Quantum Mechanical Operators and Wavefunctions

"well behaved" functions (φ), have the following properties

- must be continuous (no "breaks")
- must have continuous derivatives (no "kinks")
- must be normalizable. Mathematically, this means ("$d\tau$" implies integration over all space):

$$\int \varphi^* \varphi \, d\tau = C, (C \text{ is a finite constant}).$$

if we multiply φ by $1/\sqrt{C}$,

$$\int \left(\frac{\varphi^*}{\sqrt{C}} \right) \left(\frac{\varphi}{\sqrt{C}} \right) d\tau = 1, \quad \frac{\varphi}{\sqrt{C}} \text{ is said to be "normalized"}$$

Orthogonality of Wavefunctions
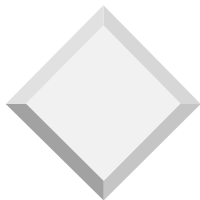
✿ Two functions, φ and χ, are *orthogonal* if

$$\int \varphi^* \chi \, d\tau = 0$$

✿ Eigenfunctions of QM operators are orthogonal (proof - handout). If 2 or more eigenfunctions (eg., φ_1 & φ_2) have the same eigenvalue, then

orthogonal eigenfunctions can be "made":
$$\chi_1 = \varphi_1 \text{ and } \chi_2 = \varphi_2 + c\varphi_1$$
$$\text{where } c = -\int \varphi_1^* \varphi_2 \, d\tau \bigg/ \int \varphi_1^* \varphi_1 \, d\tau.$$

Commuting Operators have Common Eigenfunctions

✿ This is shown on your handout

✿ Symmetry operators can't change the energy of wavefunctions after they "operate". Symmetry operators therefore commute with the Hamiltonian ($\mathcal{H}$).

✿ A set of commuting operators including $\mathcal{H}$ and the symmetry operators **A, B,** . . . have common eigenfunctions.

Example: The H-Atom (Digression)

$$\mathcal{H}\psi_{nlm}(r,\theta,\varphi) = E_{nlm}\psi_{nlm}(r,\theta,\varphi)$$

$$\mathcal{H} = \mathcal{T} + \mathcal{V}(r) = \frac{-\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r}$$

$$= \frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{1}{2mr^2}\mathcal{L}^2 - \frac{Ze^2}{r}$$

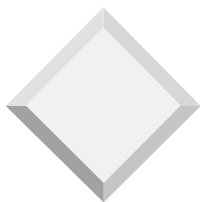where $\mathcal{L}^2$ is the (squared) angular momentum operator:

$$\mathcal{L}^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right) = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta}\right) + \frac{\mathcal{L}_z^2}{\sin^2\theta}$$

$\boxed{\mathcal{L}^2}$ operates only on θ and φ $\Rightarrow$ $\boxed{\text{commutes with }\mathcal{H}}$

$\boxed{\mathcal{L}_z} = \frac{\hbar}{i}\left(\frac{\partial}{\partial\varphi}\right)$ operates only on φ $\Rightarrow$ $\boxed{\text{commutes with }\mathcal{H}\text{ and }\mathcal{L}^2}$

Since $\mathcal{H}$ does not operate on spin variables $\Rightarrow$

$\boxed{\mathcal{S}^2\text{ and }\mathcal{S}_z\text{ also commute with }\mathcal{H},\ \mathcal{L}^2,\text{ and }\mathcal{L}_z}$

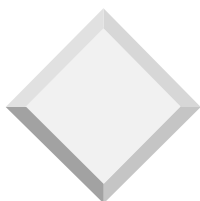# Commuting Operators have Common Eigenfunctions

❖ For the hydrogen atom, operators that commute with $\mathcal{H}$ are $\mathcal{L}^2$, $\mathcal{L}_z$, $\mathcal{S}^2$, and $\mathcal{S}_z$.

❖ Therefore, the eigenfunctions of $\mathcal{H}$ are also eigenfunctions of $\mathcal{L}^2$, $\mathcal{L}_z$, $\mathcal{S}^2$, and $\mathcal{S}_z$.

$\mathcal{L}^2$: $l = 0, 1, ..., n\text{-}1$

$\mathcal{L}_z$: $m_l = -l, -l+1, ..., l-1, l$ ($2l+1$ values)

$\mathcal{S}^2$: ($s = {}^1/_2$ for one electron)

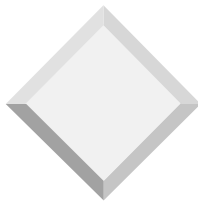$\mathcal{S}_z$: ($m_s = -{}^1/_2, +{}^1/_2$ for one electron, $2S+1$ values in general)

Group Theory & Quantum Mechanics

❖ Symmetry Operators commute with the <u>molecular</u> electronic or vibrational Hamiltonian:

$$[R,\mathcal{H}] = R\mathcal{H} - \mathcal{H}R = 0 \quad \text{or} \quad R\mathcal{H} = \mathcal{H}R$$

$$\mathcal{H}\psi_i = \varepsilon_i\psi_i \quad \text{where} \quad \{\varepsilon_i\} \text{ and } \{\psi_i\}$$

are sets of energies and wavefunctions for that Hamiltonian

Group Theory & QM, cont.

