

MATRIX ELEMENT FOR THE 1 → 2 TRANSITION AT THE FIRST ORDER IN A PERTURBATIVE REGIME NOW WE NOTE THAT $\vec{p} = m \frac{d\vec{r}}{dt}$ SO WE CAN WRITE (IN GENERAL) THE MOTION EQ. OF AN OPERATOR TIME DEPENDENT, $\hat{O}(t)$, AS

$$\frac{d\hat{O}(t)}{dt} = \frac{i}{\hbar} [\hat{H}_0, \hat{O}]$$

$$= \frac{i}{\hbar} [\hat{H}_0 \hat{O} - \hat{O} \hat{H}_0]$$

(154)

IF $\hat{O}(t) = \hat{p} \Rightarrow$

$$\langle 2 | \hat{p} | 1 \rangle = m \langle 2 | \frac{d\hat{r}}{dt} | 1 \rangle \Rightarrow \frac{i m}{\hbar} \langle 2 | \hat{H}_0 \hat{r} | 1 \rangle$$

← OPERATOR ↓

FROM THE EIGENVALUES DERIVED FROM THE S. EQ $\hat{H}_0 \psi = E_n \psi$ THE MOTION EQ BECOMES

$$- \frac{i m}{\hbar} [E_2 - E_1] \langle 2 | \hat{r} | 1 \rangle, \text{ BUT } E_2 - E_1 = \Delta E$$

AND $\Delta E = \hbar \omega_{12}$ AND $\vec{E}_0 = i \omega \vec{A}_0 \Rightarrow$

$$M_{12} = \langle 2 | e \hat{r} \cdot \vec{E}_0 | 1 \rangle, \vec{E} = E_0 \hat{\epsilon}$$

DIPOLE

← UNIT VECTOR

$$M_{12} = i E_0 e \langle 2 | \hat{r} \cdot \hat{\epsilon} | 1 \rangle$$

(155)

THE TRANSITION PROBABILITY IS GIVEN BY A RELATION, THAT WE DO NOT DERIVE HERE (SEE FOR EXAMPLE B.H. BRANSDEN AND C.J. JOACHAIN - PHYSICS OF ATOMS AND MOLECULES)

$$W_{12} = \frac{2\pi}{\hbar} |M_{12}|^2 \delta(E_2 - E_1 - \hbar\omega)$$

(156)

FOR THE PRESENT CASE $M_{12} = -i E_0 \mu_{12}$
 WHERE $\mu_{12} = e \hat{r}$

$$W_{12} = \frac{2\pi}{\hbar} E_0^2 |\mu_{12}|^2 \delta(E_2 - E_1 - \hbar\omega)$$

(157)

FROM THIS RELATION WE CAN DERIVE THE TRANSITION PROBABILITIES $B_{12} = B_{21}$, A_{21} OF THE EINSTEIN'S MODEL.

OF COURSE THERE IS A DIRECT RELATION BETWEEN W_{12} AND $B_{12} = B_{21}$. THEY BOTH REPRESENT THE TRANSITION PROBABILITY FROM THE QUANTUM STATE $|1\rangle$ TO THE QUANTUM STATE $|2\rangle$, THEREFORE, $W_{12} \equiv B_{12} u(\nu)$. AS WE KNOW THE ENERGY DENSITY $u(\nu)$ OF AN E.M. FIELD IS PROPORTIONAL TO E_0^2 (BEING E_0 THE ELECTRIC FIELD AMPLITUDE), IN DIFFERENT WORDS $\vec{S} = \vec{E} \times \vec{H}$ GIVES THE POWER FLOW IN $W \cdot m^{-2} \equiv$ INTENSITY, IN FACT, THE INTENSITY IS DEFINED AS THE ENERGY CROSSING THE UNIT AREA FOR UNIT TIME. THEREFORE, IS GIVEN BY $\vec{I} = v \vec{u}$ WHERE v IS THE VELOCITY OF THE WAVE. IN THE M.K.S.A. SYSTEM $\vec{I} = \frac{1}{2} c \epsilon_0 n E_0^2$ ($n \equiv$ REFRACTIVE INDEX) $\Rightarrow \frac{1}{2} c \epsilon_0 n E_0^2 = v u$. WITH $cn = v \Rightarrow$

$\frac{1}{2} \epsilon_0 E_0^2 = u$. THUS WE CAN FINALLY OBTAIN B_{12} FROM W_{12} AND ALSO A_{21} . THE FINAL RESULT (NOT DERIVED HERE) REPORTED IN THE

LITERATURE FOR TRANSITIONS BETWEEN NON-DEGENERATE DISCRETE ATOMIC LEVELS FOR ABSORPTION OR STIMULATED EMISSION OF UNPOLARIZED RADIATION FIELD IS

158

WHEREAS

$$B = \frac{\pi e^2}{3\epsilon_0 \hbar^2} |\langle 2 | \hat{r} | 1 \rangle|^2$$

$$A_{21} = \frac{e^2 \omega_{21}^3}{3\pi \epsilon_0 \hbar c^3} |\langle 2 | \hat{r} | 1 \rangle|^2$$

(SEE 137).

SELECTION RULES IN OPTICAL TRANSITIONS

AS FOR THE CLASSICAL E.D. THERE ARE

NO SYMMETRY CONDITIONS (RULES) FOR

THE RADIATION EMISSION (ABSORPTION). HOWEVER,

IN Q.M. THE DEFINITION ITSELF OF MATRIX ELEMENT IMPOSES SELECTION RULES, IN

AGREEMENT WITH THE EXPERIMENTAL OBSERVATIONS.

