowed and forbidden transitions; symmetry considerations
7. Conical intersections
8. Examples: Ethene, Protonated Schiff Bases (Retinal), Azobenzene
9. Some electronic structure aspects
10. Dynamics: trajectories or wavefunctions?

11. **Wavefunction propagation techniques**
12. **Trajectory surface hopping techniques**
13. **Non-linear optical spectroscopy: calculation of spectroscopic signals**
14. **Extended systems: Excitons, light-harvesting, etc.**
15. **Solvent/environmental effects**

Are the relevant transitions "allowed" or "forbidden"?

transition dipole moment:

$$\langle \psi_n^E | \mu | \psi_i^G \rangle \sim \mu_{EG} \langle \psi_n | \psi_i \rangle$$

with the Franck-Condon factors $S_{ni} = \langle \psi_n | \psi_i \rangle$

oscillator strength:

(dimensionless quantity which measures the total area under the absorption band $\sigma(\omega_I) = \frac{4\pi^2 \omega_I}{3\hbar c} \sum_n |\langle \psi_n | \mu | \psi_i \rangle|^2 \delta(\omega_I - \omega_n)$):

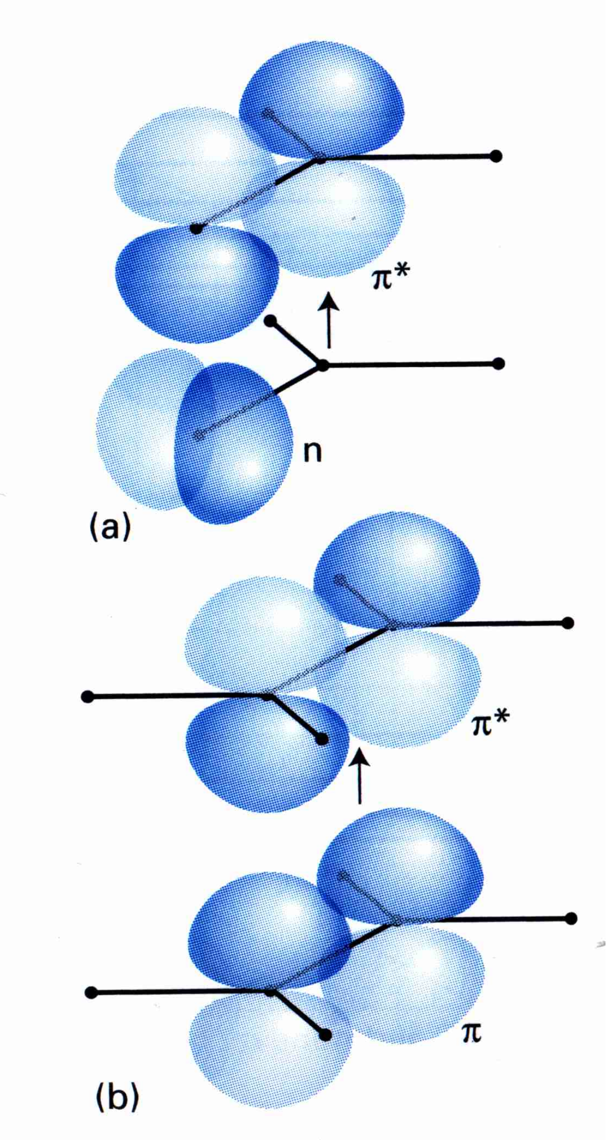
$$f = \left(\frac{4\pi m_e \omega_{EG}}{3e^2 \hbar} \right) |\mu_{EG}|^2$$

Are the relevant transitions “allowed” or “forbidden”?

1. **check whether the electronic transition dipole moment μ_{EG} is non-zero (and, hence, the oscillator strength f)**

2. **if (1) points towards an *electronically forbidden* transition, check whether the transition is vibronically allowed**

1. Electronically allowed/forbidden transitions



(a) carbonyl (C=O) group:
$\pi^* \leftarrow n$ transition is forbidden

$$n \sim O2p_y$$
$$\psi_{\pi^*} = c'\chi(C2p_x) + c\chi(O2p_x)$$

$$\langle \pi^* | \mu | n \rangle \sim c\langle Op_x | \mu | Op_y \rangle = 0$$

but: intensity borrowing possible

(b) ethene:
$\pi^* \leftarrow \pi$ transition is allowed

transition to π^* induces twisting

E.g., calculations for the anionic PYP chromophore

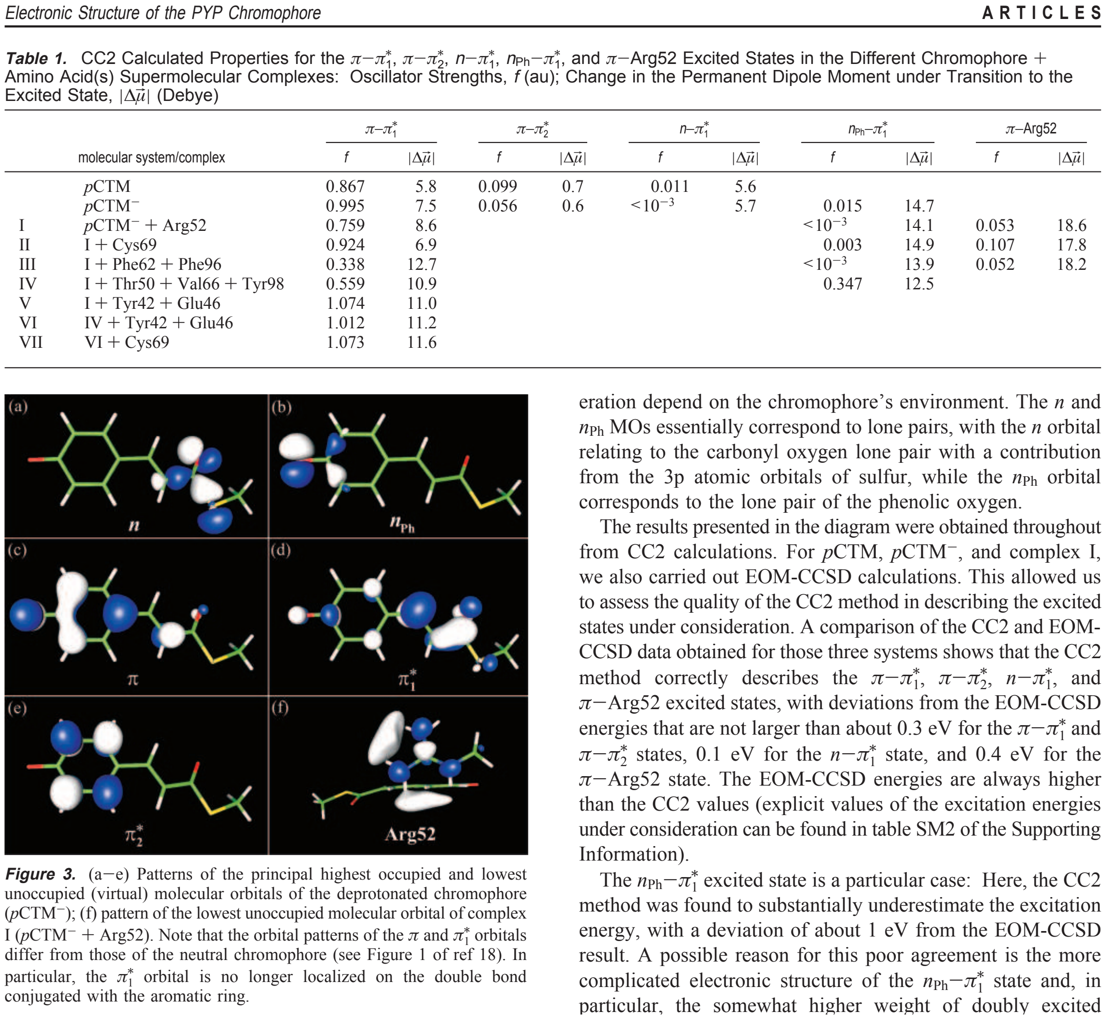


Table 1. CC2 Calculated Properties for the $\pi-\pi_1^*$, $\pi-\pi_2^*$, $n-\pi_1^*$, $n_{Ph}-\pi_1^*$, and $\pi-$Arg52 Excited States in the Different Chromophore + Amino Acid(s) Supermolecular Complexes: Oscillator Strengths, *f* (au); Change in the Permanent Dipole Moment under Transition to the Excited State, $|\Delta\vec{\mu}|$ (Debye)

		$\pi-\pi_1^*$		$\pi-\pi_2^*$		$n-\pi_1^*$		$n_{Ph}-\pi_1^*$		$\pi-$Arg52	
	molecular system/complex	*f*	$\lvert\Delta\vec{\mu}\rvert$	*f*	$\lvert\Delta\vec{\mu}\rvert$	*f*	$\lvert\Delta\vec{\mu}\rvert$	*f*	$\lvert\Delta\vec{\mu}\rvert$	*f*	$\lvert\Delta\vec{\mu}\rvert$
	*p*CTM	0.867	5.8	0.099	0.7	0.011	5.6				
	*p*CTM$^-$	0.995	7.5	0.056	0.6	$<10^{-3}$	5.7	0.015	14.7		
I	*p*CTM$^-$ + Arg52	0.759	8.6					$<10^{-3}$	14.1	0.053	18.6
II	I + Cys69	0.924	6.9					0.003	14.9	0.107	17.8
III	I + Phe62 + Phe96	0.338	12.7					$<10^{-3}$	13.9	0.052	18.2
IV	I + Thr50 + Val66 + Tyr98	0.559	10.9					0.347	12.5		
V	I + Tyr42 + Glu46	1.074	11.0								
VI	IV + Tyr42 + Glu46	1.012	11.2								
VII	VI + Cys69	1.073	11.6								