✿ <u>Nondegenerate case</u>: only one wavefunction has energy ε_i. Then,

$$\mathcal{H}R\psi_i = R\mathcal{H}\psi_i$$
$$\mathcal{H}(R\psi_i) = R\varepsilon_i\psi_i = \varepsilon_i(R\psi_i)$$
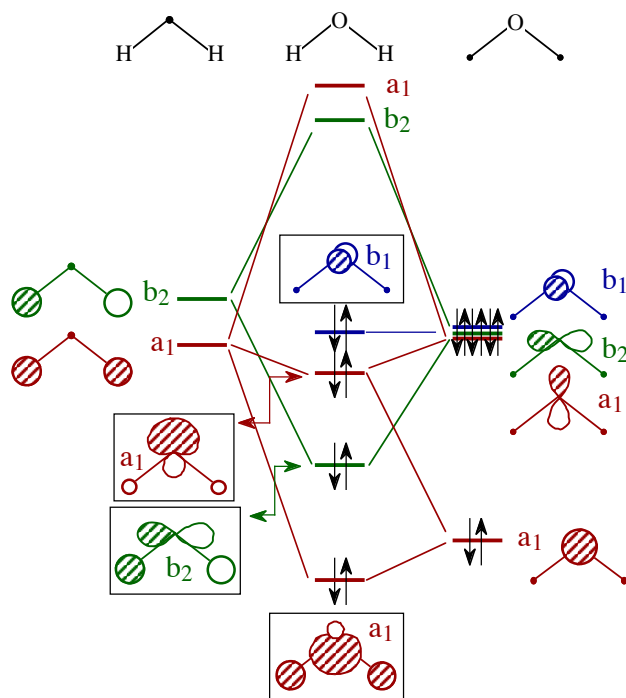
$R\psi_i$ is a wavefunction with the same energy.

Therefore, $R\psi_i = C\psi_i$, where C is a constant with a magnitude of 1 (usually $C = \pm 1$, but it could be complex, $C = e^{i\alpha}$, where α is const.)
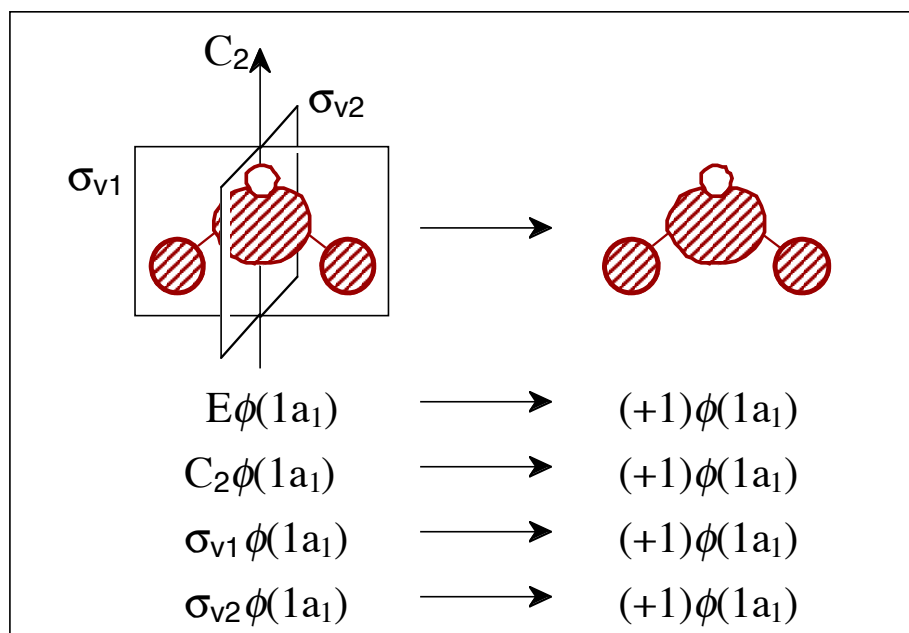
Example: Valence MOs of Water

✿ H_2O has C_{2v} symmetry.

✿ The symmetry operators of the C_{2v} group all commute with each other (each is in its own class).