FROM THE DEFINITION GIVEN FOR

A GENERIC MATRIX ELEMENT M_{ij} (WE USE

M_{ij} ONLY FOR ELECTRIC DIPOLE TRANSITIONS)

WE OBTAIN

$$M_{ij} \equiv \langle \psi_j | \hat{O}(t) | \psi_i \rangle = \int \psi_j^* \hat{O}(t) \psi_i dV$$

159

WHERE $\hat{O}(t)$ IS AN OPERATOR THAT "MAKES"

THE TRANSITION. IT CAN BE AN ELECTRIC

DIPOLE OPERATOR, AS FOR THE PRESENT

CASE ($e\hat{r}$), OR AN ELECTRIC QUADRUPOLE

OPERATOR (THAT DEPENDS ON $(\hat{r})^2$), OR

A MAGNETIC DIPOLE OPERATOR (THAT ALSO DEPENDS ON $(\hat{r})^2$. OF COURSE THE PARITY SYMMETRY OF \hat{r} IS ODD, WHEREAS FOR $(\hat{r})^2$ IS EVEN, AS A CONSEQUENCE THE MATRIX ELEMENT INTEGRAL VALUE DEPENDS ON THE SYMMETRY OF THE OPERATOR \hat{O} AND THE SYMMETRY OF THE STATE $|1\rangle$ AND $|2\rangle$, FOR ATOMIC TRANSITIONS THESE STATES ARE REPRESENTED BY WAVEFUNCTIONS.

IN A MORE GENERAL CASE THE MATRIX ELEMENT INTEGRALS ARE

1) $\langle 2 | \hat{O} | 1 \rangle = 0$ IF \hat{O} IS ODD AND THE $|1\rangle$ AND $|2\rangle$ STATES HAVE THE SAME SYMMETRY (BOTH ODD OR BOTH EVEN). IT IS $\neq 0$ IN ALL THE OTHER CASES.

2) $\langle 2 | \hat{O} | 1 \rangle = 0$ IF \hat{O} IS EVEN AND THE $|1\rangle$ AND $|2\rangle$ STATES HAVE DIFFERENT SYMMETRY (ONE ODD AND THE OTHER EVEN). IT IS $\neq 0$ FOR ALL THE OTHER CASES.

THESE NOTIONS LEAD TO THE CONCEPT OF SELECTION RULES FOR OPTICAL TRANSITIONS, FOR THE CASE OF THE ELECTRIC DIPOLE TRANSITIONS WE MUST APPLY THE FIRST CASE (\hat{r} IS ODD BY PARITY) \Rightarrow THE ALLOWED TRANSITIONS ARE THOSE BETWEEN STATES WITH OPPOSITE SYMMETRY WAVEFUNCTION, OR INITIAL AND FINAL STATES WITH OPPOSITE SYMMETRY, IN THE FOLLOWING SOME FACULTATIVE MATERIAL IS GIVEN

SYMMETRIES AND SELECTION RULES.

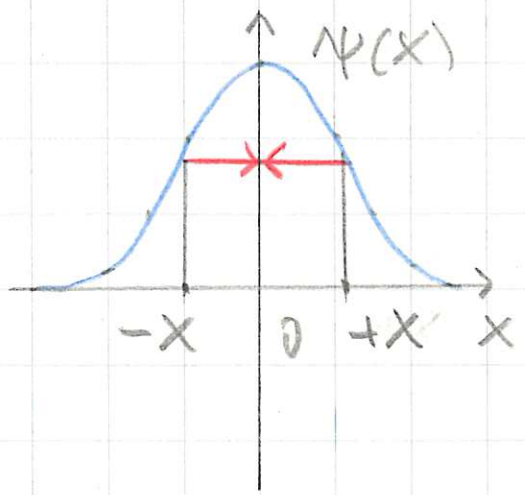
WITH SELECTION RULES, FOR PERTURBATIVE OPTICAL TRANSITIONS, WE MEAN TO MAP THE CASES WHERE THE MATRIX ELEMENT, AND GIVEN BY

(160)
$$M_{nm} \equiv \langle \psi_m | \hat{O}(t) | \psi_n \rangle \equiv \int_V \psi_m^* \hat{O}(t) \psi_n dV$$

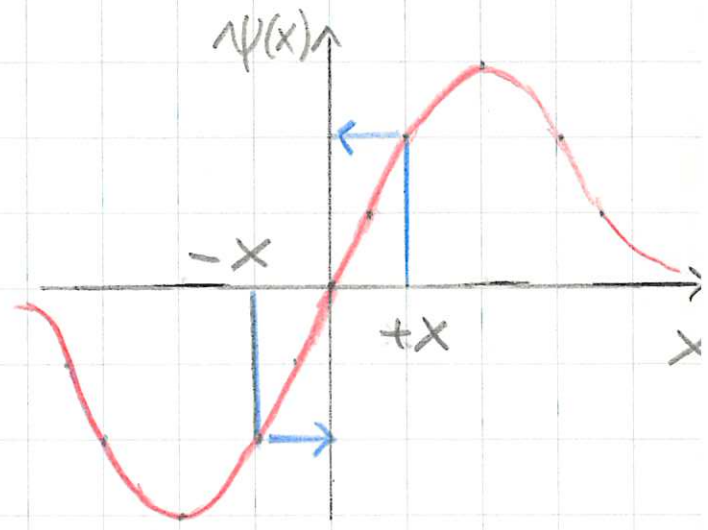
$$\hat{O}(t) \equiv \hat{H}_{INT}(t)$$

IS $\neq 0$ OR $= 0$ ON THE BASE OF THE SYMMETRY OF ψ_m , ψ_n AND $\hat{O}(t)$.