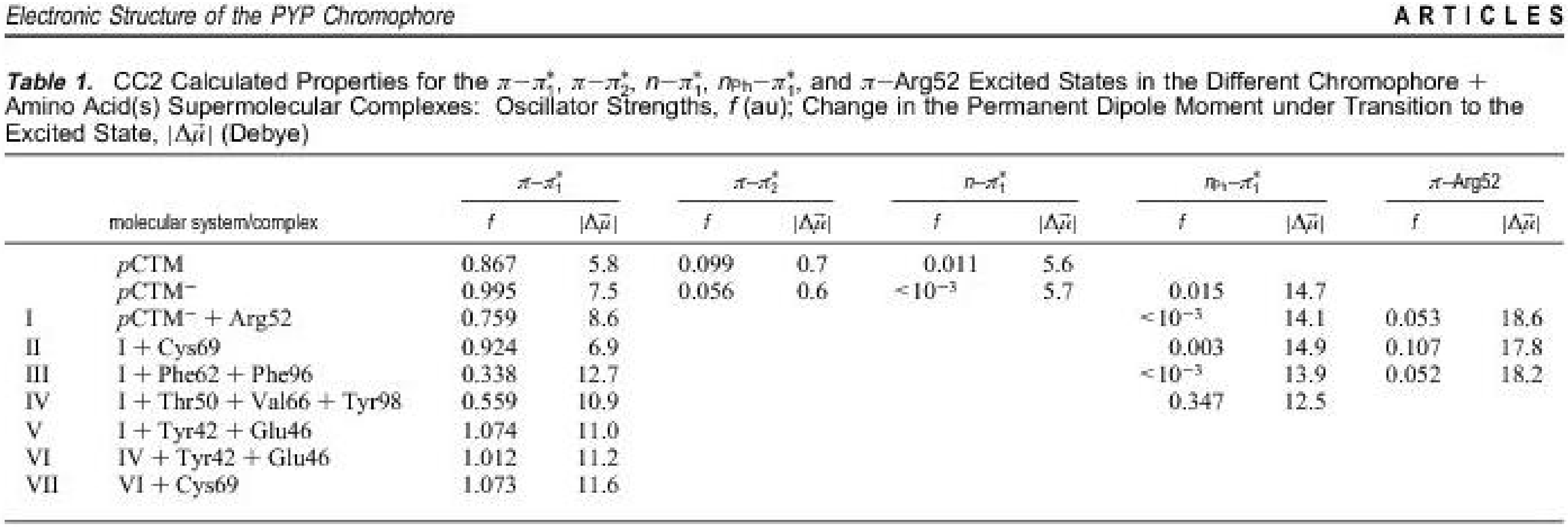
Figure 3. (a−e) Patterns of the principal highest occupied and lowest unoccupied (virtual) molecular orbitals of the deprotonated chromophore (*p*CTM$^-$); (f) pattern of the lowest unoccupied molecular orbital of complex I (*p*CTM$^-$ + Arg52). Note that the orbital patterns of the π and π_1^* orbitals differ from those of the neutral chromophore (see Figure 1 of ref 18). In particular, the π_1^* orbital is no longer localized on the double bond conjugated with the aromatic ring.

eration depend on the chromophore's environment. The *n* and n_{Ph} MOs essentially correspond to lone pairs, with the *n* orbital relating to the carbonyl oxygen lone pair with a contribution from the 3p atomic orbitals of sulfur, while the n_{Ph} orbital corresponds to the lone pair of the phenolic oxygen.

The results presented in the diagram were obtained throughout from CC2 calculations. For *p*CTM, *p*CTM$^-$, and complex I, we also carried out EOM-CCSD calculations. This allowed us to assess the quality of the CC2 method in describing the excited states under consideration. A comparison of the CC2 and EOM-CCSD data obtained for those three systems shows that the CC2 method correctly describes the $\pi-\pi_1^*$, $\pi-\pi_2^*$, $n-\pi_1^*$, and $\pi-$Arg52 excited states, with deviations from the EOM-CCSD energies that are not larger than about 0.3 eV for the $\pi-\pi_1^*$ and $\pi-\pi_2^*$ states, 0.1 eV for the $n-\pi_1^*$ state, and 0.4 eV for the $\pi-$Arg52 state. The EOM-CCSD energies are always higher than the CC2 values (explicit values of the excitation energies under consideration can be found in table SM2 of the Supporting Information).

The $n_{Ph}-\pi_1^*$ excited state is a particular case: Here, the CC2 method was found to substantially underestimate the excitation energy, with a deviation of about 1 eV from the EOM-CCSD result. A possible reason for this poor agreement is the more complicated electronic structure of the $n_{Ph}-\pi_1^*$ state and, in particular, the somewhat higher weight of doubly excited

E.g., calculations for the anionic PYP chromophore



Electronic Structure of the PYP Chromophore **ARTICLES**

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		$\pi-\pi_1^*$		$\pi-\pi_2^*$		$n-\pi_1^*$		$n_{Ph}-\pi_1^*$		π–Arg52	
	molecular system/complex	f	$\lvert\Delta\vec{\mu}\rvert$	f	$\lvert\Delta\vec{\mu}\rvert$	f	$\lvert\Delta\vec{\mu}\rvert$	f	$\lvert\Delta\vec{\mu}\rvert$	f	$\lvert\Delta\vec{\mu}\rvert$
	*p*CTM	0.867	5.8	0.099	0.7	0.011	5.6				
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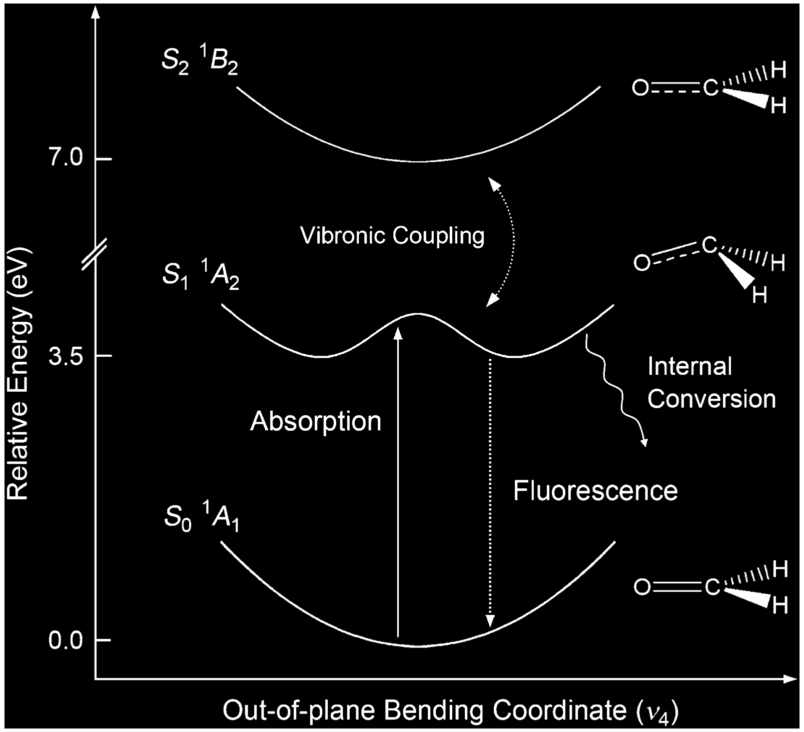
2. Vibronically allowed transitions



- formaldehyde: the $S_0 - S_1(n - \pi^*)$ transition is electronically forbidden – but becomes allowed through vibronic coupling
- the out-of-plane bending mode acts as a symmetry-breaking mode

Vibronically allowed transitions

- expand the electronic Hamiltonian in a Taylor expansion with respect to nuclear displacements:

$$H = H^{(0)} + \sum_i \Big(\frac{\partial H}{\partial Q_i}\Big)_0 Q_i + \ldots$$

- The second term is a perturbation that mixes the electronic eigenfunctions:

$$\psi = \psi_{\epsilon'} + \sum_{\epsilon \neq \epsilon'} c_\epsilon \psi_\epsilon \qquad\qquad c_\epsilon = \frac{\langle \epsilon | \sum_i (\partial H / \partial Q_i)_0 | \epsilon' \rangle Q_i}{E_{\epsilon'} - E_\epsilon} = \sum_i \kappa_i Q_i$$

- **Dipole transition moment, e.g., from the ground state (ϵ'')**

$$\mu_{\epsilon',\epsilon''} = \langle\epsilon'|\mu|\epsilon''\rangle + \sum_{\epsilon\neq\epsilon'} c^*_{\epsilon'}\langle\epsilon|\mu|\epsilon''\rangle$$

"Intensity borrowing" due to vibronic coupling

NB. The perturbation matrix elements are non-zero if $\Gamma^{(\epsilon)} \otimes \Gamma^{(i)} \otimes \Gamma^{(\epsilon')}$ contains the totally symmetric representation

Symmetry considerations

Objective (in our context): use molecular symmetry to determine whether perturbation matrix elements, or transition dipole moments are zero or not (i.e., is the transition dipole-allowed, or vibronically allowed, or neither of the two?)

