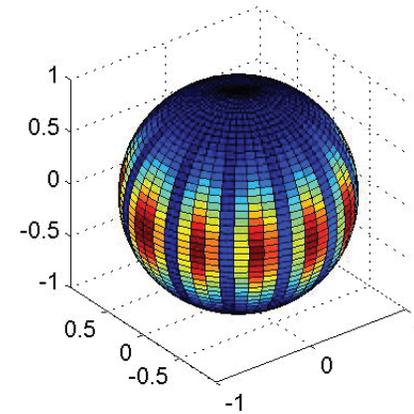
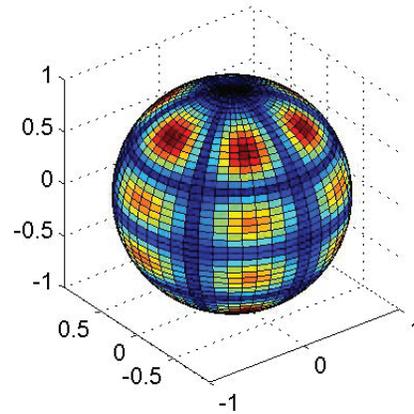
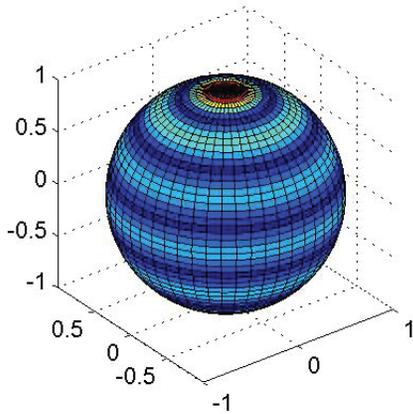


Photoelectron Angular  
Distributions Seminar Series  
*II) Very Brief Introduction to Angular  
Momentum*

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# contents/aims

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## Part I - Very Brief Introduction to Scattering Theory

- Scattering theory overview (stationary-state picture).
- Partial wave expansion.
- Radial continuum wavefunctions for Coulombic and non-Coulombic potentials.
- The importance of the scattering phase shift.

## Part II - Very Brief Introduction to Angular Momentum

- Angular momentum overview - what is angular momentum?
- Angular momentum wavefunctions - the spherical harmonics.
- Angular momentum coupling - Clebsch-Gordan coefficients and Wigner  $3j$  symbols.
- Transformation under rotation - rotation matrix elements.
- Angular part of the scattering problem.

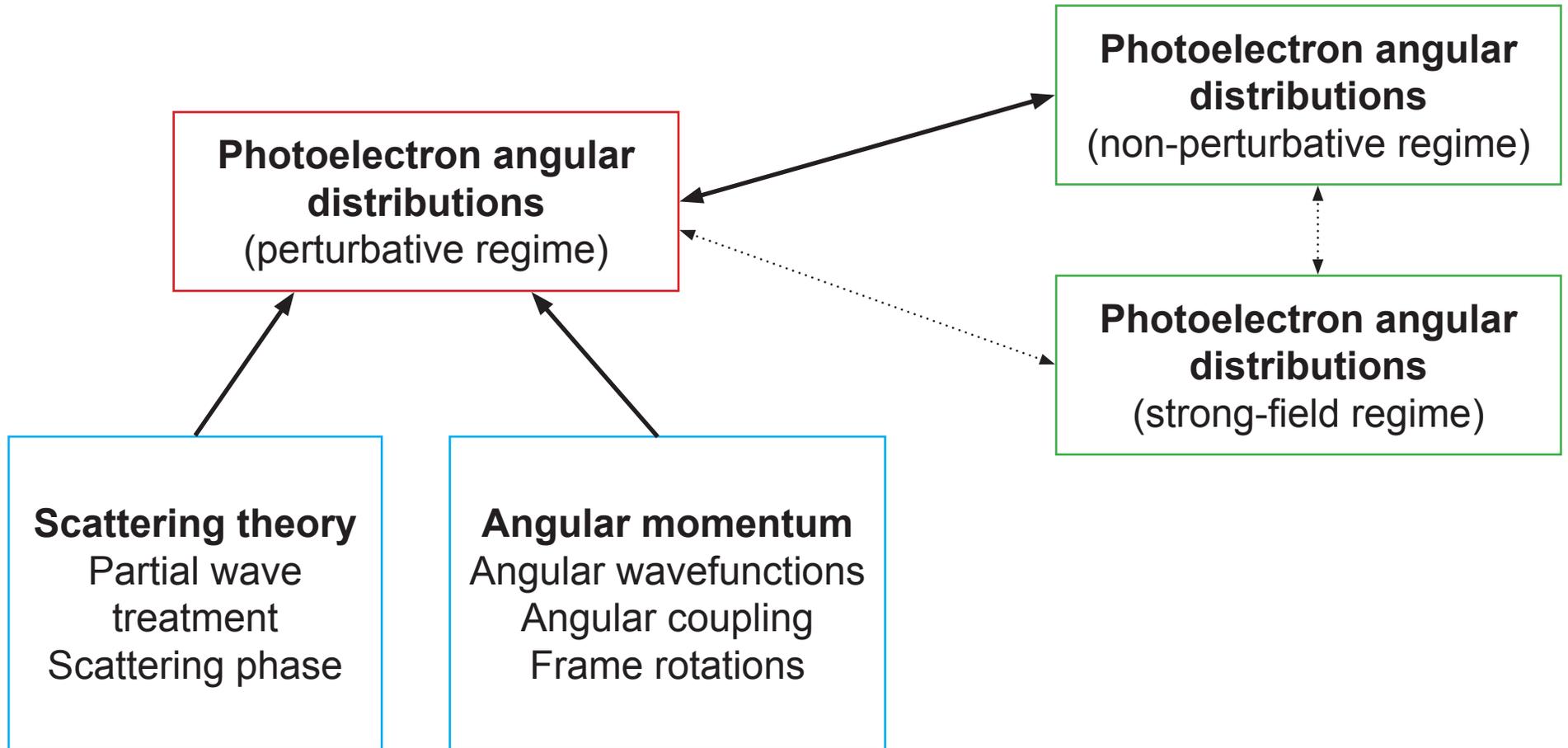
## Part III - Very Brief Introduction to Photoionization & Photoelectron Angular Distributions

- Dipole approximation, dipole matrix elements, explicit formulation of matrix elements from bound and continuum wavefunctions.
- Integrated and differential cross-sections, including exact result for 1-electron system (Cooper & Zare).
- Examples of PADs from atomic systems, in particular case of  $O^-$  photodetachment and s-d wave interference.
- Examples of PADs from molecular systems - case of many partial wave components due to non-central potentials, l-mixing/scattering etc.

Written notes will be available at the end of the seminars!

# background road map

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# what is angular momentum?

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- (i) The angular extension of linear momentum - a dynamical quantity. Quantum theory can be developed from classical mechanics to describe ***orbital angular momentum***.
- (ii) Geometric properties of a system under coordinate frame rotations. Applicable to classical and quantum systems. Gives rise to essentially the same machinery as (i), but more intuitive picture for, e.g., molecular rotations.

References for angular momentum:

*Zare*, Angular Momentum - standard reference.