LET'S START WITH THE DEFINITION OF PARITY SYMMETRY. DEF: $\underline{P} \equiv \vec{r} \rightarrow -\vec{r}$, APPLIED TO A SPATIAL FUNCTION $\psi(\vec{r})$. IF $\psi(\vec{r}) = \psi(-\vec{r})$, $\psi(\vec{r})$ HAS AN EVEN SYMMETRY. IF $\psi(\vec{r}) = -\psi(-\vec{r})$, ψ HAS AN ODD SYMMETRY. EXAMPLE IN 1D



EVEN



ODD

LET'S START FIRST WITH THE SYMMETRY PROPERTIES OF \hat{H} FOR THE HARMONIC OSCILLATOR. SINCE THE POTENTIAL ENERGY OF THE H.O. IS $\propto x^2$

$\Rightarrow V(x) = V(-x) \Rightarrow V(x)$ IS PARITY INVARIANT
IN ANALOGY THE OPERATOR $\frac{d}{dx^2} \xrightarrow{P} \frac{d}{d(-x)^2} = \frac{d}{dx^2}$

IS PARITY INVARIANT \Rightarrow FOR THIS 1D EXAMPLE
ALSO \hat{H} IS PARITY INVARIANT.

$$\hat{H}(x)\psi(x) = E\psi(x) \xrightarrow{P} \hat{H}(-x)\psi(-x) = E\psi(-x)$$

HOWEVER, BECAUSE \hat{H} IS PARITY INVARIANT

$$\hat{H}(-x) \equiv \hat{H}(x) \Rightarrow \hat{H}(x)\psi(-x) = E\psi(-x)$$

IN ORDER TO BE SIMPLE LET'S ASSUME ONLY
ONE WAVEFUNCTION $\Rightarrow \psi(x) \propto \psi(-x) \Rightarrow$

$$\psi(-x) = \alpha\psi(x) \xrightarrow{P} \psi(x) = \alpha\psi(-x)$$

WE REPLACE NOW $\psi(x)$ ON THE RIGHT SIDE

$$\text{OF } \psi(-x) = \alpha\psi(x) \text{ BY } \psi(-x) \Rightarrow$$

$$\psi(-x) = \alpha\alpha\psi(-x) = \alpha^2\psi(-x) \Rightarrow$$

$$\alpha^2 = 1 \Rightarrow \alpha = \pm 1 \Rightarrow \psi(-x) = \pm\psi(x)$$

IN 3D $\psi(-\vec{r}) = \pm\psi(\vec{r}) \Rightarrow$ THIS BEHAVIOR
IS DENOTED AS PARITY. CORRESPONDINGLY,

THE OSCILLATOR WAVEFUNCTION HAS EVEN
PARITY FOR $n = 0, 2, 4, \dots$ AND ODD PARITY

FOR $n = 1, 3, 5, \dots$ IN ANALOGY IT CAN BE
SHOWN THAT THE PARITY OPERATION CAN

BE APPLIED WHEN WE ROTATE THE COORDINATES

$$\psi(\vec{r}, 0 + \phi_j) = X_{\phi_j} \psi(\vec{r}, 0) \text{ WHERE}$$

$$X_{\phi_j} = e^{im\phi} \text{ FOR A ROTATION OF } \phi \text{ AROUND AN AXIS}$$

$m =$ INTEGER. AS THIS EXAMPLE INDICATES,

VERY GENERAL CONCLUSION ABOUT THE SYMMETRY
OPERATIONS ON A WAVEFUNCTIONS

MAY BE DRAWN, THESE TRANSFORMATIONS ARE TREATED BY THE THEORY OF REPRESENTATIONS OF ROTATION GROUP. OPTIONAL

ELECTRIC DIPOLE OPTICAL TRANSITIONS SELECTION RULES

AS A FIRST EXAMPLE WE CONSIDER AN INTEGRAL WHICH RESULTS FROM LEAVING OUT THE FACTOR "e" (CHARGE OF THE PARTICLE) FROM THE MATRIX ELEMENT OF THE ELECTRIC DIPOLE OPTICAL TRANSITION:

$$M_{mn} \equiv \langle \psi_m(\vec{r}) | e \hat{r} | \psi_n(\vec{r}) \rangle = \int \psi_m^*(\vec{r}) e \hat{r} \psi_n(\vec{r}) dV$$

(161) $\propto \int_{-W}^{+W} \psi_m^*(\vec{r}) \hat{r} \psi_n(\vec{r}) dV$

IF WE REPLACE $\psi_m(\vec{r})$ AND $\psi_n(\vec{r})$ WITH $\psi(x)$

(FOR SIMPLICITY) $\Rightarrow I = \int_{-W}^{+W} \psi^*(x) \hat{x} \psi(x) dx$

(162) $\xrightarrow{P} I = \int_{+W}^{-W} \psi^*(-x) (-\hat{x}) \psi(-x) d(-x)$. BY EXCHANGING