More generally: consider a matrix element

$$\langle a|\Omega|b\rangle = \int d\tau \psi_a^* \Omega \psi_b$$

determine the symmetry of the wavefunctions and operators within the molecular point group and decide if the integral can be non-zero

Or, even more generally, consider an integral over a product of functions

$$I = \int d\tau \, f^{(l)*} f^{(l')} f^{(l'')}$$

where l, l', l'' label different symmetries within a point group

The integrand has to be "totally symmetric" overall to have $I \neq 0$

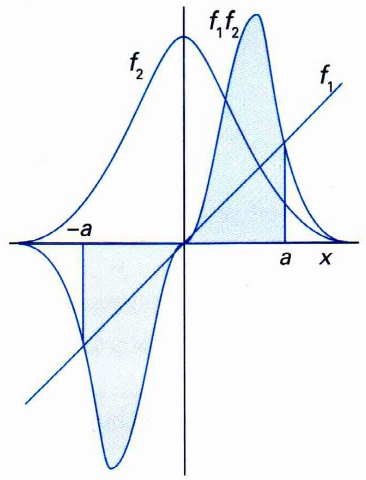
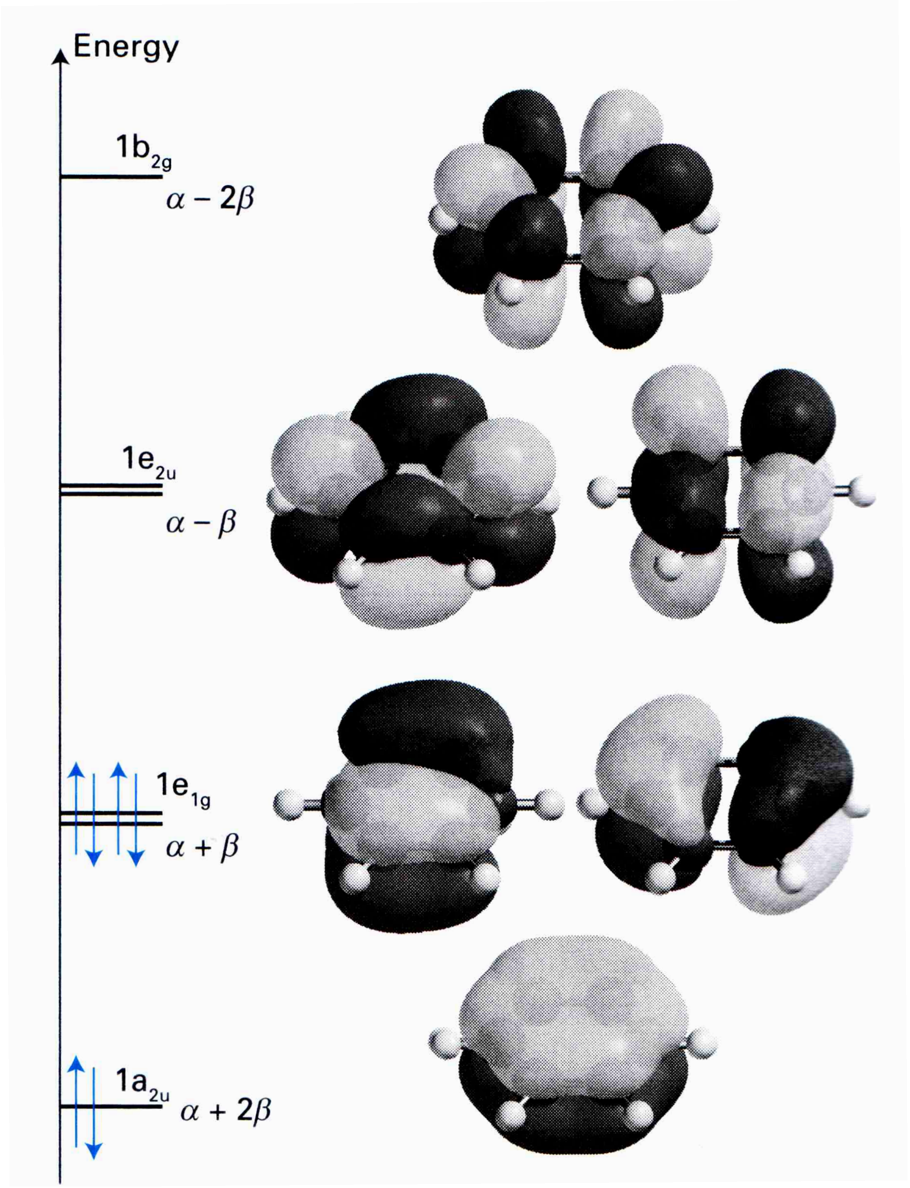


Fig. 5.1 The integral over a symmetric range of the product of a symmetric and antisymmetric function (f_2 and f_1, respectively) is zero.

General procedure

- assign a point group to the molecule in question
- with regard to an integral $I = \int d\tau\, f^{(l)*} f^{(l')} f^{(l'')}$ determine the symmetry of the individual functions with respect to the point group in question
- determine whether the symmetry of the product corresponds to the "totally symmetric" representation

Example: Benzene (D$_{6h}$)



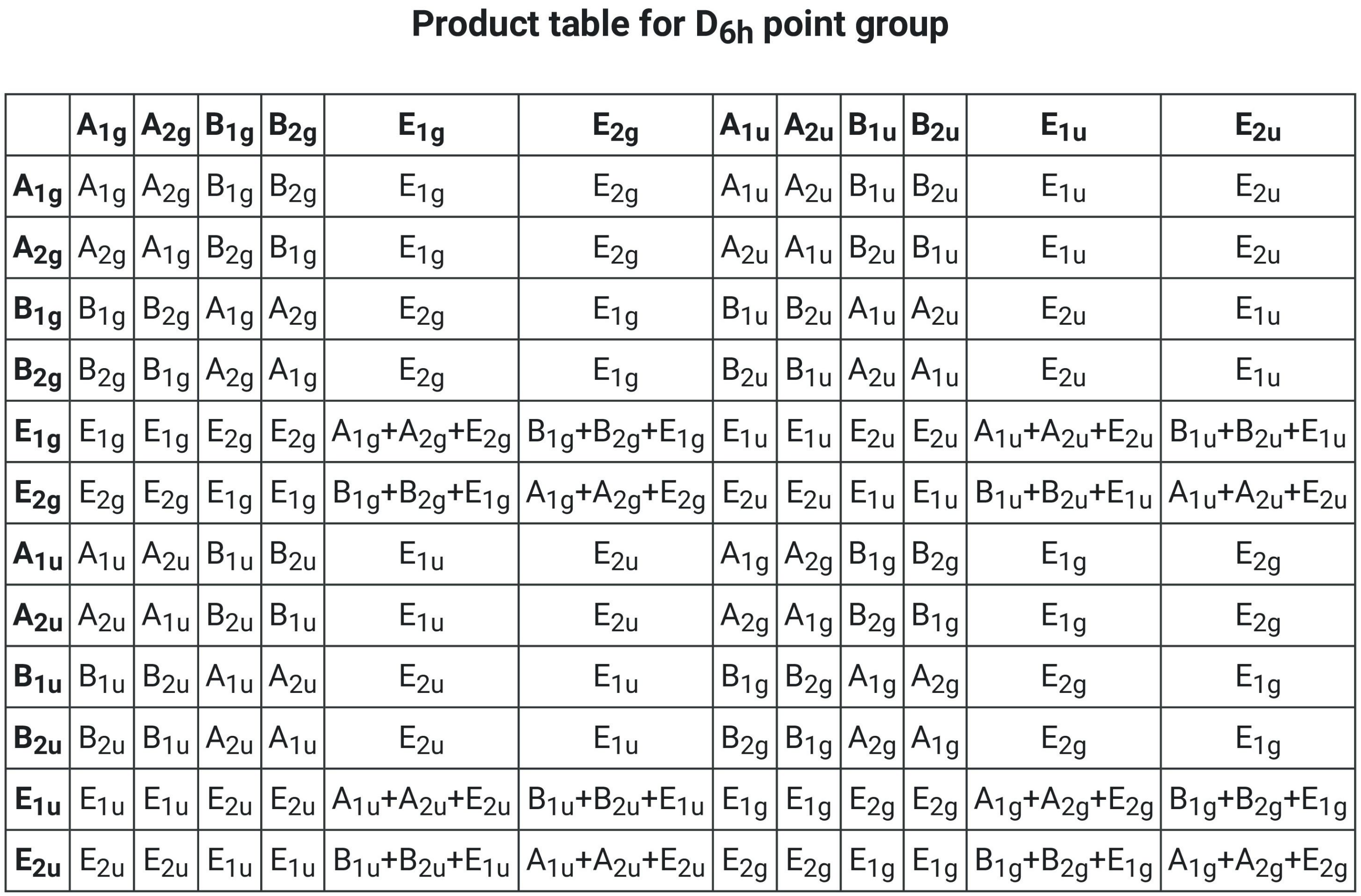
three important bands in the UV:
185 nm – symmetry-allowed, intense
200 nm – symmetry-forbidden, weak
260 nm – symmetry-forbidden, weak

ground state: G($^1A_{1g}$)

electric dipole operator:
$A_{2u}(z) + E_{1u}(x, y)$

allowed transitions:
$E_{1u} \leftarrow {}^1A_{1g}$ **(185 nm)**
$^1A_{2u} \leftarrow {}^1A_{1g}$

forbidden (but weak) transitions:
$^1B_{1u} \leftarrow {}^1A_{1g}$ **(200 nm)**
$^1B_{2u} \leftarrow {}^1A_{1g}$ **(260 nm)**