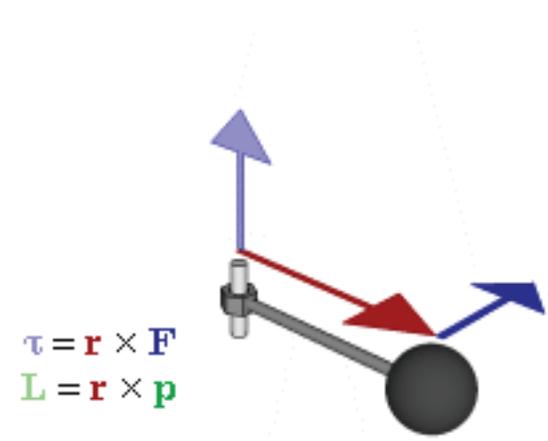
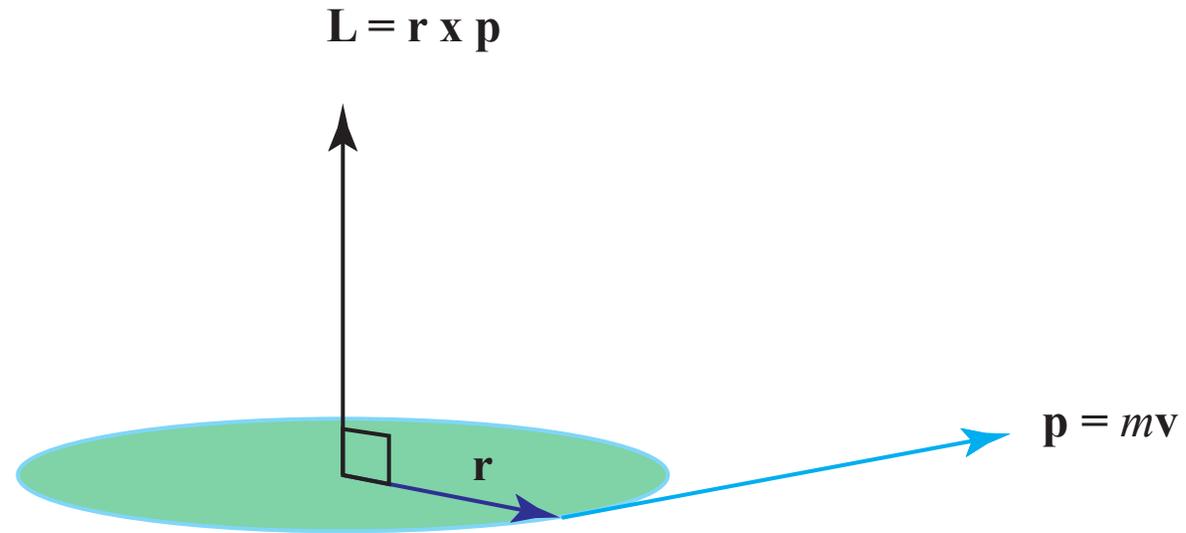
*Edmunds*, Angular Momentum - very mathematical treatment.

*Thompson*, Angular Momentum - more visual/geometric treatment.

Most standard Q.M. textbooks will also have introductory material.

# classical picture

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# quantum correspondence

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Replace  $\mathbf{p}$  with  $\hat{\mathbf{p}} = \frac{\hbar}{i} \nabla$   Note - following Zare  $\hbar=1$

Expand in cartesian form:

$$l_x = y\hat{p}_z - z\hat{p}_y = -i \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$$

$$l_y = z\hat{p}_x - x\hat{p}_z = -i \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$$

$$l_z = \underline{x\hat{p}_y - y\hat{p}_x} = -i \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

Cross-products

 Angular momentum components

# quantum correspondence

---

Commutation relations

$$[l_x, l_y] = il_z$$

$$[l_y, l_z] = il_x$$

$$[l_z, l_x] = il_y$$

Total angular momentum,

$$\mathbf{l}^2 = l_x^2 + l_y^2 + l_z^2$$

$$[\mathbf{l}^2, l_{x,y,z}] = 0$$

Commutation properties mean we can define the total angular momentum of the system, but only one cartesian component. We will see later how this relates to the uncertainty principle.

# quantum correspondence

---

So far we have defined the properties of the orbital angular momentum  $\mathbf{L}$  by comparison with classical angular momentum.

This has given us the operator  $\mathbf{L}$  and commutation relations, but no real physical picture of what we're considering beyond the classical.

If we carry on to consider a general eigenfunction treatment we can develop a vector picture of angular momentum which gives more insight.

# eigenfunctions

---

Define general angular momentum operator as  $\mathbf{j}$  ( $\mathbf{L}$  will be reserved for orbital ang. mom.)

$$\mathbf{j}^2 = j_x^2 + j_y^2 + j_z^2$$

Define states which are eigenfunctions of the total angular momentum, and one projection term (chosen by convention as  $j_z$ ):

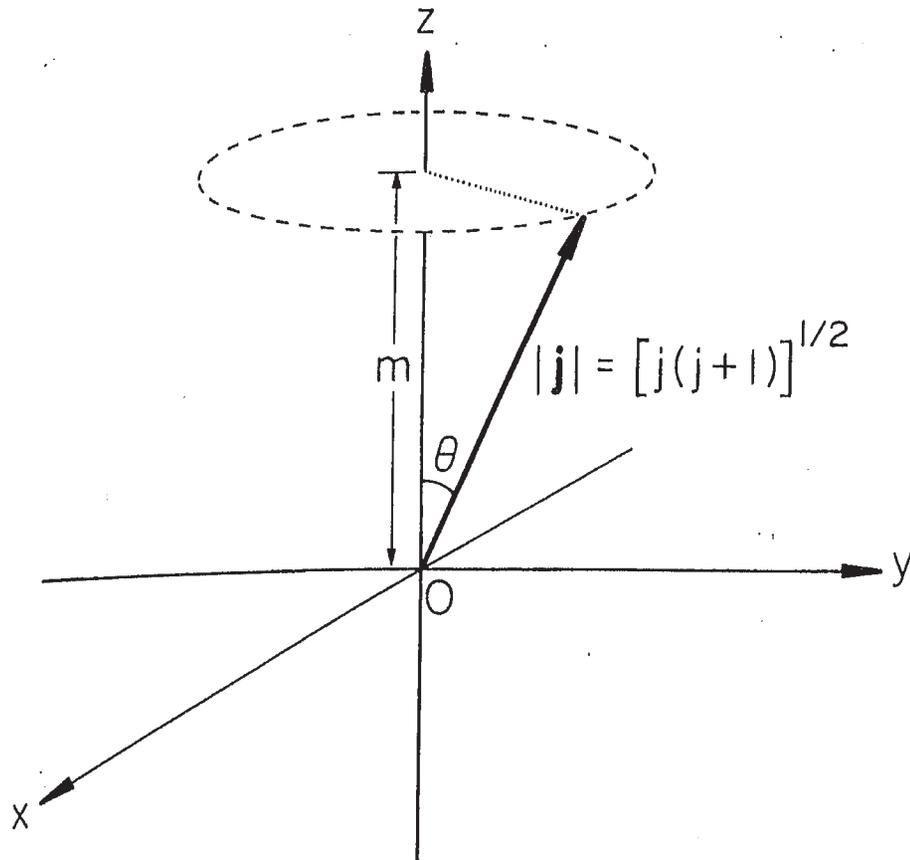
$$\mathbf{j}^2 |jm\rangle = j(j+1) |jm\rangle$$

$$j_z |jm\rangle = m |jm\rangle$$

$m$  takes values  $-j..j$  in integer steps.

# vector model

---



In this picture the total angular momentum defines a vector  $\mathbf{j}$ .