THE LIMITS AND ACCORDINGLY CHANGING THE SIGN OF THE DIFFERENTIAL, WE OBTAIN

$I = \int_{-W}^{+W} \psi^*(-x) (-\hat{x}) \psi(-x) dx$. NOW WE MAKE

USE OF A SYMMETRY PROPERTIES OF THE WAVE FUNCTION, $\psi(-x) = \pm \psi(x)$. THE TRANSFORMATION $\xrightarrow{P} (x \rightarrow -x)$ LEAVES $\psi \psi^*$ INVARIANT, SO $\int_{-W}^{+W} \psi^*(-x) (-\hat{x}) \psi(x) dx$ DIFFERS FROM

$$\int_{-a}^{+a} \psi^*(x) \hat{x} \psi(x) dx \text{ ONLY WITH RESPECT TO THE}$$

SIGN. THUS WE OBTAIN $I = -I$ WHICH IS TRUE ONLY IF $I = 0$. THIS RESULT IS VERY IMPORTANT FOR IT SHOWS THAT ITS VALUE CAN BE FOUND WITHOUT CALCULATING THE INTEGRAL BUT ONLY CONSIDERING THE SYMMETRY PROPERTIES OF THE WAVEFUNCTION AND OF THE OPERATOR. LET'S NOW SEE THE CASE OF A MATRIX ELEMENT WITH DIFFERENT INDEXED WAVEFUNC. $\psi_m(F); \psi_n(F)$. IF THE PERTURBATION OPERATOR IS STILL \hat{x}^n (ODD) THE INTEGRAL IS $\neq 0$ ONLY IF $\psi_m(F)$ AND $\psi_n(F)$ HAVE DIFFERENT SYMMETRY. THIS IS THE SIMPLES EXAMPLE OF OPTICAL TRANSITION SELECTION RULES. THIS CASE CAN BE EXTENDED TO ELECTRIC DIPOLE OPTICAL TRANSITIONS BETWEEN STATES REPRESENTED BY $\psi_{n,l,m}(F)$ AND

$\psi_{n',l',m'}(F)$ WAVEFUNCTIONS.

(163) $I_z = \int_V \psi_{n,l,m}^*(F) \hat{z} \psi_{n',l',m'}(F) dV$ THAT IN POLAR

COORDINATES BECOMES

$$I_z = \int_V dV \psi_{n,l,m}^*(r, \theta, \phi) r \cos \theta \psi_{n',l',m'}(r, \theta, \phi)$$

IN ORDER TO CALCULATE I WE MAKE USE AGAIN OF THE SYMMETRY OPERATIONS AND PROPERTIES. THIS TIME HOWEVER, WE CONSIDER THE ROTATION AROUND Z. IF THE ROTATION IS ϕ_0 THE PREVIOUS INTEGRAL IS CONVERTED INTO

(165)
$$\frac{I}{Z} = e^{-i(m-m')\phi_0} I_Z$$
 AS WE CAN SEE FROM THE TRANS-

FORMATION PROPERTIES GIVEN BY

$\psi(r, \phi) = e^{im\phi} \psi(r, \theta)$. THIS EQ. CAN BE SATISFIED IN TWO WAYS. EITHER $I_Z = 0$ OR $I_Z \neq 0$ BUT IN THE LATTER CASE m MUST BE EQUAL TO m' ($m = m'$). THIS IS ANOTHER CASE OF SELECTION RULE. \Rightarrow IF THE PERTURBATION OPERATOR CONTAINS THE DIPOLE MOMENT IN THE Z DIRECTION $M_{m, m'} \neq 0$ ONLY IF $m = m'$

WE CAN DERIVE NOW THE SELECTION RULE FOR THE X AND Y COMPONENTS OF THE DIPOLE MOMENT:

$$I_x = \int dV \psi_{n, l, m}^*(r, \theta, \phi) x \psi_{n', l', m'}(r, \theta, \phi)$$

$$\text{AND } I_y = \int dV \psi_{n, l, m}^*(r, \theta, \phi) y \psi_{n', l', m'}(r, \theta, \phi)$$

WE CAN MULTIPLY I_y BY i AND ADD IT TO I_x

$$I_x + iI_y = \int dV \psi_{n, l, m}^* r \sin \theta e^{i\phi} \psi_{n', l', m'}$$

BY ROTATING OF ϕ_0 AROUND Z WE OBTAIN

✓ 99

IN ANALOGY TO WHAT HAS BEEN DONE BEFORE,

$$I_x + iI_y = e^{-i(m-1-m')\phi_0} (I_x + iI_y) \Rightarrow$$

$$I_x + iI_y = 0 \text{ FOR } m \neq m' + 1$$

$$I_x - iI_y = 0 \text{ FOR } m \neq m' - 1 \Rightarrow I_x = 0 \text{ AND}$$

$$I_y = 0 \text{ IF } m - m' \neq \Delta m = \pm 1 \Rightarrow I_x \text{ AND } I_y$$

CAN BE $\neq 0$ ONLY IF $\Delta m = \pm 1$ THAT WITH SELECTION RULE FOR Z GIVES

THESE ARE THE SELECTION RULES FOR THE MAGNETIC Q.N. (166)

$\Delta m = 0, \pm 1$

THE SELECTION RULE FOR THE ANGULAR MOMENTUM OF THE ELECTRON CAN ALSO BE DERIVED FROM THE PREVIOUS MATRIX ELEMENTS AND THEY ARE SIMILAR IN PRINCIPLE BUT WITH A MORE EXTENSIVE MATHEMATICS. HOWEVER, IN THIS CASE WE MUST CONSIDER THE ANGULAR MOMENTUM OF THE LIGHT (IF ANY) \Rightarrow THE LIGHT IS CIRCULARLY (ELLIPTICALLY) POLARIZED. IN THE INTERACTION THE OVERALL ANGULAR MOMENTUM (LIGHT + MATTER) MUST BE CONSERVED. IN SUMMARY ALSO FOR THE l QUANTUM NUMBER WE OBTAIN

$\Delta l = 0, \pm 1$ | THESE ARE THE SELECTION RULES FOR THE AZIMUTHAL Q.N. (167)

THE INVARIANCE PROPERTIES OF \hat{H}_{INT} LEAD TO CERTAIN TRANSFORMATION PROPERTIES OF THE

WAVEFUNCTIONS. FROM THE TRANSFORMATION PROPERTIES OF THE W.F. AND THE PERTURBATION OPERATOR (ELECTRIC DIPOLE OPERATOR IN THE GIVEN EXAMPLES) IT CAN BE RIGOROUSLY DETERMINED WHICH MATRIX ELEMENTS ARE $\neq 0$ AND WHICH ARE $= 0$.