Product table for D_{6h} point group

	A_{1g}	**A_{2g}**	**B_{1g}**	**B_{2g}**	**E_{1g}**	**E_{2g}**	**A_{1u}**	**A_{2u}**	**B_{1u}**	**B_{2u}**	**E_{1u}**	**E_{2u}**
A_{1g}	A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_{1g}	E_{2g}	A_{1u}	A_{2u}	B_{1u}	B_{2u}	E_{1u}	E_{2u}
A_{2g}	A_{2g}	A_{1g}	B_{2g}	B_{1g}	E_{1g}	E_{2g}	A_{2u}	A_{1u}	B_{2u}	B_{1u}	E_{1u}	E_{2u}
B_{1g}	B_{1g}	B_{2g}	A_{1g}	A_{2g}	E_{2g}	E_{1g}	B_{1u}	B_{2u}	A_{1u}	A_{2u}	E_{2u}	E_{1u}
B_{2g}	B_{2g}	B_{1g}	A_{2g}	A_{1g}	E_{2g}	E_{1g}	B_{2u}	B_{1u}	A_{2u}	A_{1u}	E_{2u}	E_{1u}
E_{1g}	E_{1g}	E_{1g}	E_{2g}	E_{2g}	$A_{1g}+A_{2g}+E_{2g}$	$B_{1g}+B_{2g}+E_{1g}$	E_{1u}	E_{1u}	E_{2u}	E_{2u}	$A_{1u}+A_{2u}+E_{2u}$	$B_{1u}+B_{2u}+E_{1u}$
E_{2g}	E_{2g}	E_{2g}	E_{1g}	E_{1g}	$B_{1g}+B_{2g}+E_{1g}$	$A_{1g}+A_{2g}+E_{2g}$	E_{2u}	E_{2u}	E_{1u}	E_{1u}	$B_{1u}+B_{2u}+E_{1u}$	$A_{1u}+A_{2u}+E_{2u}$
A_{1u}	A_{1u}	A_{2u}	B_{1u}	B_{2u}	E_{1u}	E_{2u}	A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_{1g}	E_{2g}
A_{2u}	A_{2u}	A_{1u}	B_{2u}	B_{1u}	E_{1u}	E_{2u}	A_{2g}	A_{1g}	B_{2g}	B_{1g}	E_{1g}	E_{2g}
B_{1u}	B_{1u}	B_{2u}	A_{1u}	A_{2u}	E_{2u}	E_{1u}	B_{1g}	B_{2g}	A_{1g}	A_{2g}	E_{2g}	E_{1g}
B_{2u}	B_{2u}	B_{1u}	A_{2u}	A_{1u}	E_{2u}	E_{1u}	B_{2g}	B_{1g}	A_{2g}	A_{1g}	E_{2g}	E_{1g}
E_{1u}	E_{1u}	E_{1u}	E_{2u}	E_{2u}	$A_{1u}+A_{2u}+E_{2u}$	$B_{1u}+B_{2u}+E_{1u}$	E_{1g}	E_{1g}	E_{2g}	E_{2g}	$A_{1g}+A_{2g}+E_{2g}$	$B_{1g}+B_{2g}+E_{1g}$
E_{2u}	E_{2u}	E_{2u}	E_{1u}	E_{1u}	$B_{1u}+B_{2u}+E_{1u}$	$A_{1u}+A_{2u}+E_{2u}$	E_{2g}	E_{2g}	E_{1g}	E_{1g}	$B_{1g}+B_{2g}+E_{1g}$	$A_{1g}+A_{2g}+E_{2g}$

- **for a matrix element $\langle \psi_1 | \hat{\mu} | \psi_2 \rangle$, check whether the direct product $\Gamma_{\psi_1} \otimes \Gamma_{\mu} \otimes \Gamma_{\psi_2}$ contains the totally symmetric representation A_{1g}**

Character table for point group D_{6h}

(x axis coincident with C'_2 axis)

D_{6h}	E	$2C_6$ (z)	$2C_3$	C_2	$3C'_2$	$3C''_2$	i	$2S_3$	$2S_6$	σ_h (xy)	$3\sigma_d$	$3\sigma_v$	linear functions, rotations	quadratic functions	cubic functions
A_{1g}	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	-	x^2+y^2, z^2	-
A_{2g}	+1	+1	+1	+1	-1	-1	+1	+1	+1	+1	-1	-1	R_z	-	-
B_{1g}	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1	-	-	-
B_{2g}	+1	-1	+1	-1	-1	+1	+1	-1	+1	-1	-1	+1	-	-	-
E_{1g}	+2	+1	-1	-2	0	0	+2	+1	-1	-2	0	0	(R_x, R_y)	(xz, yz)	-
E_{2g}	+2	-1	-1	+2	0	0	+2	-1	-1	+2	0	0	-	(x^2-y^2, xy)	-
A_{1u}	+1	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1	-1	-	-	-
A_{2u}	+1	+1	+1	+1	-1	-1	-1	-1	-1	-1	+1	+1	z	-	z^3, $z(x^2+y^2)$
B_{1u}	+1	-1	+1	-1	+1	-1	-1	+1	-1	+1	-1	+1	-	-	$x(x^2-3y^2)$
B_{2u}	+1	-1	+1	-1	-1	+1	-1	+1	-1	+1	+1	-1	-	-	$y(3x^2-y^2)$
E_{1u}	+2	+1	-1	-2	0	0	-2	-1	+1	+2	0	0	(x, y)	-	(xz^2, yz^2) $[x(x^2+y^2), y(x^2+y^2)]$
E_{2u}	+2	-1	-1	+2	0	0	-2	+1	+1	-2	0	0	-	-	$[xyz, z(x^2-y^2)]$

Additional information

Number of symmetry elements	h = 24
Number of irreducible representations	n = 12

Symmetry operations

Symmetry operations = operations that leave the object (molecule) apparently unchanged

The ensemble of symmetry operations for a given molecule define the point group.

Symmetry operations and symmetry elements

E = identity – the symmetry element is the object itself

C_n = n-fold rotation – the symmetry element is the axis of rotation

σ = reflection – the symmetry element is the mirror plane
($\sigma_v, \sigma_h, \sigma_d$ = vertical, horizontal, dihedral plane)

i = inversion – the symmetry element is the inversion center

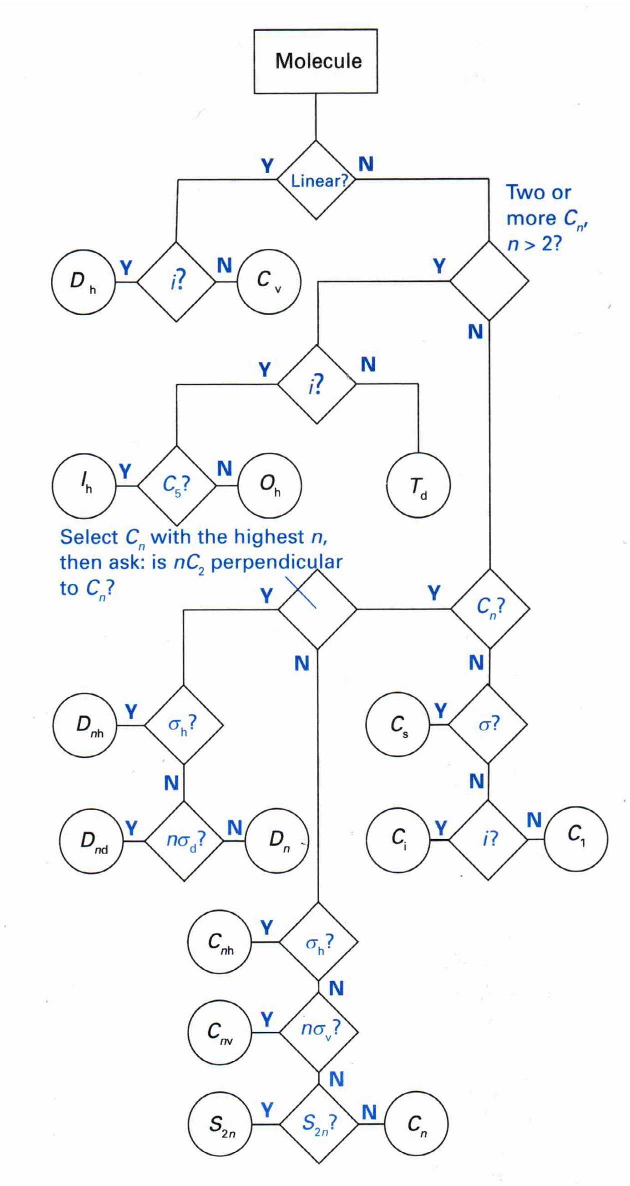
S_n = n-fold improper rotation ("rotary-reflection") = rotation + horizontal reflection

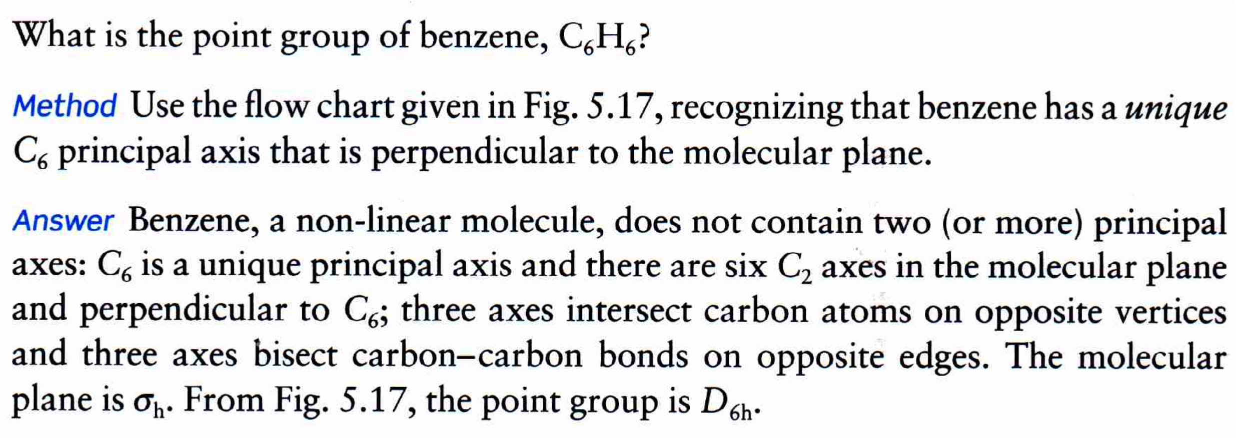
Group property

The set of symmetry operations of an object (e.g., a molecule) constitute a group in a mathematical sense:

1. The identity is a symmetry operation
2. Symmetry operations combine in accord with the associative law of multiplication
3. If R and S are symmetry operations, then RS is also a symmetry operation
4. The inverse of each symmetry operation is also a symmetry operation

Identifying point groups



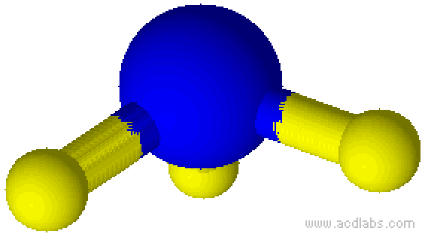


What is the point group of benzene, C_6H_6?