$\mathbf{j}$  has a fixed projection onto the  $z$ -axis, and also precesses about the axis.

The precession ensures that the  $x$  and  $y$  components are undefined, as required by the commutation relations.

We can also consider this in terms of uncertainty - if we try to fix all components then we would have a classical orbit in which both  $\mathbf{r}$  and  $\mathbf{p}$  are defined.

# spherical harmonics

It can be shown (e.g. Zare section 1.3) that the spherical harmonics provide suitable eigenfunctions for integer values of  $j$  in spherical polar coordinates.

$$|lm\rangle = Y_{lm}(\theta, \phi)$$

The functional form of the spherical harmonic is quite complex:

$$Y_{lm}(\theta, \phi) = (-1)^m \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P_l^m(\cos\theta) e^{im\phi}$$

Annotations:

- Red arrow: Parity (points to  $(-1)^m$ )
- Blue arrow: Normalisation (points to the square root)
- Black arrow:  $\phi$  dependence (points to  $e^{im\phi}$ )

**Associated Legendre Function**

$$P_l^m(\cos\theta) = \sin^m\theta \left( \frac{d}{d(\cos\theta)} \right)^m P_l(\cos\theta)$$

**Legendre Polynomial**

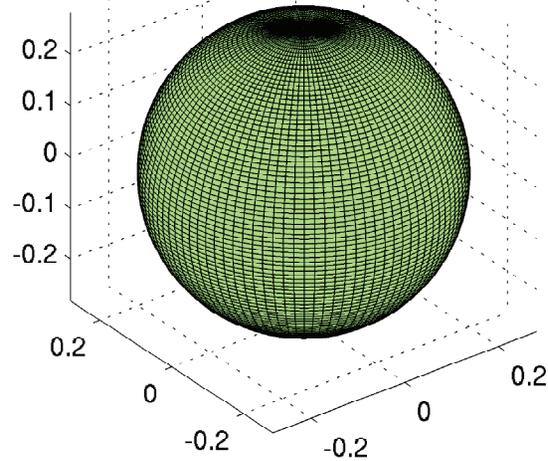
$$P_l(\cos\theta) = \frac{1}{2^l l!} \left( \frac{d}{d(\cos\theta)} \right)^l (\cos^2\theta - 1)^l$$

# spherical harmonics

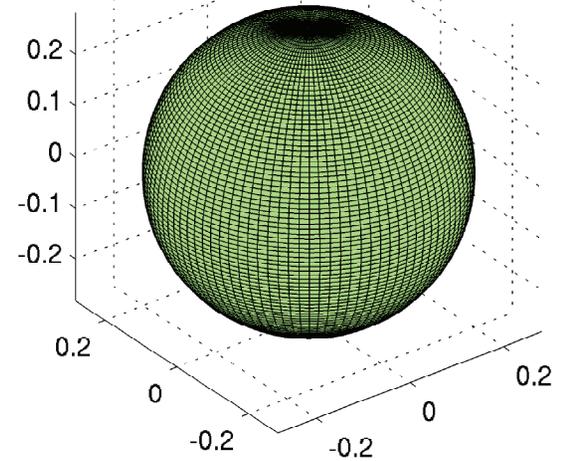
The spherical harmonics are much easier to visualize....

$$Y_{00}$$

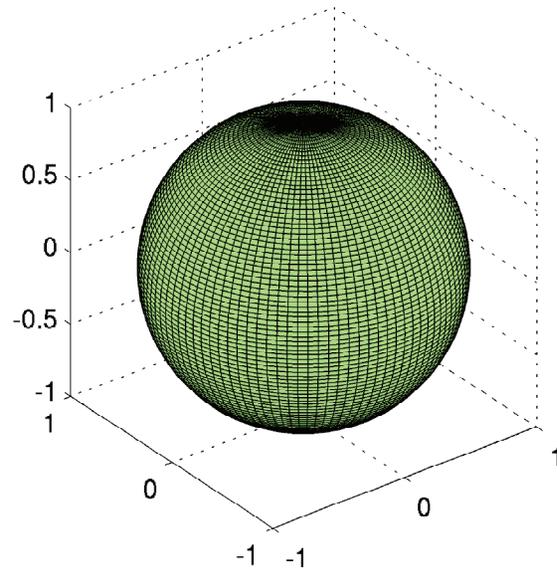
$$|Y_{lm}(\theta, \phi)|$$



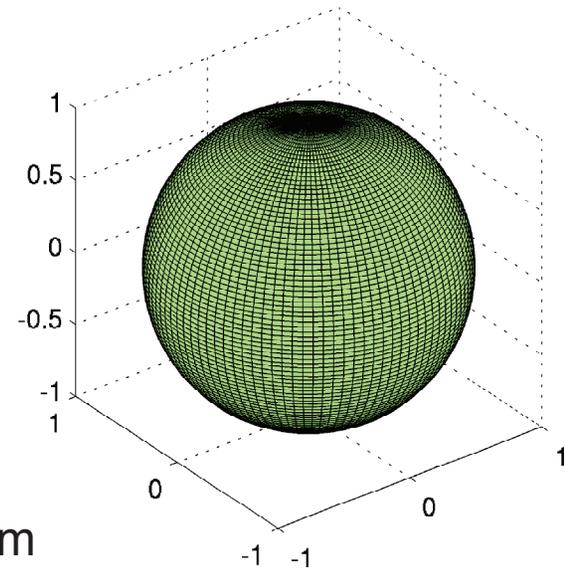
$$\arg[Y_{lm}(\theta, \phi)]$$



Just a sphere!  
Zero phase.  
*s* orbital.