✿ The eigenfunctions of $\mathcal{H}$ must also be eigenfunctions of the symmetry operators $\mathbf{E}$, C_2, σ_{v1}, and σ_{v2}.
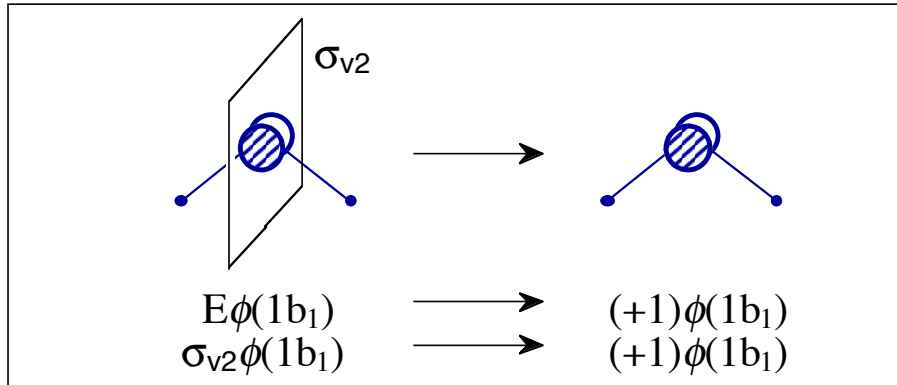
Building a MO diagram for H_2O

a_1 orbital of H_2O

$$E\phi(1a_1) \longrightarrow (+1)\phi(1a_1)$$

$$C_2\phi(1a_1) \longrightarrow (+1)\phi(1a_1)$$

$$\sigma_{v1}\phi(1a_1) \longrightarrow (+1)\phi(1a_1)$$

$$\sigma_{v2}\phi(1a_1) \longrightarrow (+1)\phi(1a_1)$$

b_1 orbital of H_2O

$$E\phi(1b_1) \longrightarrow (+1)\phi(1b_1)$$
$$\sigma_{v2}\phi(1b_1) \longrightarrow (+1)\phi(1b_1)$$

b_1 orbital of H_2O, cont.

$$C_2\phi(1b_1) \longrightarrow (-1)\phi(1b_1)$$
$$\sigma_{v1}\phi(1b_1) \longrightarrow (-1)\phi(1b_1)$$

b_2 orbital of H_2O

$$\sigma_{v1}$$

$$E\phi(1b_2) \longrightarrow (+1)\phi(1b_2)$$
$$\sigma_{v1}\phi(1b_2) \longrightarrow (+1)\phi(1b_2)$$

b_2 orbital of H_2O, cont.

$$C_2$$
$$\sigma_{v2}$$

$$C_2\phi(1b_2) \longrightarrow (-1)\phi(1b_2)$$
$$\sigma_{v2}\phi(1b_2) \longrightarrow (-1)\phi(1b_2)$$
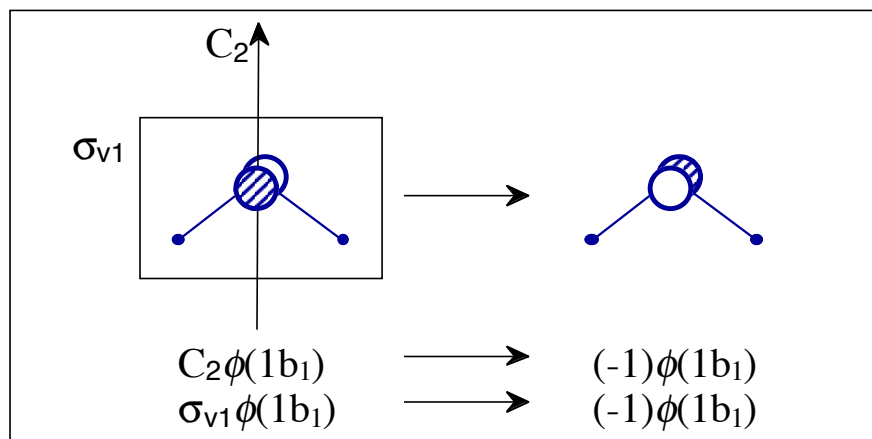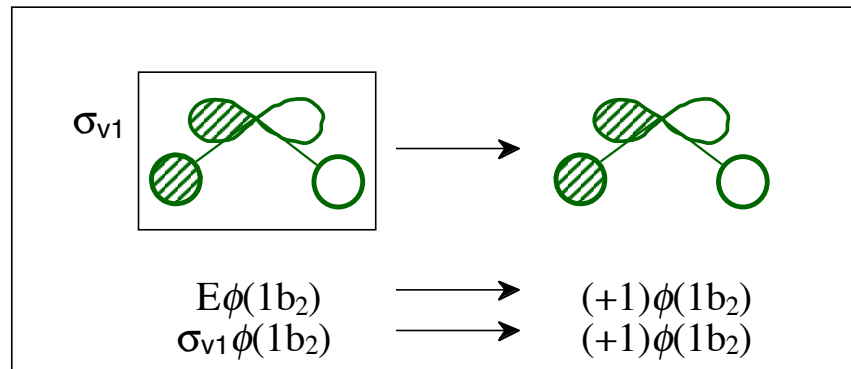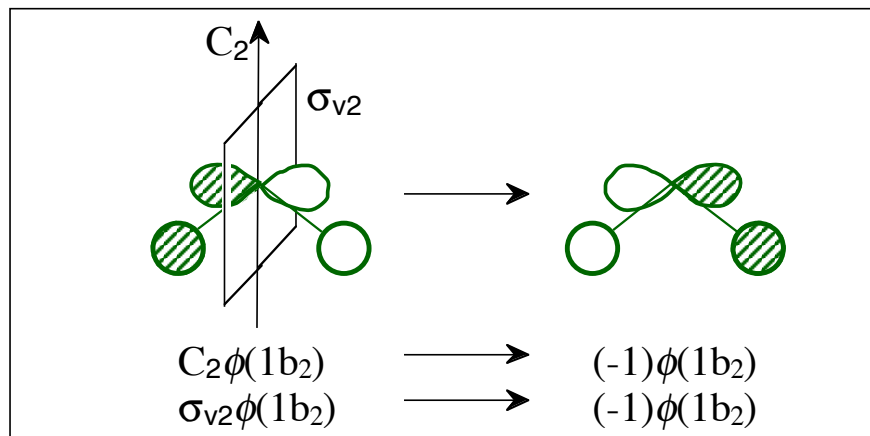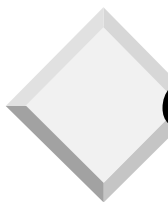
Group Theory & QM, cont.