Method Use the flow chart given in Fig. 5.17, recognizing that benzene has a ***unique*** C_6 principal axis that is perpendicular to the molecular plane.

Answer Benzene, a non-linear molecule, does not contain two (or more) principal axes: C_6 is a unique principal axis and there are six C_2 axes in the molecular plane and perpendicular to C_6; three axes intersect carbon atoms on opposite vertices and three axes bisect carbon–carbon bonds on opposite edges. The molecular plane is σ_h. From Fig. 5.17, the point group is D_{6h}.

Group multiplication tables



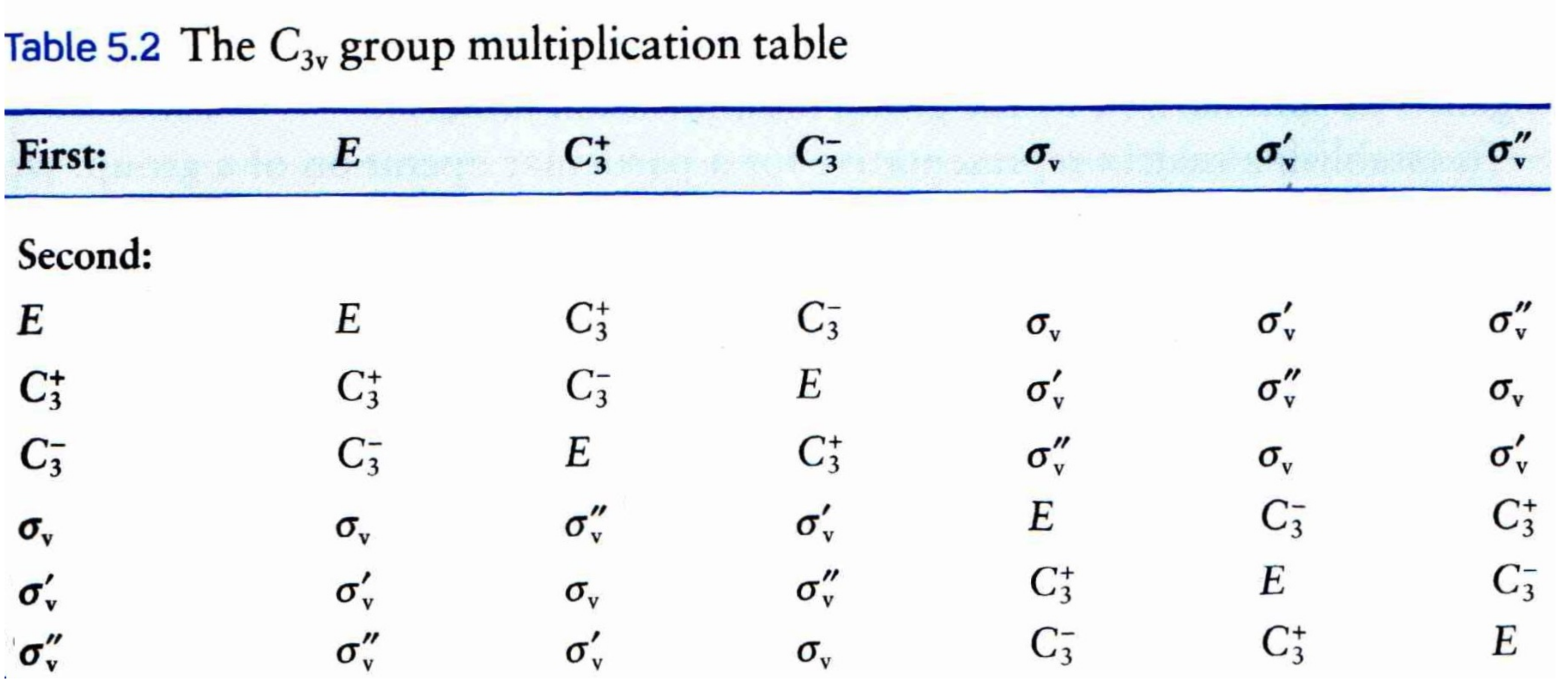


Table 5.2 The C_{3v} group multiplication table

First:	E	C_3^+	C_3^-	σ_v	σ_v'	σ_v''
Second:						
E	E	C_3^+	C_3^-	σ_v	σ_v'	σ_v''
C_3^+	C_3^+	C_3^-	E	σ_v'	σ_v''	σ_v
C_3^-	C_3^-	E	C_3^+	σ_v''	σ_v	σ_v'
σ_v	σ_v	σ_v''	σ_v'	E	C_3^-	C_3^+
σ_v'	σ_v'	σ_v	σ_v''	C_3^+	E	C_3^-
σ_v''	σ_v''	σ_v'	σ_v	C_3^-	C_3^+	E

Matrix representations

Choose a basis, e.g., the s orbitals of NH$_3$: (s_n, s_A, s_B, s_C)

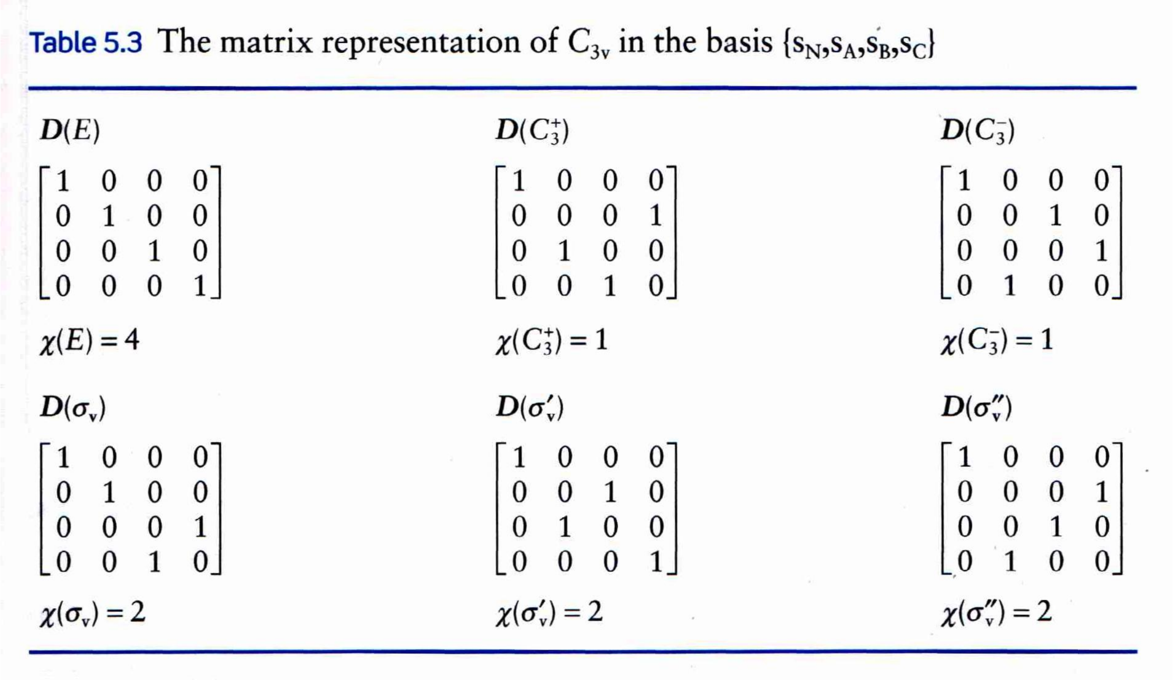


Table 5.3 The matrix representation of C_{3v} in the basis $\{s_N, s_A, s_B, s_C\}$

$\boldsymbol{D}(E)$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

$\chi(E) = 4$

$\boldsymbol{D}(C_3^+)$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix}$$

$\chi(C_3^+) = 1$

$\boldsymbol{D}(C_3^-)$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{bmatrix}$$

$\chi(C_3^-) = 1$

$\boldsymbol{D}(\sigma_v)$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$$

$\chi(\sigma_v) = 2$

$\boldsymbol{D}(\sigma_v')$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

$\chi(\sigma_v') = 2$

$\boldsymbol{D}(\sigma_v'')$

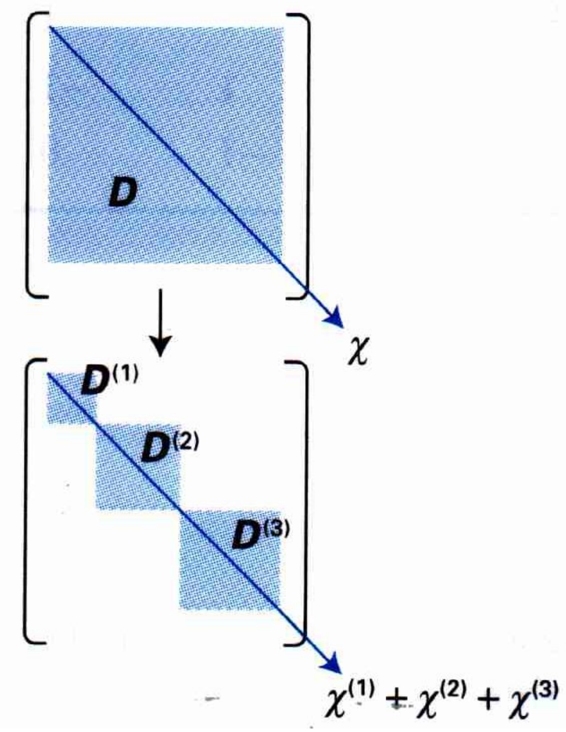
$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$$