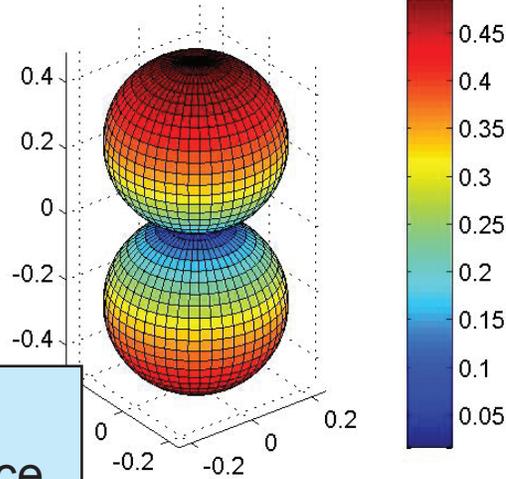
Cartesian form



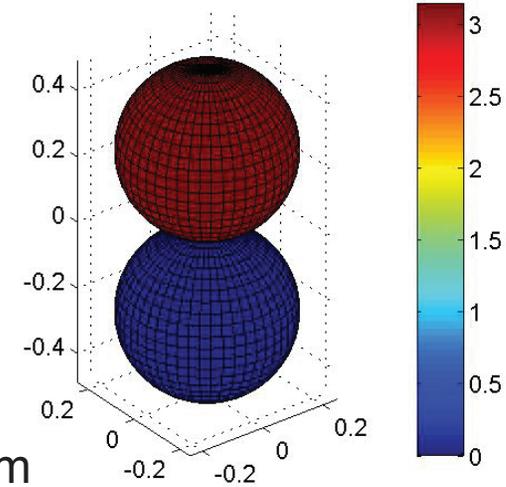
# spherical harmonics

$$Y_{10}$$

$$|Y_{lm}(\theta, \phi)|$$



$$\arg[Y_{lm}(\theta, \phi)]$$

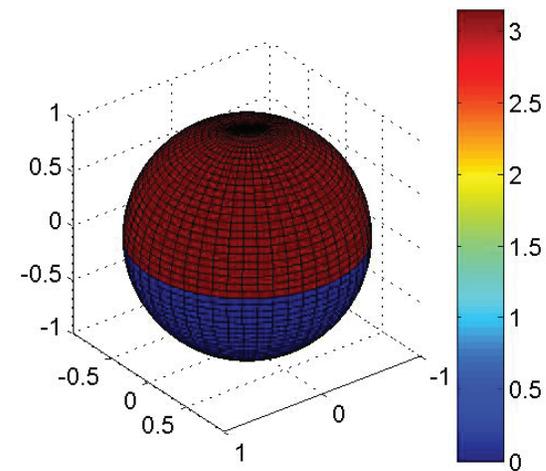
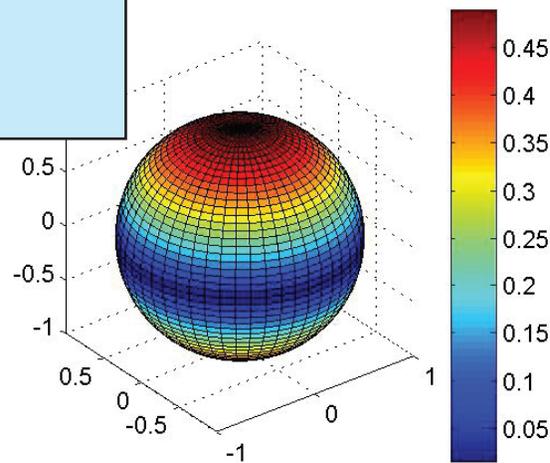


Polar form

$l=1 \rightarrow$  one node in  $\theta$   
 $m=0 \rightarrow$  no  $\phi$  dependence.

$\pi$  phase jump at node.

$p_z$  orbital.

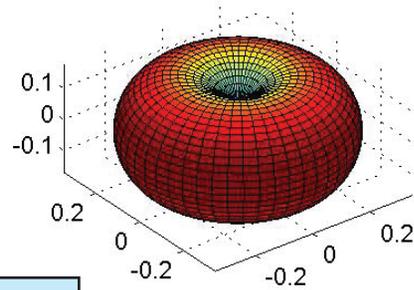


Cartesian form

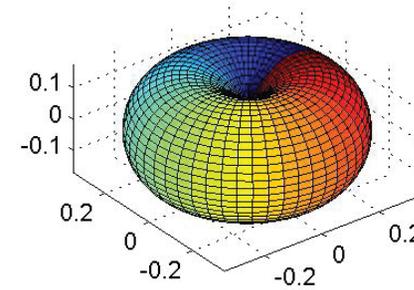
# spherical harmonics

$$Y_{11}$$

$$|Y_{lm}(\theta, \phi)|$$



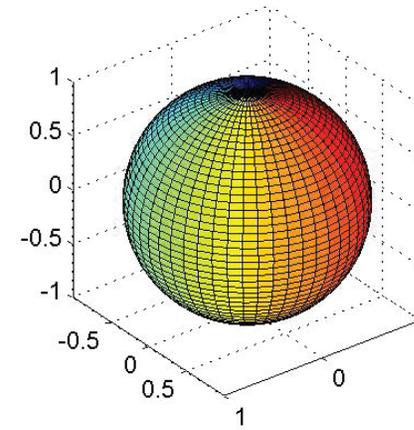
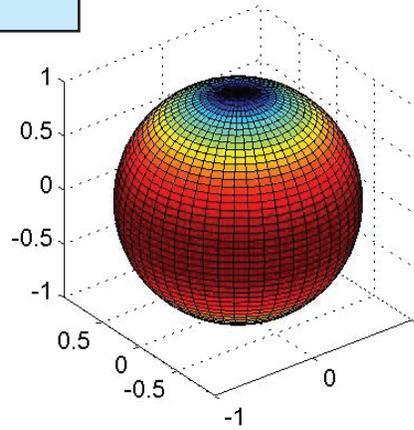
$$\arg[Y_{lm}(\theta, \phi)]$$



Polar form

$l=1 \rightarrow$  one node.  
 $m=1 \rightarrow e^{i\phi}$  phase.

$p_{x,y}$  orbital.

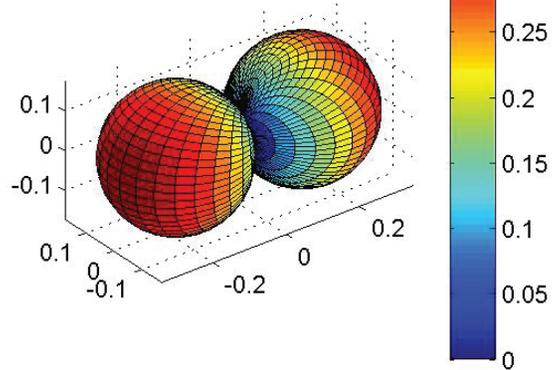


Cartesian form

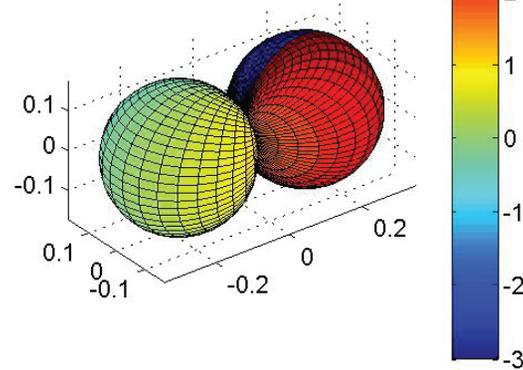
# spherical harmonics

$$Y_{11}$$

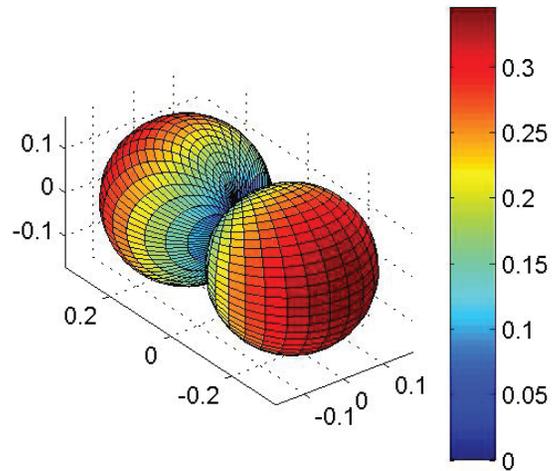
$$\text{Re}[Y_{lm}(\theta, \phi)]$$



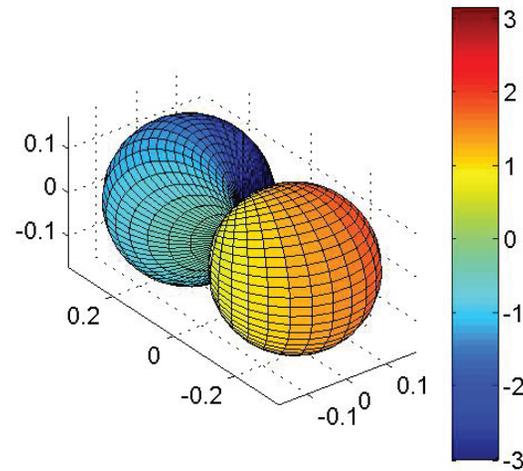
$$\text{arg}[Y_{lm}(\theta, \phi)]$$



$$\text{Im}[Y_{lm}(\theta, \phi)]$$



$$\text{arg}[Y_{lm}(\theta, \phi)]$$

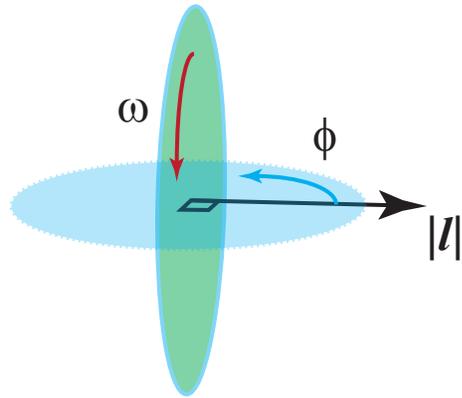


Real and imaginary parts are “rotations”. Can form cartesian  $x$  and  $y$  forms from linear combinations of  $\pm m$ .