✿ <u>Degenerate case</u>: more than one wavefunction has energy ε_i. We still write

$$\mathcal{H}R\psi_i = R\mathcal{H}\psi_i$$

$$\mathcal{H}(R\psi_i) = R\varepsilon_i\psi_i = \varepsilon_i(R\psi_i)$$

Again, $R\psi_i$ is a wavefunction with the same

energy, but it is possible that $R\psi_i = \Sigma_j c_j \psi_j$ where

the sum is over the all wavefunctions with the same energy $(\varepsilon_i = \varepsilon_j)$ — for molecules the

degeneracy is usually only 2- or 3-fold.

Higher Dimensional Representations and Degeneracy

✿ k-fold degenerate wavefunctions form a basis for a k-dimensional irreducible rep.

✿ Example: For a molecule with octahedral (O_h) symmetry three p orbitals (p_x, p_y, p_z) on the central atom must be degenerate, $\varepsilon_x = \varepsilon_y = \varepsilon_z$. Demonstrate that the p orbitals form a basis for the T_{1u} representation in O_h symmetry.

✿ The converse is true: If k wavefunctions are degenerate, they form a basis for a k-dimensional irreducible representation.
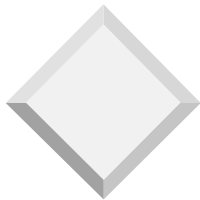
The Direct Product - What is it for?

✿ It is often important to know whether integrals involving bases of IRs are zero. i.e., if f and g are basis functions belonging to Γ_1 and Γ_2,   ?

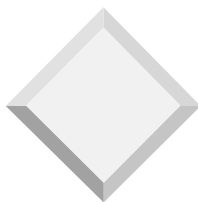$$\int_{\substack{\text{all} \\ \text{space}}} fg \ \mathrm{d}\tau = 0$$

If the integrand, fg, belongs to the totally symmetric IR, then this is nonzero. Otherwise it is identically zero.

Direct Products:
Is there nothing else?

"The universe is an enormous direct product of representations of symmetry groups." – *Steven Weinberg*[1]

[1]Steven Weinberg, Sheldon Glashow, and Abdus Salam were awarded the 1979 Nobel Prize in Physics for their incorporation of the weak and electromagnetic 'forces' into a single theory.

States and Configurations

✿ Each of the electronic <u>states</u> of an atom or a molecule are usually described as being built up from one (or perhaps more than one) <u>configuration</u>.

✿ Similarly, the total vibrational state of a molecule derives from a description of which individual modes are excited.

✿ Atomic Example: What states arise from a $1s^2$ $2s^2$ $2p^2$ (C atom ground) configuration?

Read: Harris & Bertolucci, *Symmetry and Spectroscopy...*, Chapter 4, pp. 225-45.