$\chi(\sigma_v'') = 2$

The matrix representatives multiply in exactly the same way as the symmetry operations

Irreducible representations ("irreps")

Apply similarity transformations to reduce a given matrix representation to a block-diagonal, "irreducible" form



"character" (trace) is invariant:

$$\chi(R) = \sum_i D_{ii}(R)$$

$$\chi(R) = \sum_l a_l \chi^{(l)}(R)$$

determine coefficients:

$$a_l = 1/h \sum_R \chi^{(l)*}(R)\chi(R)$$

Similarity transformations: NH_3

Choose a new basis, e.g., linear combinations of the s orbitals of NH_3:

$s_N = s_N$
$s_1 = s_A + s_B + s_C$
$s_2 = 2s_A - s_B - s_C$
$s_3 = s_B - s_C$

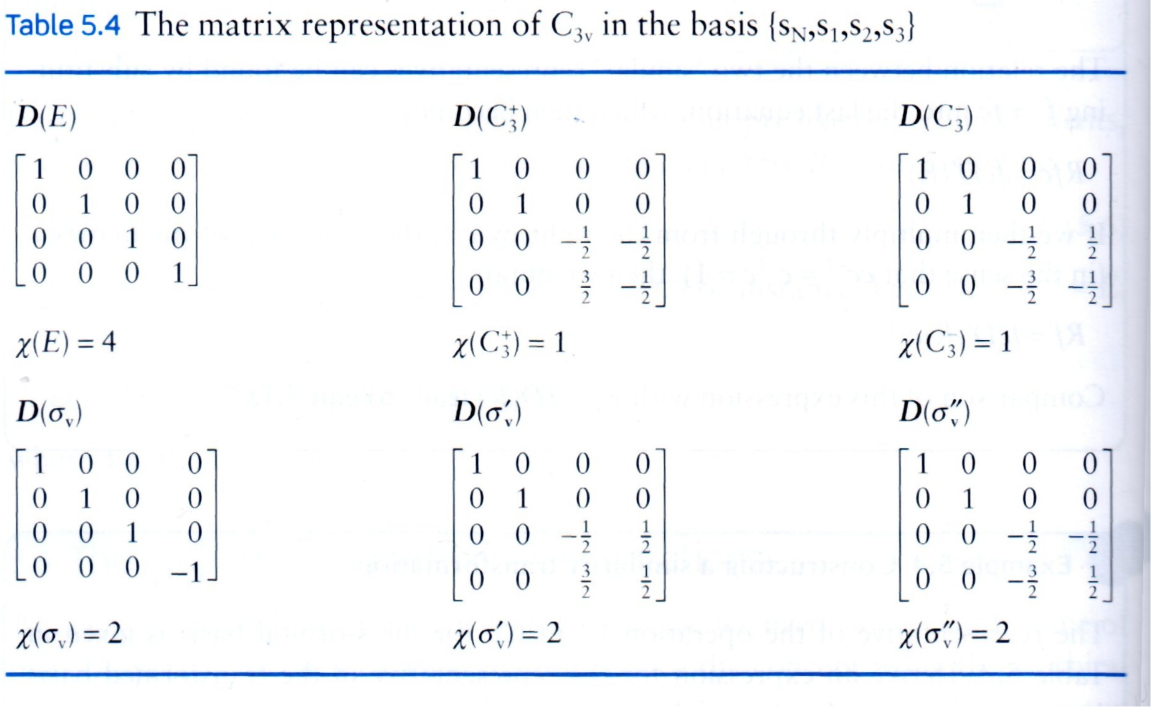


Table 5.4 The matrix representation of C_{3v} in the basis $\{s_N, s_1, s_2, s_3\}$

$\boldsymbol{D}(E)$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

$\chi(E) = 4$

$\boldsymbol{D}(C_3^+)$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & -\frac{1}{2} \\ 0 & 0 & \frac{3}{2} & -\frac{1}{2} \end{bmatrix}$$

$\chi(C_3^+) = 1$

$\boldsymbol{D}(C_3^-)$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & \frac{1}{2} \\ 0 & 0 & -\frac{3}{2} & -\frac{1}{2} \end{bmatrix}$$

$\chi(C_3^-) = 1$

$\boldsymbol{D}(\sigma_v)$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$$

$\chi(\sigma_v) = 2$

$\boldsymbol{D}(\sigma_v')$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & \frac{1}{2} \\ 0 & 0 & \frac{3}{2} & \frac{1}{2} \end{bmatrix}$$

$\chi(\sigma_v') = 2$

$\boldsymbol{D}(\sigma_v'')$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & -\frac{1}{2} \\ 0 & 0 & -\frac{3}{2} & \frac{1}{2} \end{bmatrix}$$

$\chi(\sigma_v'') = 2$

Obtain a block-diagonal representation!

Irreducible representations: character tables

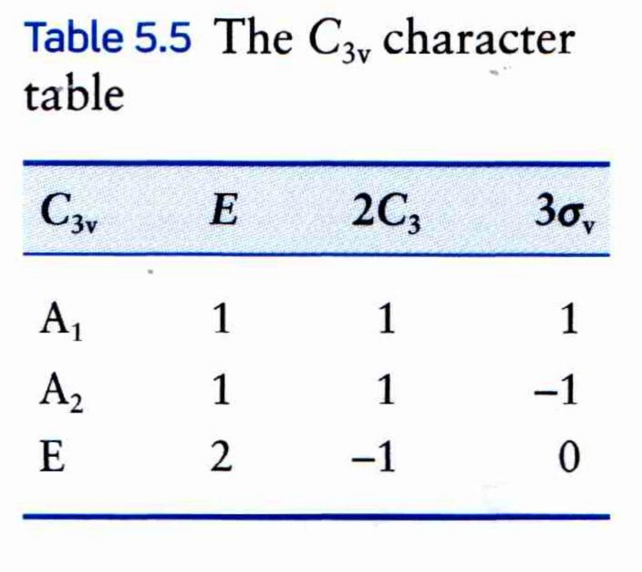


Table 5.5 The C_{3v} character table

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	–1
E	2	–1	0

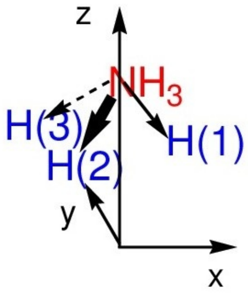
A, B: symmetry species of one-dimensional irreps

E: two-dimensional irreps

T: three-dimensional irreps

Molecular Orbitals of NH_3 (C_{3v})

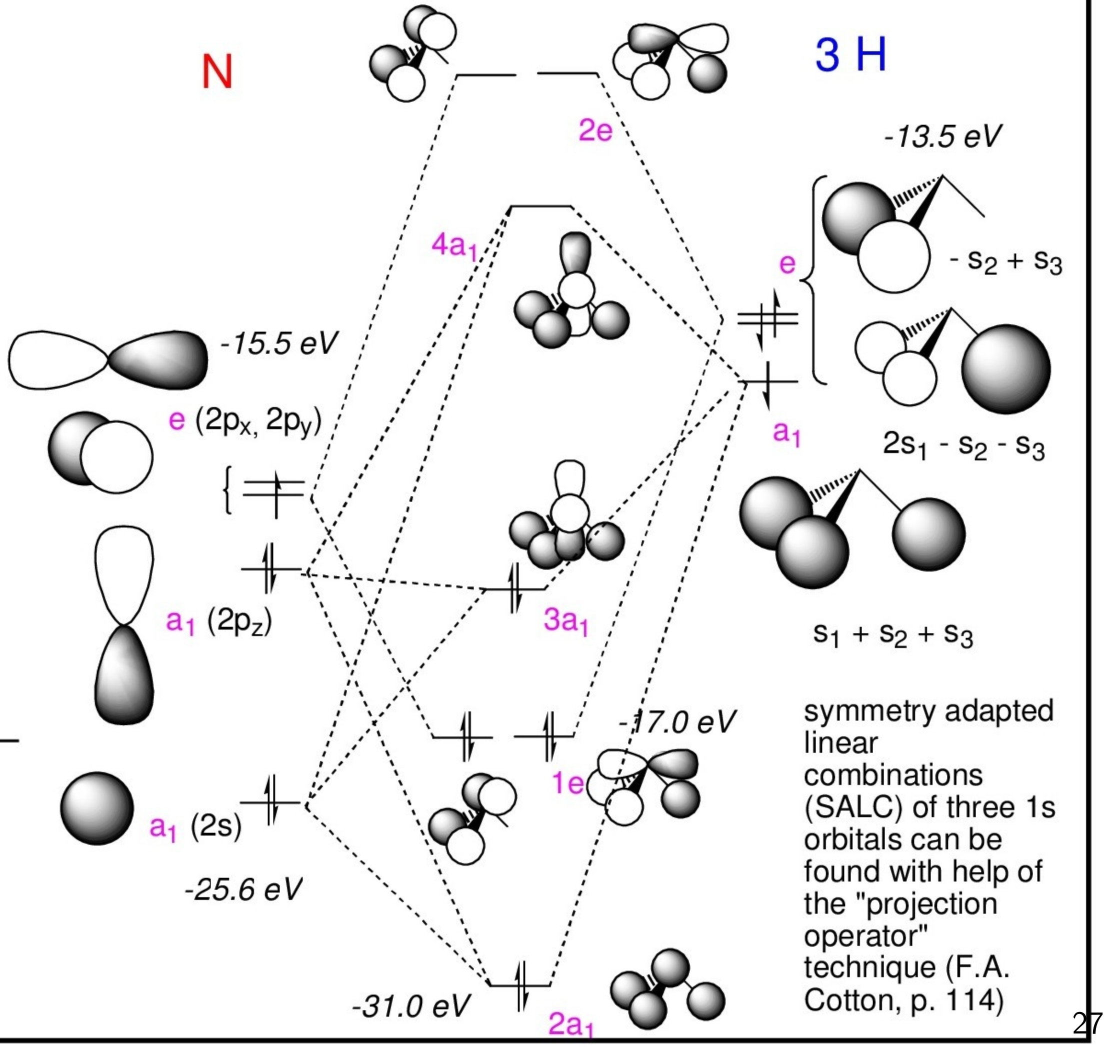
- NH_3 (C_{3v}: E, $2C_3$, $3\sigma_v$)