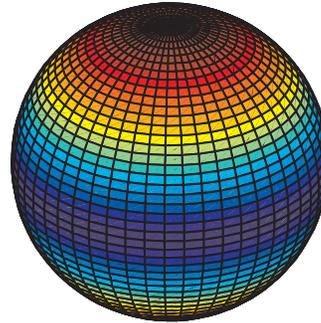
# spherical harmonics

How do the spherical harmonics link to the vector picture?

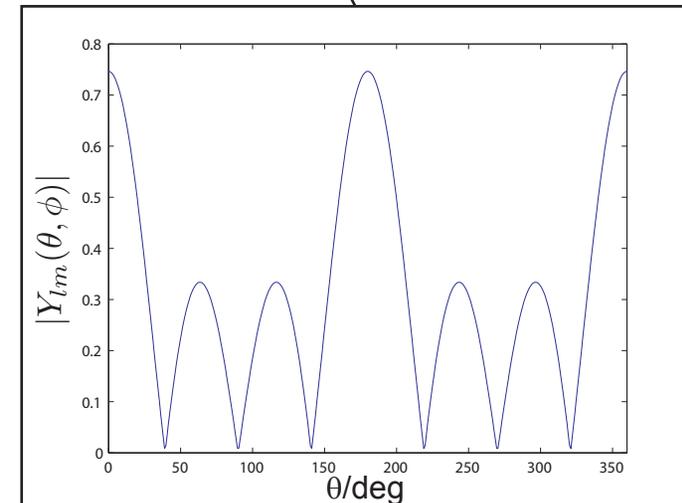
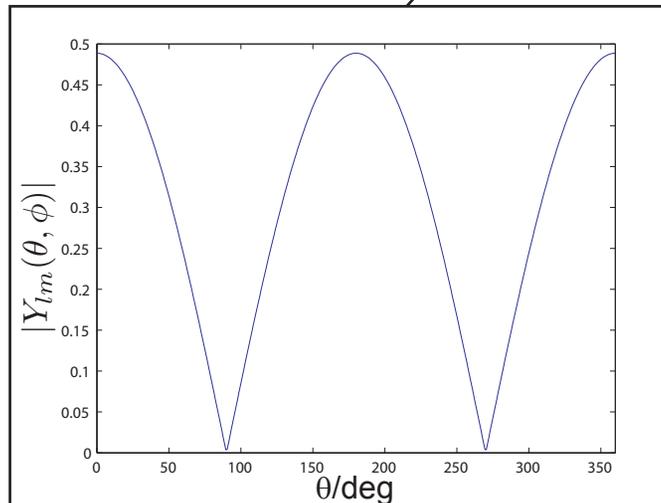
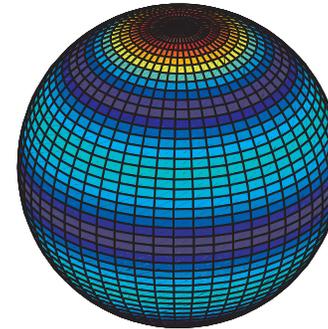
For  $m=0$



$l=1$

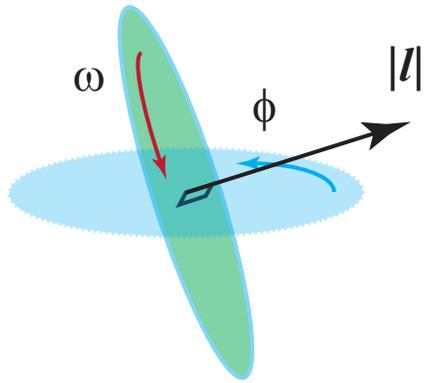


$l=3$



This is a standing-wave on the 'classical' orbit which is azimuthally averaged. Hence larger angular momentum, more nodes in the standing-wave.

# spherical harmonics

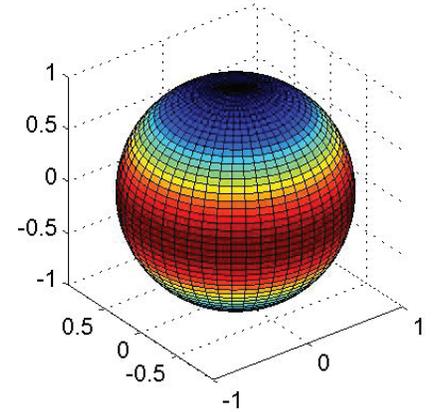
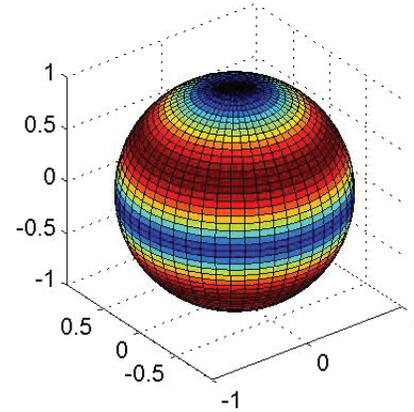
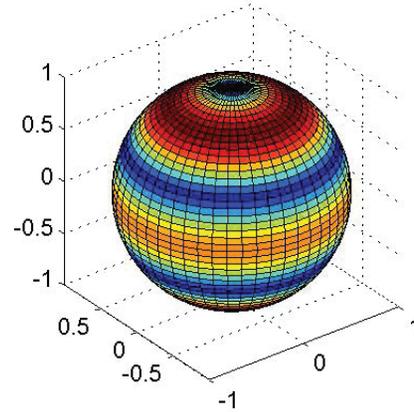


$l=3$

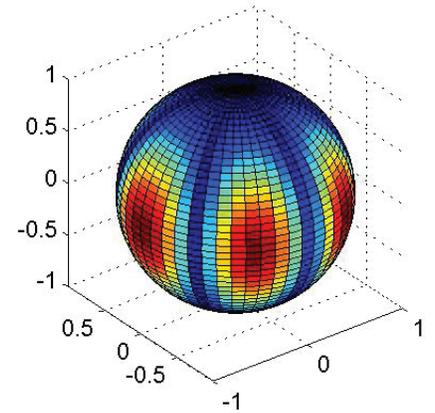
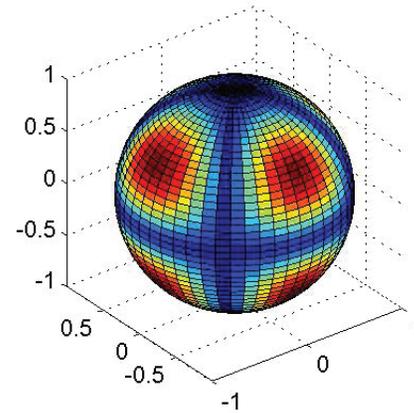
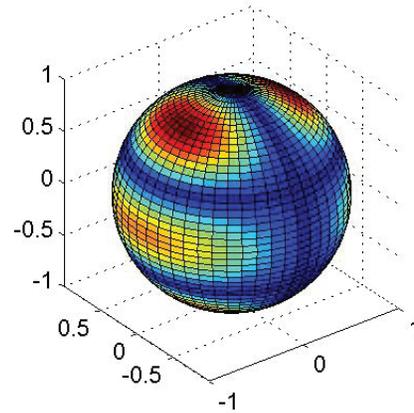
$m=1$

$m=2$

$m=3$



$|Y_{lm}(\theta, \phi)|$



$Re[Y_{lm}(\theta, \phi)]$

For high  $m$  we approach a classical orbit confined to the  $xy$  plane.