$2p_x$, $2p_y$, $2p_{\pm 1}$
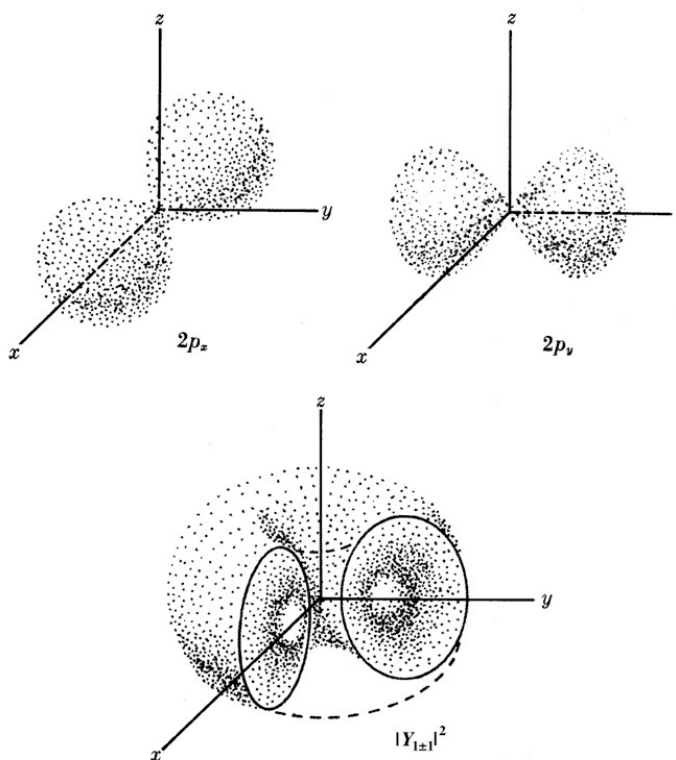
Carbon: Atomic Energy Levels

Experimental atomic energy levels are shown, with energies in cm^{-1}.

Configuration	Term	J	Level (cm^{-1})
$2s^2 2p^2$	^3P	0	0
		1	16.40
		2	43.40
	term		29.58
$2s^2 2p^2$	^1D	2	10 192.63
	term		10 192.63
$2s^2 2p^2$	^1S	0	21 648.01
	term		21 648.01
$2s2p^3$	$^5S°$	2	33 735.20
	term		33 735.20
$2s^2 2p(^2P°)3s$	$^3P°$	0	60 333.43
		1	60 352.63
		2	60 393.14
	term		60 373.00
$2s^2 2p(^2P°)3s$	$^1P°$	1	61 981.82
	term		61 981.82

http://physics.nist.gov/ PhysRefData/ASD/ index.html

Carbon: Atomic Energy Levels
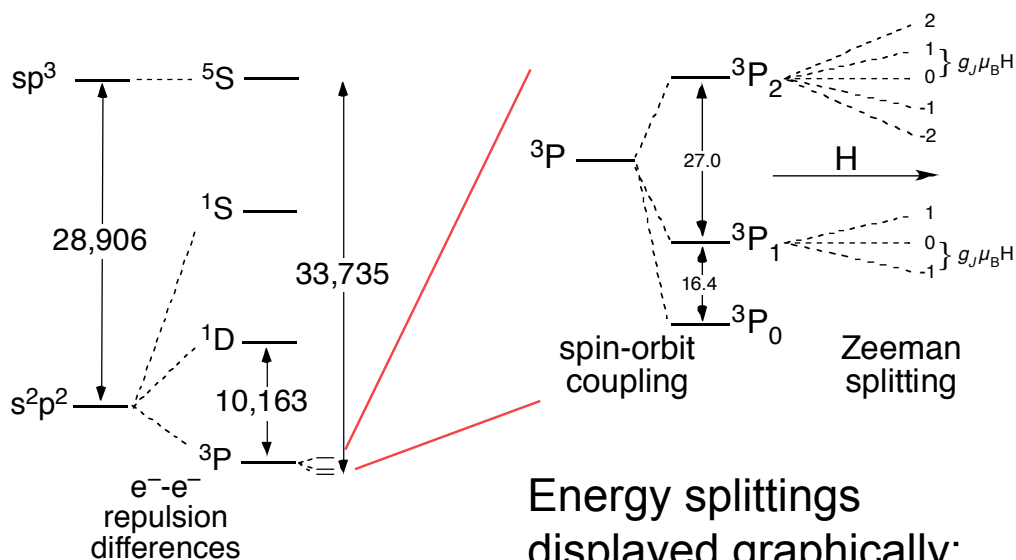
Energy splittings displayed graphically; energies in cm^{-1}

$$\mu_B H = 5.6711 \times 10^{-5} \text{ eV} \sim 0.4574 \text{ cm}^{-1} \text{, at } H = 1.0T$$

The Direct Product - What is it for?

✿ We often seek to know the symmetries of electronic <u>states</u> that arise from configuration with partially filled orbital subshells. For example, what <u>states</u> arise from $(t_{2g})^1 (e_g)^1$ configuration for a d^2 octahedral complex?

↑ —— e_g

↑ ——— t_{2g}
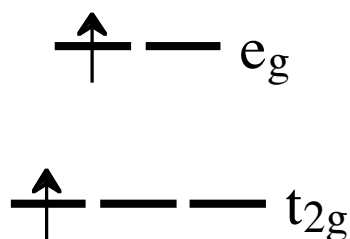
The Direct Product - What is it?