The symmetry of 3H's group orbitals:

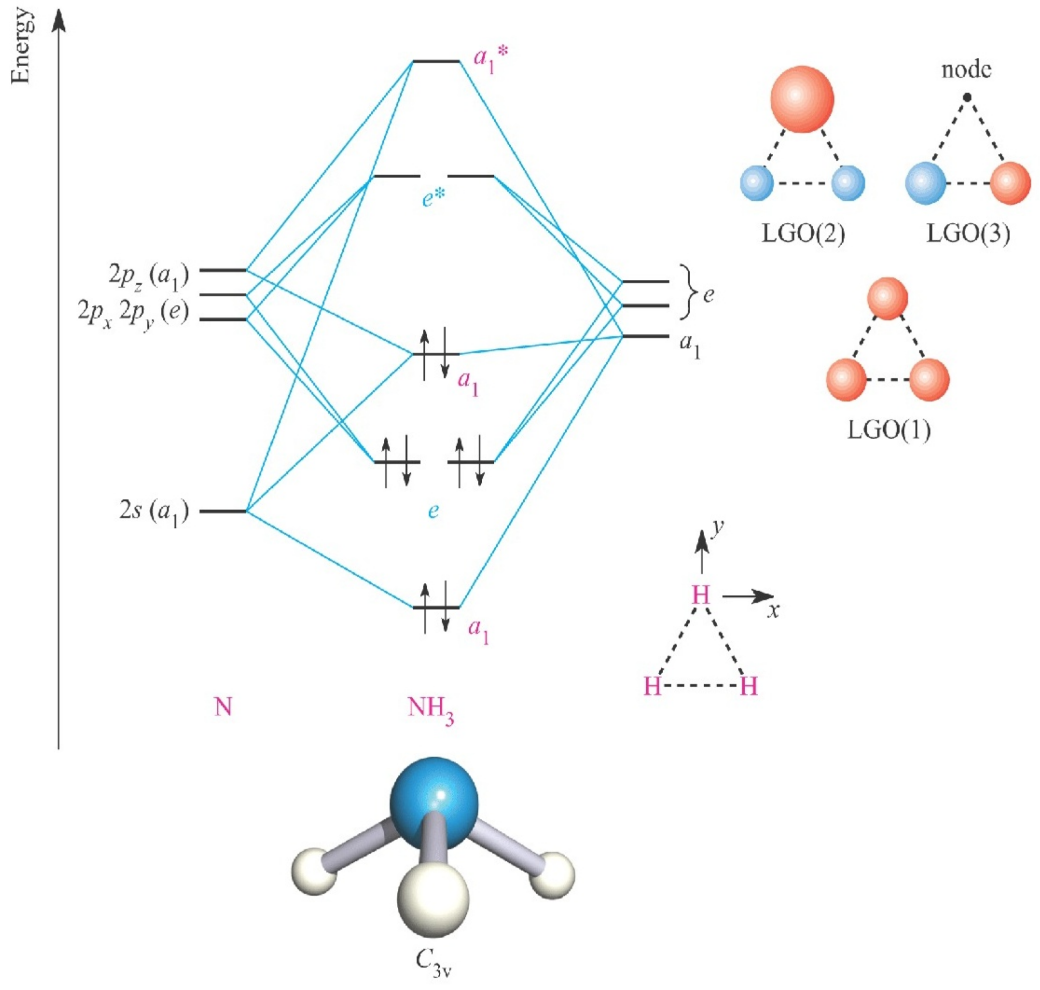
$\Gamma_r = 3E + 0C_3 + \sigma_v = A_1 + E$

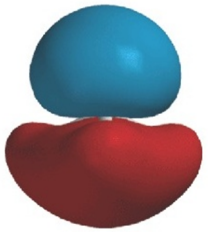
C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1		
E	2	-1	0	(x,y)	



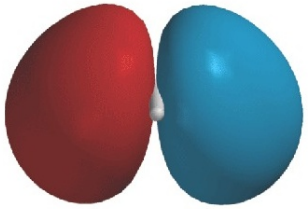
symmetry adapted linear combinations (SALC) of three 1s orbitals can be found with help of the "projection operator" technique (F.A. Cotton, p. 114)

Molecular Orbital Theory

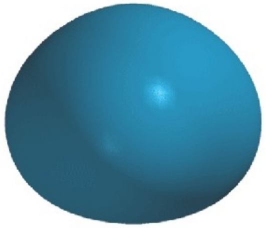




Representation of the HOMO (a_1)

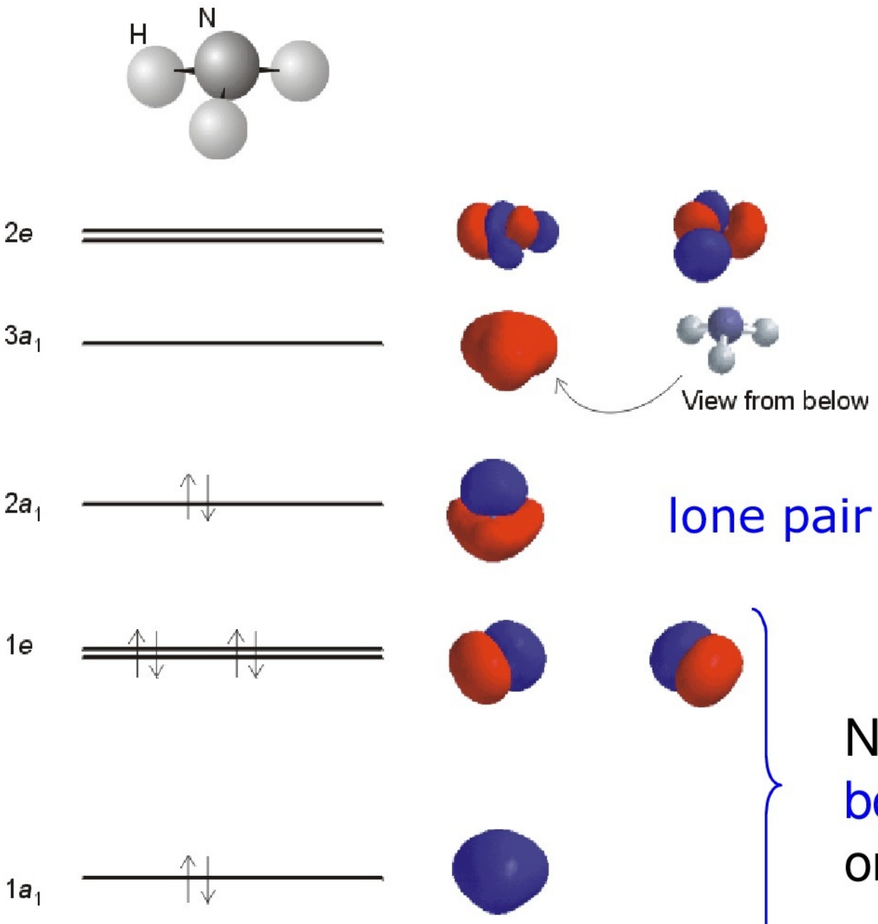


Representation of one of the e MOs



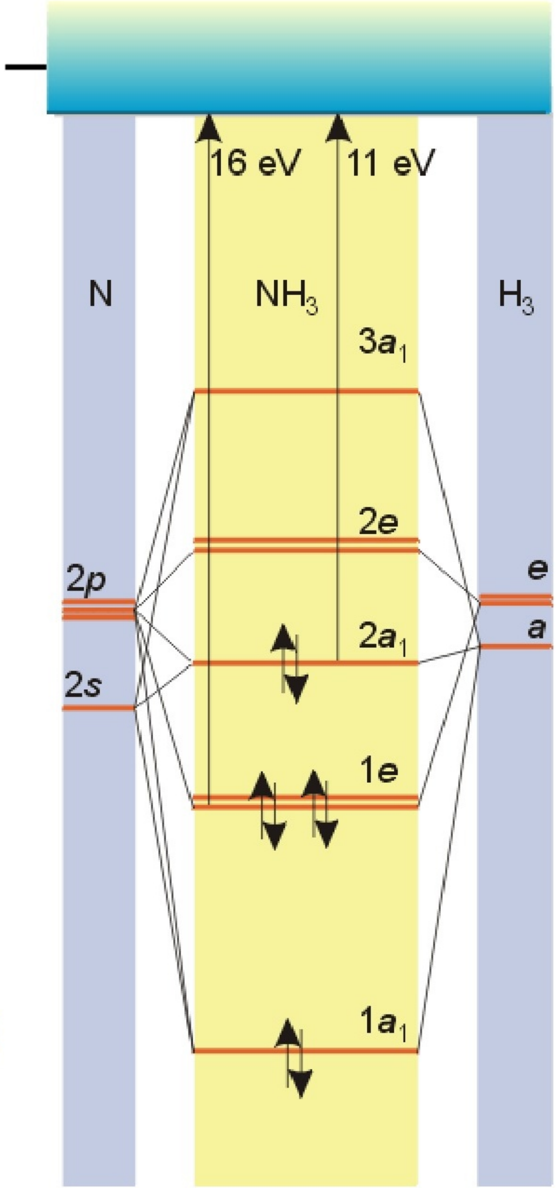
Representation of the lowest lying a_1 MO

Molecular Orbital Theory –



lone pair on N

N-H
bonding
orbitals



Which irreps are spanned by a reducible representation?