This is even more apparent for high  $l$ , high  $m$  cases...

# spherical harmonics

$l=6$

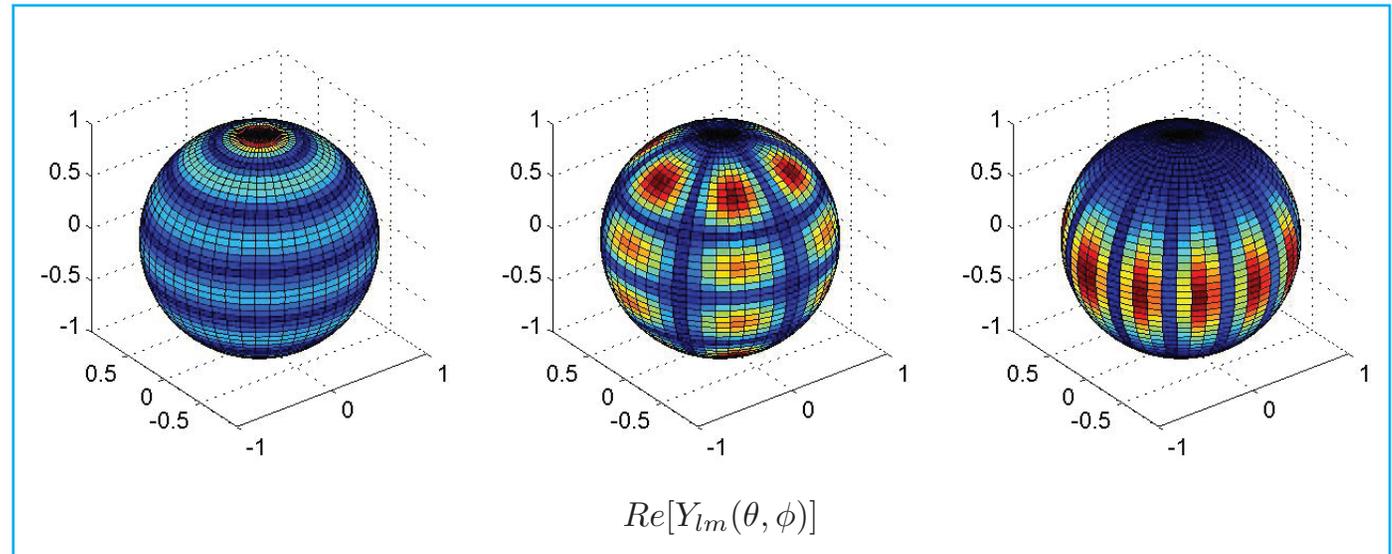
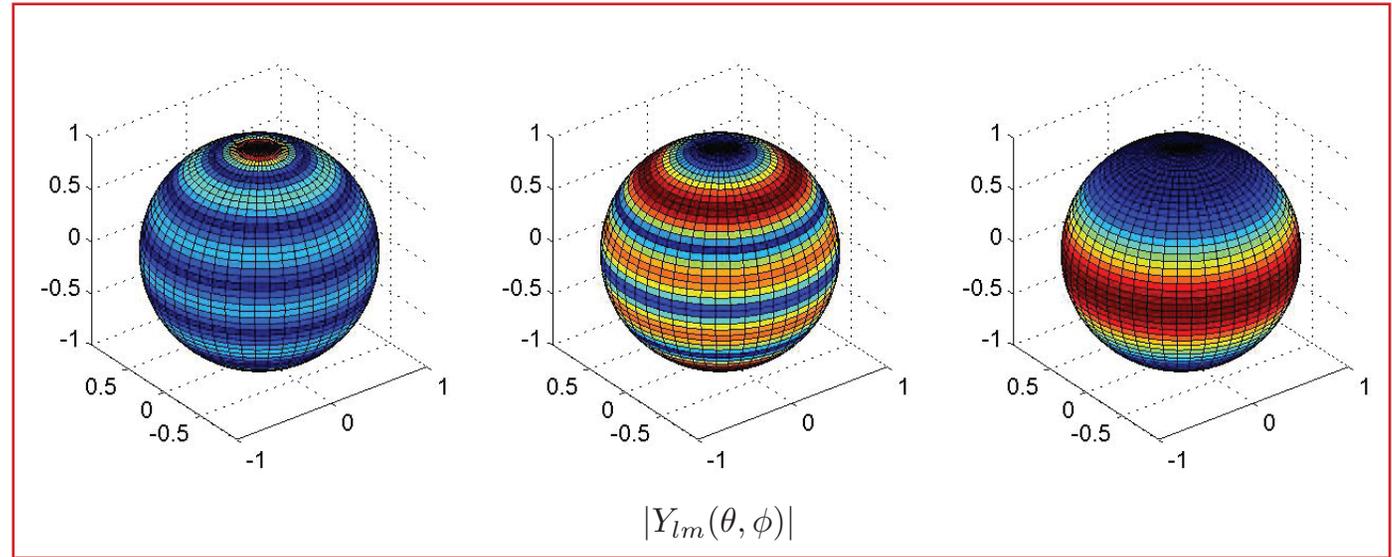
$m=0$

$m=3$

$m=6$

For high  $l$  we approach the classical result for  $m=0$  and  $m=j$ .

Other values still look quite different from the classical case due to the nodal structure of the standing wave.



# rotations

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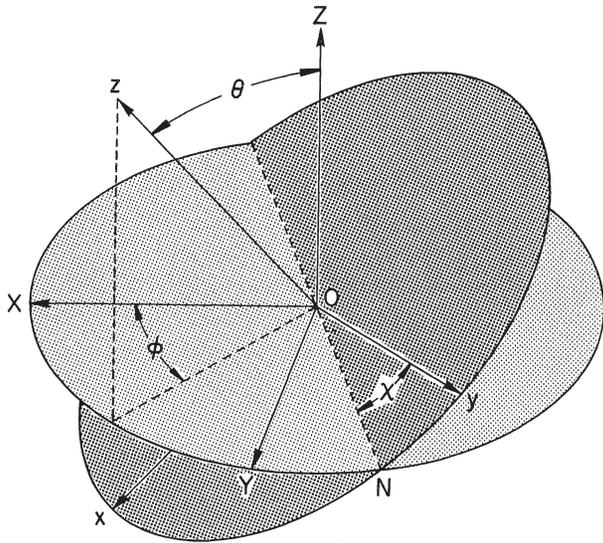
We have so far considered ***dynamical*** angular momentum, building up from a classical orbital picture. In this picture we can consider a particle undergoing ‘classical’ orbits on a ring (albeit with wave structure) which are azimuthally averaged.