✿ Basis Functions: If two sets of functions $\{X_j, j = 1, m\}$ and $\{Y_j, j = 1, n\}$ form bases for two representations, then the representation spanned by the $m \times n$ product functions, $\{X_i Y_j\}$ is called a <u>direct product</u> representation.

Direct Product Representations

$\Gamma(R_i)$ in 1st 2-D basis $\qquad$ $\Gamma(R_i)$ in 2nd 2-D basis

$$\begin{bmatrix} a & b \\ c & d \end{bmatrix} \otimes \begin{bmatrix} p & q \\ r & s \end{bmatrix} = \left[\begin{array}{c|c} a \times \begin{bmatrix} p & q \\ r & s \end{bmatrix} & b \times \begin{bmatrix} p & q \\ r & s \end{bmatrix} \\ \hline c \times \begin{bmatrix} p & q \\ r & s \end{bmatrix} & d \times \begin{bmatrix} p & q \\ r & s \end{bmatrix} \end{array} \right]$$

$$= \left[\begin{array}{cc|cc} ap & aq & bp & bq \\ ar & as & br & bs \\ \hline cp & cq & dp & dq \\ cr & cs & dr & ds \end{array} \right]$$

$\Gamma(R_i)$ in 4-D basis made up of product functions from 1st and 2nd basis

$$\begin{bmatrix} a & b \end{bmatrix} \otimes \begin{bmatrix} p & q \end{bmatrix} = \begin{bmatrix} ap & aq & bp & bq \end{bmatrix}$$

$$\begin{bmatrix} a \\ b \end{bmatrix} \otimes \begin{bmatrix} p \\ q \end{bmatrix} = \begin{bmatrix} ap \\ aq \\ bp \\ bq \end{bmatrix}$$

Illustration: S_3 Operation in D_{3h}

E' represention; x and y basis. S_3 matrix : $\begin{bmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix}$

A_2'' represention; z basis. S_3 "matrix" : -1

Direct Product rep.; xz and yz basis.

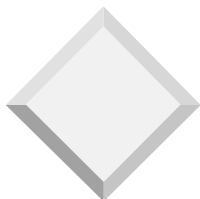S_3 matrix : $\begin{bmatrix} 1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{bmatrix}$

Illustration: S_3 Operation in D_{3h}

E' rep.; p_x and p_y basis. S_3 matrix :
$$\begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{bmatrix}$$

E'' rep.; d_{xz} and d_{yz} basis. S_3 matrix :
$$\begin{bmatrix} 1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{bmatrix}$$

Direct Product rep.; $p_x d_{xz}, p_x d_{yz}, p_y d_{xz}, p_y d_{yz}$, basis.

S_3 matrix :
$$\left[\begin{array}{cc|cc} -1/4 & -\sqrt{3}/4 & -\sqrt{3}/4 & -3/4 \\ \sqrt{3}/4 & -1/4 & 3/4 & -\sqrt{3}/4 \\ \hline \sqrt{3}/4 & 3/4 & -1/4 & -\sqrt{3}/4 \\ -3/4 & \sqrt{3}/4 & \sqrt{3}/4 & -1/4 \end{array}\right]$$

Properties and Uses of Direct Products

❀ The direct product representation Γ_{AB}, obtained from Γ_A and Γ_B, will only contain the totally symmetric representation if Γ_A and Γ_B belong to the <u>same</u> IR.

Proof

The number of times the ith IR is contained in Γ_{AB} is

$$a_i = \tfrac{1}{h}\sum_R \chi_{AB}(R)\chi_i(R)$$

$$\chi_1(R) = 1 \text{ for all } R \quad \Rightarrow \quad a_1 = \tfrac{1}{h}\sum_R \chi_{AB}(R)$$
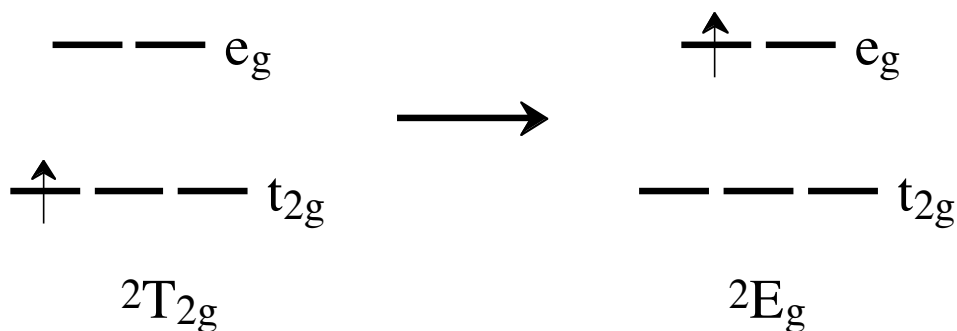
but we know that $\chi_{AB}(R) = \chi_A(R)\chi_B(R),$ so

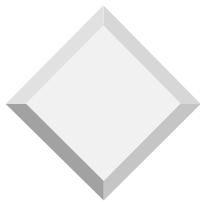$$a_1 = \tfrac{1}{h}\sum_R \chi_A(R)\chi_B(R) = \delta_{AB}$$

where the final equality arises from orthogonality.