WE CAN ALSO NOTE THAT WE HAVE NO OPERATORS THAT CAN CHANGE THE SPIN \Rightarrow

$\Delta S = 0$ 168

• PARITY OF THE ATOMIC STATES

TO ADDRESS THIS QUESTION WE MUST DETERMINE THE PARITY OF THE ATOMIC STATE.

LET'S ASSUME THAT AN e^- MOVES IN THE CENTRAL POTENTIAL OF THE NUCLEUS PLUS THE POTENTIAL OF THE OTHER ELECTRONS IN THE SYSTEM. LET'S DEFINE THE WAVEFUNCTION OF THE STATE IDENTIFIED BY THE QUANTUM NUMBERS n, l, m AS

$\psi_{nlm}(\vec{r})$ THAT IN SPHERICAL COORDINATES (POLAR) BECOMES $\psi_{nlm}(r, \theta, \varphi)$ AND LET'S SEPA-

RATE THE RADIAL FROM THE ANGULAR COMPONENTS $\psi_{nlm}(r, \theta, \varphi) = R_{nl}(r) Y_{lm}(\theta, \varphi)$

THE PARITY OPERATION $\vec{r} \rightarrow -\vec{r} \Rightarrow$

$x \rightarrow -x$	$r \rightarrow r$	
$y \rightarrow -y$	$\theta \rightarrow \pi - \theta$	\Rightarrow
$z \rightarrow -z$	$\varphi \rightarrow \varphi + \pi$	

THE RADIAL PART DOES NOT CHANGE IN PARITY
 $R_{nl}(r) \xrightarrow{P} R_{nl}(r) \Rightarrow$ THERE ARE NO SELEC-
 TION RULES ON THE PRINCIPAL QUANTUM
 NUMBER n . FROM THE PROPERTIES OF THE
 SPHERICAL FUNCTION Y_{lm}

$$Y_{lm}(\pi - \theta, \varphi + \pi) = (-1)^l Y_{lm}(\theta, \varphi)$$

SO WE HAVE SELECTION RULES ON l AND m
 QUANTUM NUMBER.

HOWEVER, FOR A MULTIELECTRON ATOM WE
 MUST CONSIDER THE TOTAL L AND THE
 TOTAL M_L QUANTUM NUMBER, AND IN THIS
 CASE THE PARITY IS DETERMINED BY n

$$P = (-1)^{l_1} (-1)^{l_2} \dots (-1)^{l_n} = (-1)^{\sum_{i=1}^n l_i}$$

EXAMPLE:

WHAT IS THE PARITY OF THE Li STATES
 $1s^2 2s$ AND $1s^2 2p$

$$1s^2 \underline{2s} \quad (-1)^l = 1 \Rightarrow \text{EVEN}$$

$l=0$

$$1s^2 \underline{2p} \quad (-1)^l = -1 \Rightarrow \text{ODD}$$

$l=1$

$$1s^2 2s^2 \underline{2p^6} 3s 3p \quad (-1)^{0+1} = -1 \text{ ODD}$$

$\downarrow \quad \downarrow$
 $l=0 \quad l=1$

$$1s^2 2s^2 \underline{2p^6} 3s 3d \quad (-1)^{0+2} = +1 \text{ EVEN}$$

$\downarrow \quad \downarrow$
 $l=0 \quad l=2$

THE SELECTION RULES BETWEEN THE STATE h AND k OF THE ATOM ARE GIVEN BY

$$\begin{array}{l}
 J = L + S \\
 \text{TOTAL ANG. MOM.}
 \end{array}
 ,
 \begin{array}{l}
 M_J \\
 \text{SECONDARY} \\
 \text{TOTAL MOM. Q.N.}
 \end{array}
 \quad
 \begin{array}{l}
 \Delta M_J = 0, \pm 1 \\
 \Delta J = 0 \pm 1
 \end{array}
 \quad
 \left|
 \begin{array}{l}
 j = l + s \\
 j_z = m_j \hbar
 \end{array}
 \right.$$