But we can also consider the spherical standing waves described by  $Y_{lm}$  to have ***geometrical*** angular momentum. They are just some set of functions which describe a complete  $(2l+1)$  basis on the surface of a sphere.

We will explore this concept in terms of ***frame rotations***, and later link this back to spherical harmonics.

# euler angles

We can parameterize rotations of a 3D body (or axis system) in terms of Euler angles. Rotation can then be described as an operator  $\mathbf{R}$  with matrix elements referred to as the **direction cosine matrix elements**.

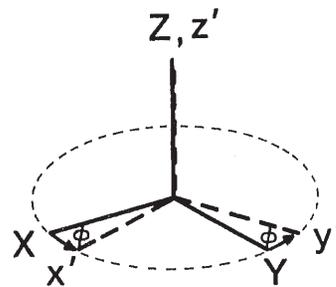


$$\mathbf{R}(\phi, \theta, \chi) f(X, Y, Z) = f(x, y, z)$$

$$\mathbf{R}(\phi, \theta, \chi) = \mathbf{R}_z(\chi) \mathbf{R}_N(\theta) \mathbf{R}_Z(\phi)$$

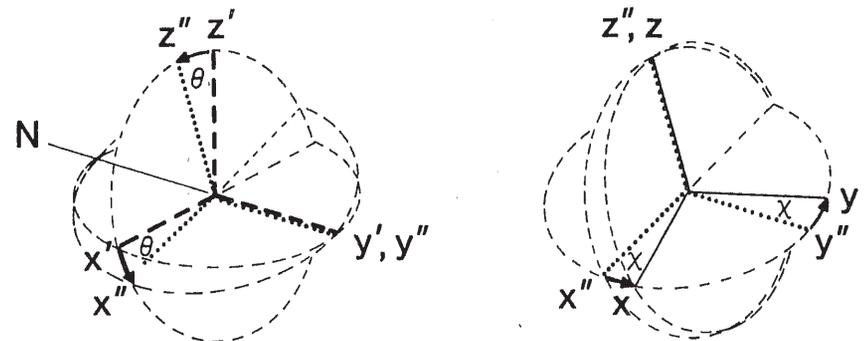
Direction cosine matrix elements

Original Frame



$\mathbf{R}_Z(\phi)$

Final Frame



$\mathbf{R}_N(\theta)$

$\mathbf{R}_z(\chi)$

Reproduced from Zare,  
Angular Momentum

# direction cosine matrix

---

As an example, consider rotations about the  $Z$ -axis.

This is rotation by  $\phi$ , so the rotated frame mixes  $X$  and  $Y$  components of the initial frame.

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \mathbf{R}_Z(\phi) \begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{pmatrix} \cos \phi & \sin \phi & 0 \\ -\sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$$

Similar transformations can be derived for the other components of  $\mathbf{R}$ .

# wigner rotation matrix

---

Wigner developed the quantum analogue of the direction cosine matrix element by considering the behaviour of  $|jm\rangle$  under rotation.

In particular we can see that rotation must commute with  $\mathbf{j}$  - the total angular momentum of the system (hence energy) is conserved under frame rotation. However, projection terms  $m$  must be mixed by rotation. This is analogous to the classical behaviour of vectors under the direction cosine matrix elements.

$$\mathbf{R}(\phi, \theta, \chi)|jm\rangle = \sum_{m'} D_{m'm}^j(\phi, \theta, \chi)|jm'\rangle$$

$$D_{m'm}^j(\phi, \theta, \chi) = \langle jm'|\mathbf{R}(\phi, \theta, \chi)|jm\rangle$$



***Wigner rotation matrix elements***

# wigner rotation matrix

What do the rotation matrix elements look like...?

Phase terms

$$D_{m'm}^j(\phi, \theta, \chi) = e^{-i\phi m'} d_{m'm}^j(\theta) e^{-i\chi m}$$

**Reduced matrix elements**

$$\begin{aligned} d_{m'm}^j(\theta) &= \langle jm' | e^{-i\theta j_y} | jm \rangle \\ &= [(j+m)!(j-m)!(j+m')!(j-m)!]^{1/2} \\ &\times \sum_v \frac{(-1)^v}{(j-m'-v)!(j+m-v)!(v+m'-m)!v!} \\ &\times \left[ \cos\left(\frac{\theta}{2}\right) \right]^{2j+m-m'-2v} \left[ \sin\left(\frac{\theta}{2}\right) \right]^{m'-m+2v} \end{aligned}$$

Summation index is defined to run over all terms for which the factorials are  $\geq 0$

# wigner rotation matrix

---

$$\begin{aligned}d_{m'm}^j(\theta) &= \langle jm' | e^{-i\theta j_y} | jm \rangle \\ &= [(j+m)!(j-m)!(j+m')!(j-m)!]^{1/2} \\ &\times \sum_v \frac{(-1)^v}{(j-m'-v)!(j+m-v)!(v+m'-m)!v!} \\ &\times \left[ \cos\left(\frac{\theta}{2}\right) \right]^{2j+m-m'-2v} \left[ \sin\left(\frac{\theta}{2}\right) \right]^{m'-m+2v}\end{aligned}$$

Rotation about the  $z$ -axis produces only phase factors, but rotation by  $\theta$  mixes  $m$  states. The mixing is defined by terms in  $\theta$ , but also by factorial terms which we can envisage as 'counting' the overlap between  $m$  and  $m'$  states.

Hence,

$$|D_{m'm}^j(\phi, \theta, \chi)|^2 = d_{m'm}^j(\theta)^2$$

# rotation matrix and $Y_{lm}$

---

What about the spherical harmonics under rotation?

$$\mathbf{R}(\phi, \theta, \chi) Y_{lm}(\theta, \phi) = \sum_{m'} D_{m'm}^l(\phi, \theta, \chi) Y_{lm'}(\theta, \phi) = Y_{lm}(\theta', \phi')$$

Hence rotation is equivalent to frame transformation from  $(\theta, \phi) \rightarrow (\theta', \phi')$ . Again this reflects an invariance due to rotation, we just rotate the  $z$ -axis to a new direction.

We can identify the rotation matrix elements with spherical harmonics for  $m'=0$  - these functions are *geometrically related*.

$$D_{m0}^l(\phi, \theta, \chi) = \left( \frac{4\pi}{2l+1} \right)^{1/2} Y_{lm}^*(\theta, \phi)$$

# rotation matrix and rotations

---

Following the above it is perhaps not surprising that the rotation matrix elements can also be used as basis functions to describe rotational motion of a symmetric top.

$$|JKM\rangle = \left[ \frac{2J+1}{8\pi^2} \right]^{1/2} D_{MK}^{J*}(\phi, \theta, \chi)$$

We will see more of the rotation matrix elements next week...



# coupling angular momenta

---

Formally the coupling follows from a treatment of the commutation relations.