$$\Gamma_{\text{red}} = \sum_l a_l \Gamma^{(l)}$$

$$a_l = \frac{1}{h} \sum_R \chi^{(l)*}(R)\chi(R)$$

h = order of the group

R = symmetry operation

$\Gamma^{(l)}$ = symmetry species of the irreducible representation

χ = character of the (reducible or irreducible) representation

How to use projection operators to generate symmetry-adapted bases

For a given basis $\{f_i\}$, apply projection operators as follows:

$$\mathcal{P}^{(l)} f_i = \frac{d_l}{h} \sum_R \chi^{(l)}(R)^* R \; f_i$$

h = order of the group

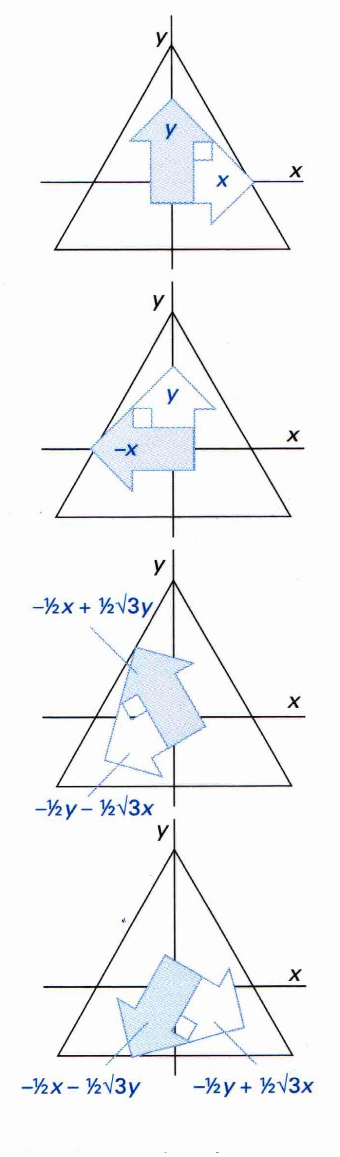
d_l = dimension of the irrep

R = symmetry operation

$\Gamma^{(l)}$ = symmetry species of the irreducible representation

χ = character of the (reducible or irreducible) representation

Symmetry properties of functions



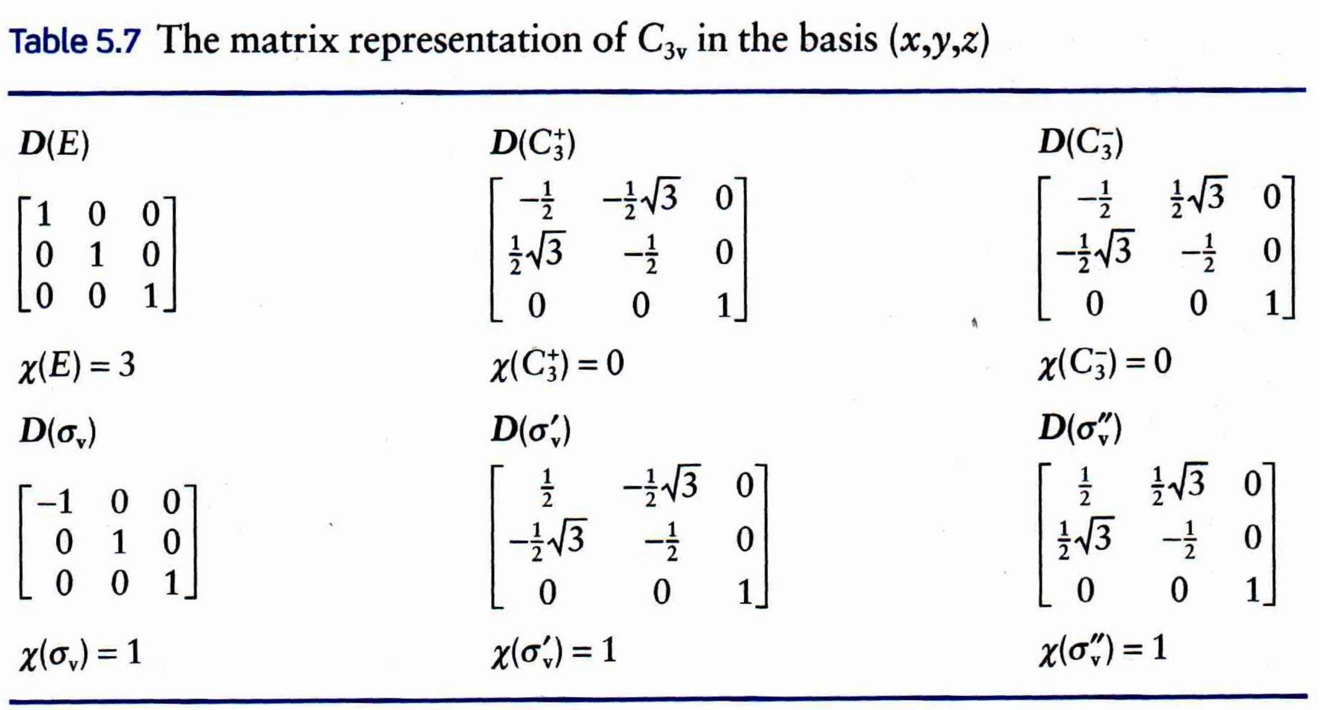


Table 5.7 The matrix representation of C_{3v} in the basis (x,y,z)

$D(E)$	$D(C_3^+)$	$D(C_3^-)$
$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & -\frac{1}{2}\sqrt{3} & 0 \\ \frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & \frac{1}{2}\sqrt{3} & 0 \\ -\frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$
$\chi(E) = 3$	$\chi(C_3^+) = 0$	$\chi(C_3^-) = 0$
$D(\sigma_v)$	$D(\sigma_v')$	$D(\sigma_v'')$
$\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} \frac{1}{2} & -\frac{1}{2}\sqrt{3} & 0 \\ -\frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} \frac{1}{2} & \frac{1}{2}\sqrt{3} & 0 \\ \frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$
$\chi(\sigma_v) = 1$	$\chi(\sigma_v') = 1$	$\chi(\sigma_v'') = 1$

(x, y, z) span $A_1 + E$

C_{3v}, again

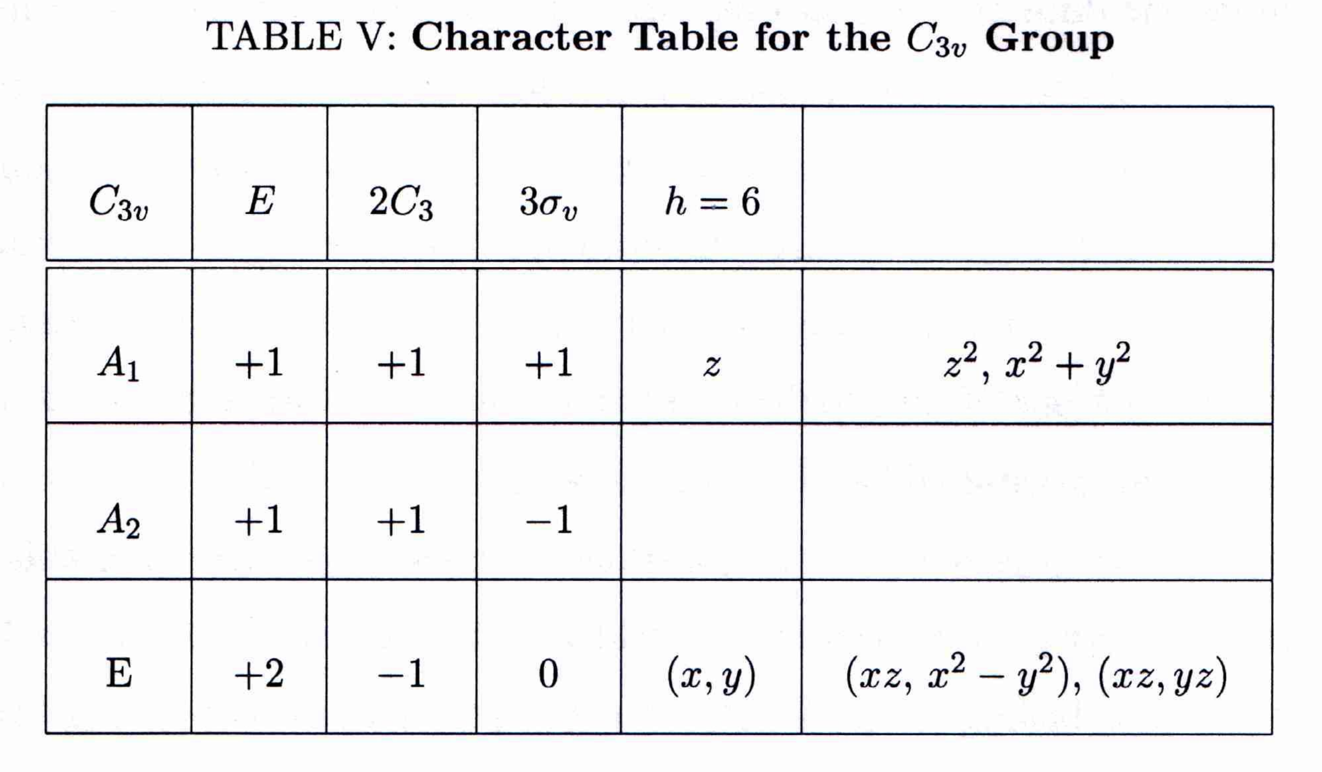


TABLE V: **Character Table for the C_{3v} Group**

C_{3v}	E	$2C_3$	$3\sigma_v$	$h = 6$	
A_1	$+1$	$+1$	$+1$	z	$z^2,\ x^2 + y^2$
A_2	$+1$	$+1$	-1		
E	$+2$	-1	0	(x, y)	$(xz,\ x^2 - y^2),\ (xz, yz)$

- **determine symmetry of dipole operator from x, y, z entries**