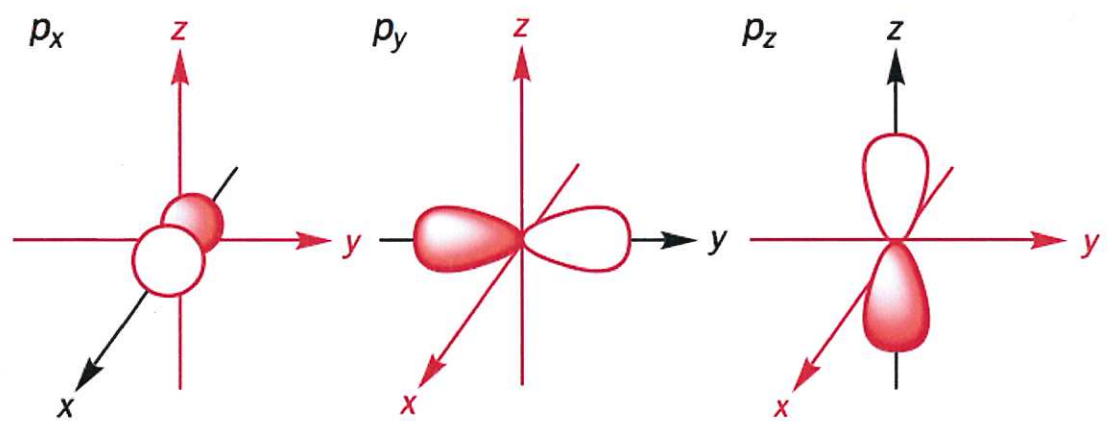
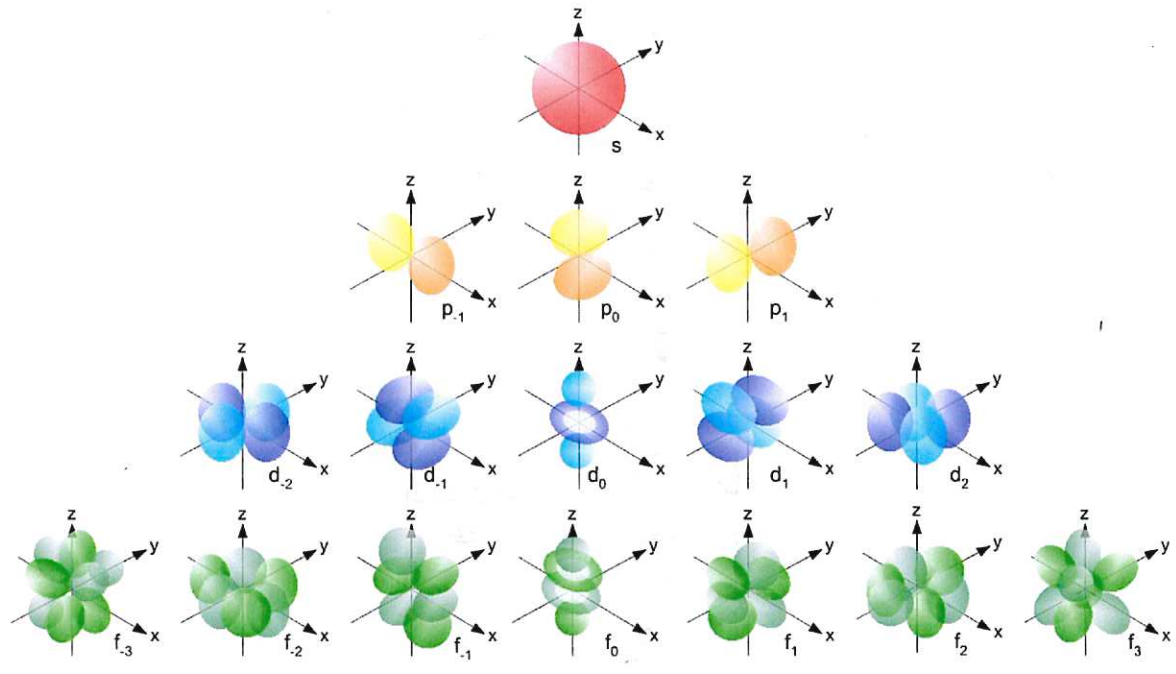
(BUT FROM $J_h = 0$ TO $J_k = 0$ IS FORBIDDEN)

(FOR 1 e^- ATOM \Rightarrow $\Delta j = 0, \pm 1, \Delta m_j = 0, \pm 1, \Delta l = \pm 1$)

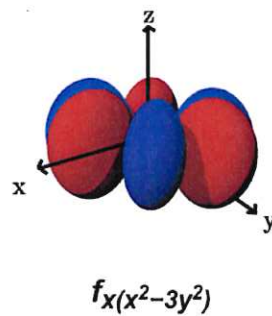
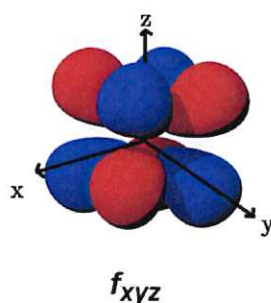
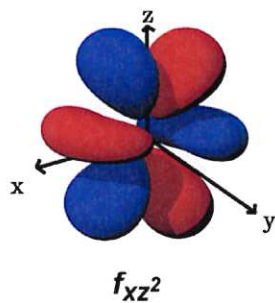
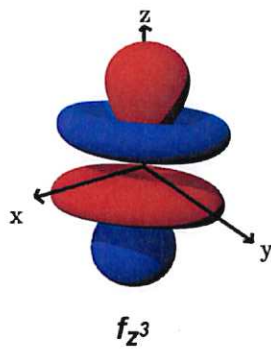
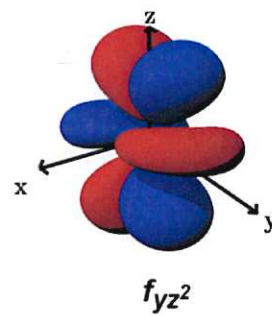
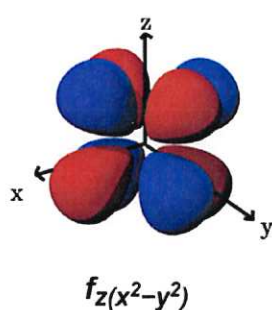
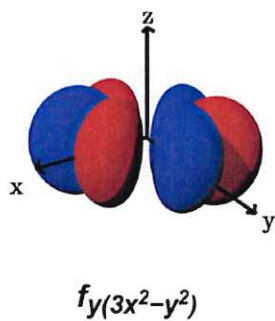
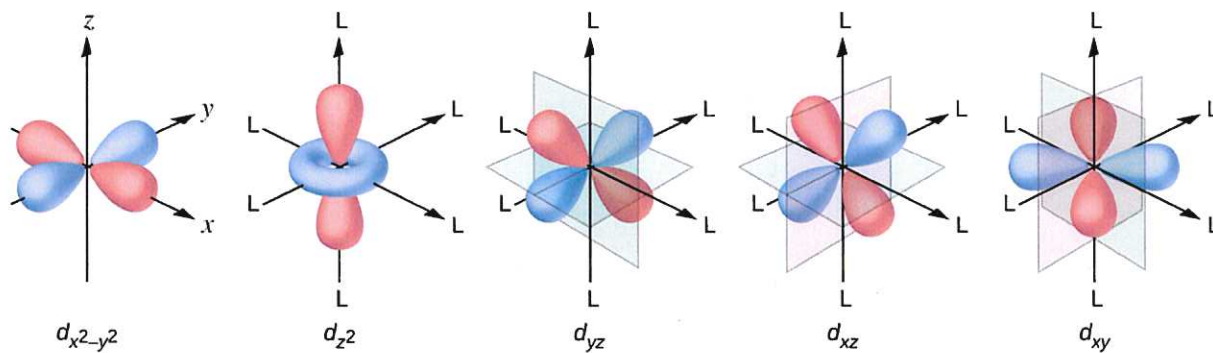
WE MUST NOTE HERE, FOR REASONS THAT OVERTAKES THE SCOPE OF THESE LECTURES THAT ΔM_J AND ΔL ARE REASONABLY GOOD QUANTUM NUMBERS. FOR MANY e^- ATOMS THEY ARE NOT BUT $J = \sum_i (l_i + s_i) = L + S$ IS A GOOD QUANTUM NUMBER