SPECTRAL TRANSITION PROBABILITIES

When are electronic transitions allowed?

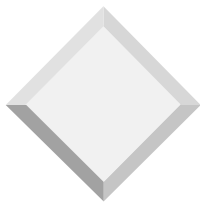For example, is the $^2T_{2g} \rightarrow {}^2E_g$ transition illustrated below "symmetry allowed"?

TRANSITION ENERGIES

The energetic restriction on the allowedness of optical transitions like the $^2T_{2g} \rightarrow \, ^2E_g$ transition illustrated earlier is familiar:

$$E_f - E_i = h\nu$$

But this doesn't deal with <u>symmetry</u>.

Transition Probabilities, Symmetry Aspects

I $\propto$ transition moment: $\quad I \, \propto \, \int \psi_i \mu \psi_j d\tau$

$$\mu \, = \, \sum_i q_i x_i \, + \, \sum_i q_i y_i \, + \, \sum_i q_i z_i$$

μ is the dipole moment operator

$$I_x \, \propto \, \int \psi_i x \psi_j d\tau$$

See Harris & Bertolucci, pp. 130-5.

$$I_y \, \propto \, \int \psi_i y \psi_j d\tau$$

$$I_z \, \propto \, \int \psi_i z \psi_j d\tau$$
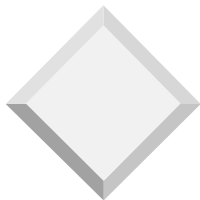
Transition Probabilities, Symmetry Rules

An electric dipole transition will be allowed with *x, y,* or *z* polarization if the direct product of the representations of the two states concerned is or contains the irreducible representation to which *x, y,* or *z*, respectively, belongs.

Summary

- In the handout, "**Transitions Between Stationary States (Adapted from *Harris* and *Bertolucci*, p. 130)**", an expression for the probability that a system in its ground state, ψ_0 can be stimulated by radiation into an excited state, ψ_1, is derived:
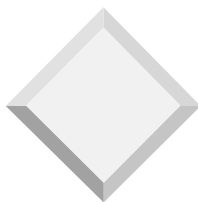
$$\Psi(\mathbf{r},t) = c_0(t)\Psi_0(\mathbf{r},t) + c_1(t)\Psi_1(\mathbf{r},t)$$

$$\boxed{\frac{d(c_1{}^*c_1)}{dt} \propto \mathcal{E}_0^2 \left(\mu_{01}^{x\,2} + \mu_{01}^{y\,2} + \mu_{01}^{z\,2} \right)}$$ assuming $c_0(0) = 1$ and $c_1(0) = 0$.

$\mathcal{E}_0^2$ is proportional to the light intensity and

$$\boxed{\mu_{01}^{x,y,z} = e\int \psi_1^* \begin{Bmatrix} x \\ y \\ z \end{Bmatrix} \psi_0 d\tau}$$ are the transition moment integrals.

- This expression applies to an integral over all wavelengths of incident light (in the dipole approximation) and was the form used to evaluate whether an electron transition was symmetry allowed.

Allowedness

- In group theory, prescription for deciding whether a transition is dipole-allowed is straightforward:

  - If the ground and excited states respectively belong to the Γ_0 and Γ_1 representations of the point group of the molecule in question, then a transition is dipole-allowed if and only if

  $$\Gamma_0 \otimes \Gamma_1 \text{ contains } \begin{cases} \Gamma_x \text{ for } x\text{-polarized light} \\ \Gamma_y \text{ for } y\text{-polarized light} \\ \Gamma_z \text{ for } z\text{-polarized light} \end{cases}$$

  - Spin doesn't change: $\Delta S = 0$. For states where large spin-orbit mixing is possible (large ζ and/or small ΔE between mixed states), the rule is weakened.
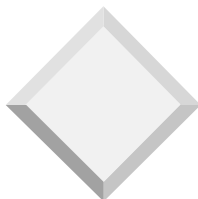
Examples

- ✿ Is the $^2T_{2g} \rightarrow {}^2E_g$ transition illustrated earlier "symmetry allowed"?

- ✿ What about a $^2E \rightarrow {}^2T_2$ transition for a tetrahedral complex?