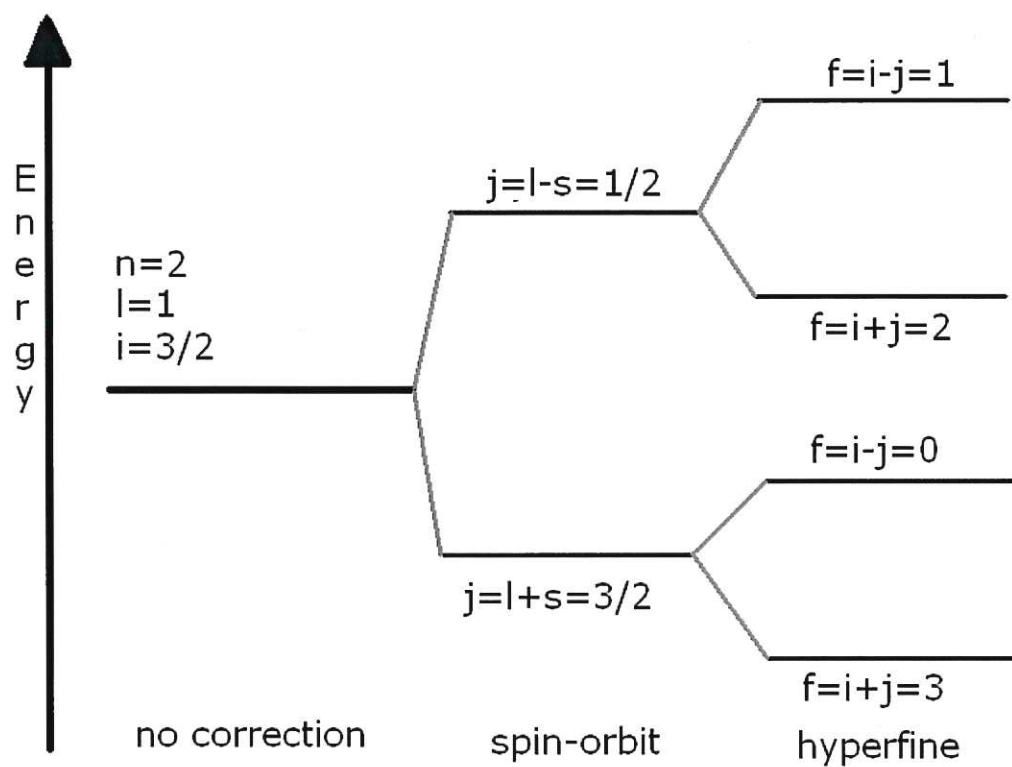
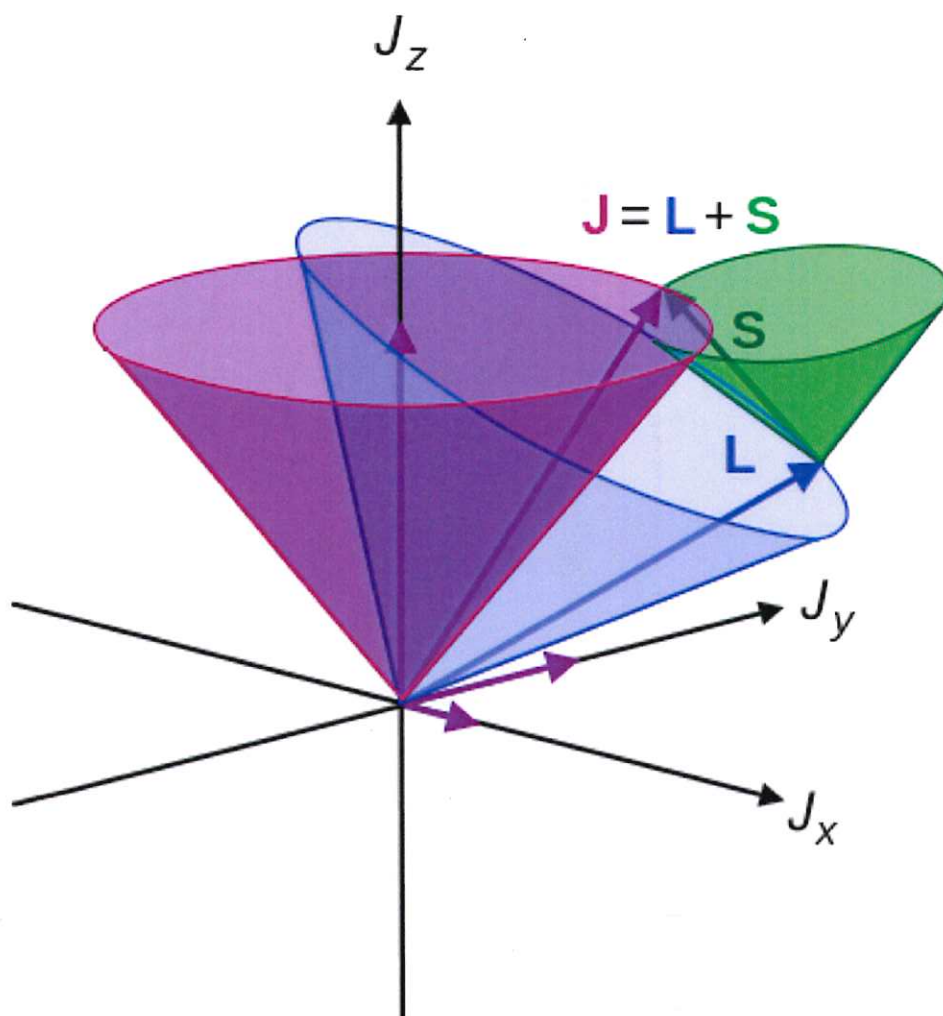
GOOD QUANTUM NUMBERS ARE ASSOCIATED WITH OPERATORS THAT COMMUTE WITH THE HAMILTONIAN. THEY CORRESPOND TO CONSERVED QUANTITIES.

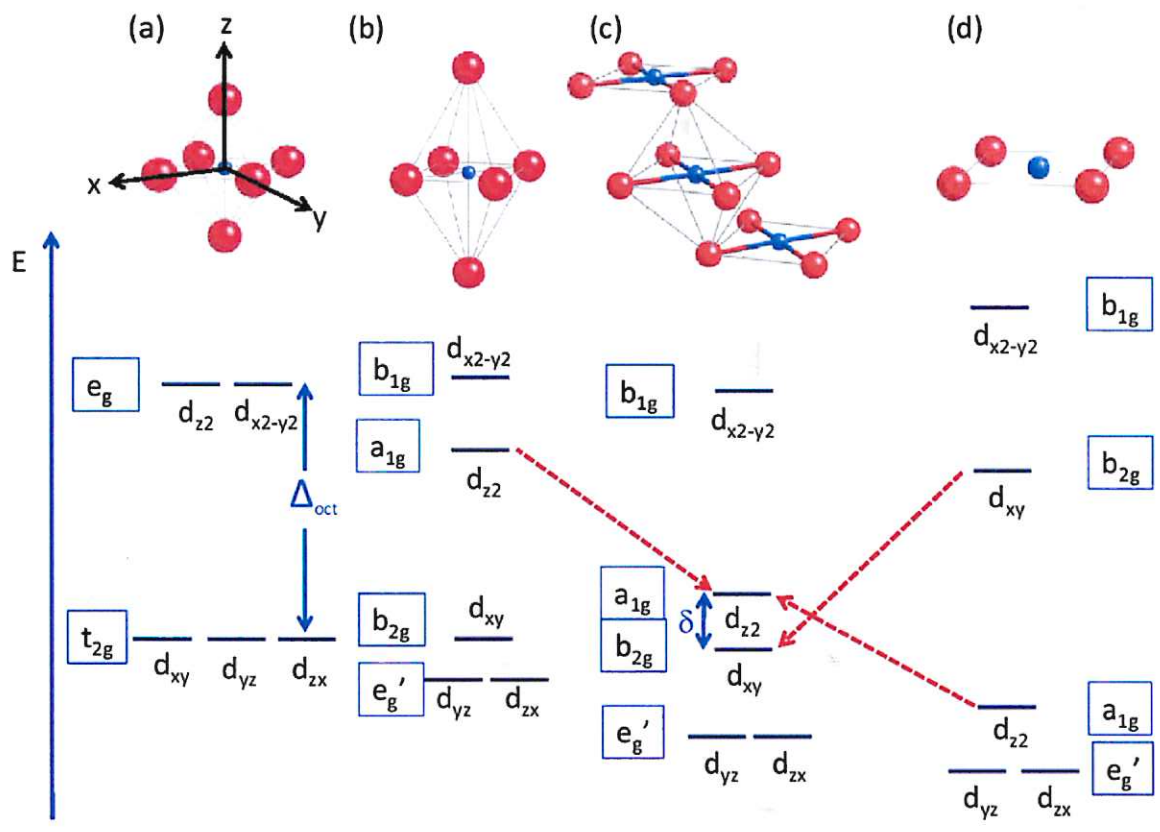
OVERALL, ANGULAR MOMENTUM IS CONSERVED BUT THE PORTION OF WHAT IS DUE TO ORBITAL MOTION AND DUE TO THE SPIN ARE NOT THEMSELVES CONSERVED. n IS "BAD" IN THAT THERE IS NO CONSERVED PHYSICAL QUANTITY RELATED TO RADIAL MOTION.



the three degenerate p orbitals are aligned along perpendicular axes







(Color online) The d-orbital energy splittings of a transition metal surrounded by oxygen ligands in (a) regular octahedral CEF in O_h symmetry, (b) octahedral CEF with principal z-axis elongation in D_{4h} symmetry, (c) the proposed CEF with weak effective charge at the apical ligand positions, and (d) the square-planar CEF in C_{4v} symmetry. 17