^2E $^2T_2$
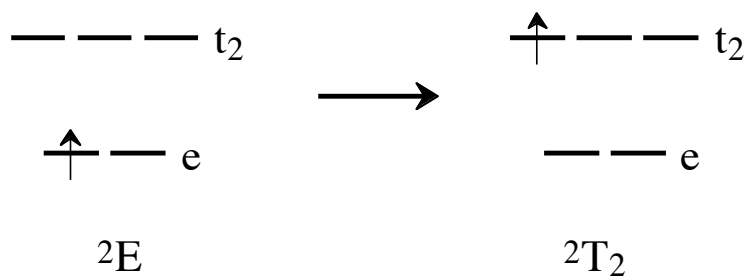
T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	−1	1	−1	(R_x, R_y, R_z)	
T_2	3	0	−1	−1	1	(x, y, z)	(xy, xz, yz)

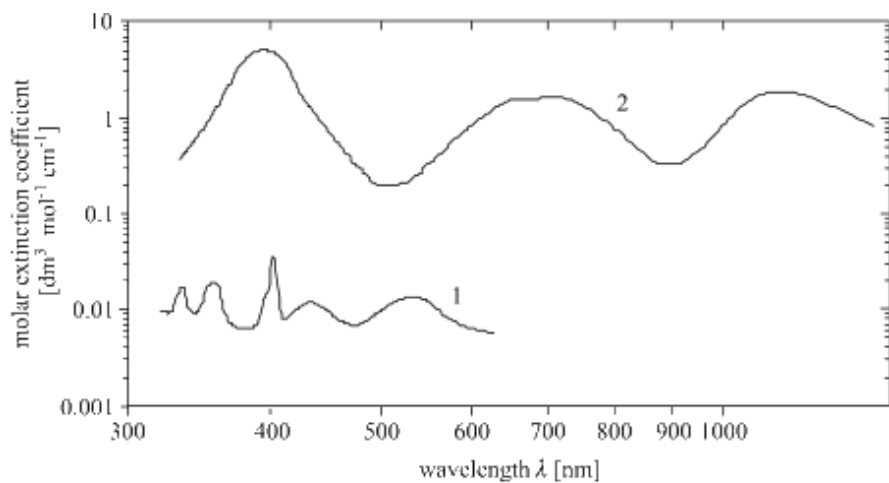| O_h	E	$8C_3$	$3C_2$ $(=C_4^2)$	$6C_4$	$6C_2$	i	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1		
E_g	2	−1	2	0	0	2	−1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	−1	1	−1	3	0	−1	1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	−1	−1	1	3	0	−1	−1	1		(xy, xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1		
E_u	2	−1	2	0	0	−2	1	−2	0	0		
T_{1u}	3	0	−1	1	−1	−3	0	1	−1	1	(x, y, z)	
T_{2u}	3	0	−1	−1	1	−3	0	1	1	−1		

FIGURE 2.17. Spectra of molar extinction coefficients ε for aqua-complexes of manganese ($[Mn(H_2O)_6]^{2+}$) (1) and nickel ($[Ni(H_2O)_6]^{2+}$) (2). (Data from Barrow (1969).)
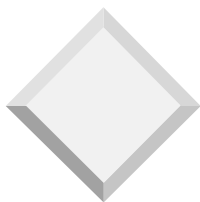
Types of Transitions: d-d

a) intramolecular e⁻ transfer within the *d*-orbital manifold

b) Values for ε vary: up to 1,000 M⁻¹ cm⁻¹ (moderately intense) for spin-allowed transitions in non-centrosymmetric molecules; ~10 M⁻¹cm⁻¹ for spin-allowed transitions in centrosymmetric molecules (weak); ~10⁻¹ M⁻¹cm⁻¹ for spin-forbidden transitions in centrosymmetric molecules (very weak).

c) 1-e⁻ transitions much more intense (2-e⁻ transitions typically 10⁻² times weaker)

d) Shoulders and/or broad peaks expected where Jahn-Teller distortions apply.
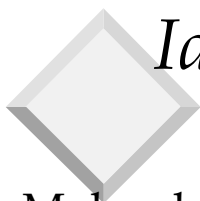
Identifying Nonzero Matrix Elements

Molecular Orbitals, ψ_μ (μ = 1, 2, …), for molecules are usually expanded in terms of basis functions: ($\psi_\mu = c_{1\mu}\phi_1 + c_{2\mu}\phi_2 + …$)

These basis functions, $\{\phi_1, \phi_2, … \}$, may be atomic orbitals, or as we shall see, they may be Symmetry Adapted Linear Combinations (SALCs) of atomic orbitals. We shall see that it is important to be able to identify whether integrals (called <u>matrix elements</u>) of the form below are zero by symmetry.

$$H_{ij} \equiv \int \phi_i \mathcal{H} \phi_j \, d\tau = 0$$
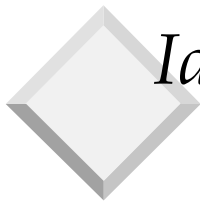
Identifying Nonzero Matrix Elements

SALCs are constructed so that they form basis functions for the IRs of the system (molecule or crystal).

Hamiltonian Matrix Elements, H_{ij}, involving SALCs are nonzero only if ϕ_i and ϕ_j belong to the same IR.