In the *uncoupled representation* we have:

$$|j_1 m_1, j_2 m_2\rangle \equiv |j_1 m_1\rangle |j_2 m_2\rangle$$

We know this is an eigenfunction of  $\mathbf{j}_1^2$  and  $\mathbf{j}_2^2$ , and their  $z$ -components:

$$\begin{aligned} \mathbf{j}_1^2 |j_1 m_1, j_2 m_2\rangle &= j_1(j_1 + 1) |j_1 m_1, j_2 m_2\rangle \\ j_{1z} |j_1 m_1, j_2 m_2\rangle &= m_1 |j_1 m_1, j_2 m_2\rangle \\ \mathbf{j}_2^2 |j_1 m_1, j_2 m_2\rangle &= j_2(j_2 + 1) |j_1 m_1, j_2 m_2\rangle \\ j_{2z} |j_1 m_1, j_2 m_2\rangle &= m_2 |j_1 m_1, j_2 m_2\rangle \end{aligned}$$

It can also be shown that another complete set of commuting angular momentum operators is given by  $\mathbf{j}_1^2$ ,  $\mathbf{j}_2^2$ ,  $\mathbf{j}^2 = (\mathbf{j}_1 + \mathbf{j}_2)^2$ , and  $j_z = j_{1z} + j_{2z}$ . This defines the coupled representation.

# coupling angular momenta

---

In the coupled representation the eigenvalues are then given by:

$$\mathbf{j}_1^2 |jm\rangle = j_1(j_1 + 1) |jm\rangle$$

$$\mathbf{j}_2^2 |jm\rangle = j_2(j_2 + 1) |jm\rangle$$

$$\mathbf{j}^2 |jm\rangle = j(j + 1) |jm\rangle$$

$$j_z |jm\rangle = m |jm\rangle$$

The representations are linked by a unitary transform - they are just expressions of the same result in different basis spaces.

$$|jm\rangle = \sum_{m_1, m_2} C(j_1 j_2 j; m_1 m_2 m) |j_1 m_1, j_2 m_2\rangle$$

$$|j_1 m_1, j_2 m_2\rangle = \sum_{j, m} C(j_1 j_2 j; m_1 m_2 m) |jm\rangle$$

**Vector coupling coefficients**  
**Clebsch-Gordan coefficients**



# clebsch-gordan coefficients

---

The Clebsch-Gordan coefficients - the vector coupling matrix elements - are real numbers given by:

$$C(j_1 j_2 j; m_1 m_2 m) \equiv \langle j_1 m_1, j_2 m_2 | j m \rangle \equiv \langle j m | j_1 m_1, j_2 m_2 \rangle$$

Where:

$$|j_1 + j_2| \geq j \geq |j_1 - j_2|$$

$$m = m_1 + m_2$$

Hence they act like (quantized) vector addition - the scalar terms add while the vector terms can be parallel, anti-parallel, or integer steps in-between.

# clebsch-gordan coefficients

What do the vector coupling coefficients look like...?

$$\begin{aligned} \langle j_1 m_1, j_2 m_2 | j m \rangle &= \delta_{m_1+m_2, m} \left[ (2j+1) \frac{(s-2j)!(s-2j_2)!(s-2j_1)!}{(s+1)!} \right]^{1/2} \\ &\times [(j_1+m_1)!(j_1-m_1)!(j_2+m_2)!(j_2-m_2)!(j+m)!(j-m)!]^{1/2} \\ &\times \sum_v \frac{(-1)^v}{v!(j_1+j_2-j-v)!(j_1-m_1-v)!(j_2+m_2-v)!(j-j_2+m_1+v)!(j-j_1-m_2+v)!} \end{aligned}$$

$$s = j_1 + j_2 + j$$



Summation index is defined to run over all terms for which the factorials are  $\geq 0$

Note the passing resemblance to the reduced rotation matrix elements - we are again dealing with quantized vector overlap integrals.

This looks nasty, but is just a number we can calculate.

# $3j$ symbols

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A useful alternative to Clebsch-Gordan coefficients are Wigner  $3j$  symbols. These can be regarded as essentially the same, but have slightly different symmetry properties which are useful when manipulating angular momentum expressions algebraically.

$$\begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix} = (-1)^{j_1 - j_2 - m} (2j + 1)^{-1/2} \langle j_1 m_1, j_2 m_2 | j m \rangle$$

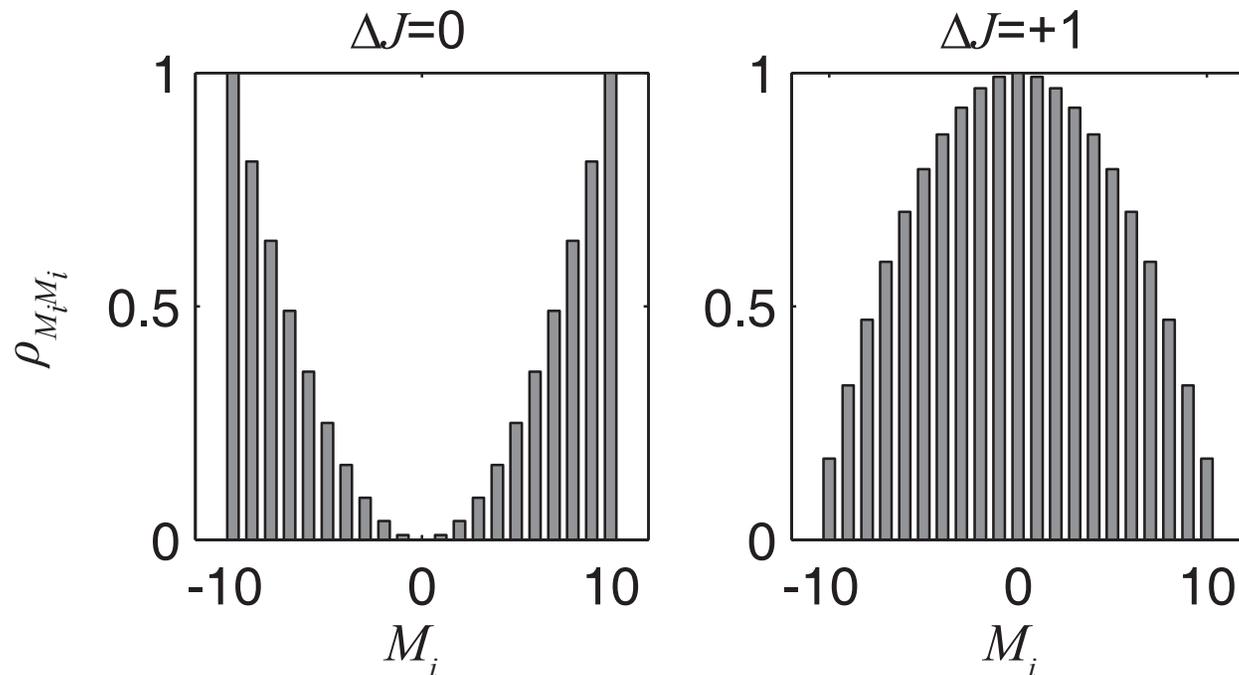
We will see a lot of these next week!

# 3j symbols - alignment

Finally, a quick example to show how we might use angular momentum coupling.

$${}^{J_i K_i} \rho_{M_i M_i} \propto \mathbf{S}(J_i K_i, J_g K_g) \sum_{M_g} \begin{pmatrix} J_g & 1 & J_i \\ M_g & 0 & M_i \end{pmatrix}^2$$

Single photon absorption, leads to a diagonal density matrix describing the excited state alignment.





# summary

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In this session we have covered:

- Dynamical and geometrical pictures of angular momentum.
- Spherical harmonics as angular momentum wavefunctions.
- Frame rotations: the Wigner rotation matrix elements.
- Angular momentum coupling: Clebsch-Gordan coefficients and  $3j$  symbols.

NEXT TIME... photoelectron angular distributions

# addendum - alignment

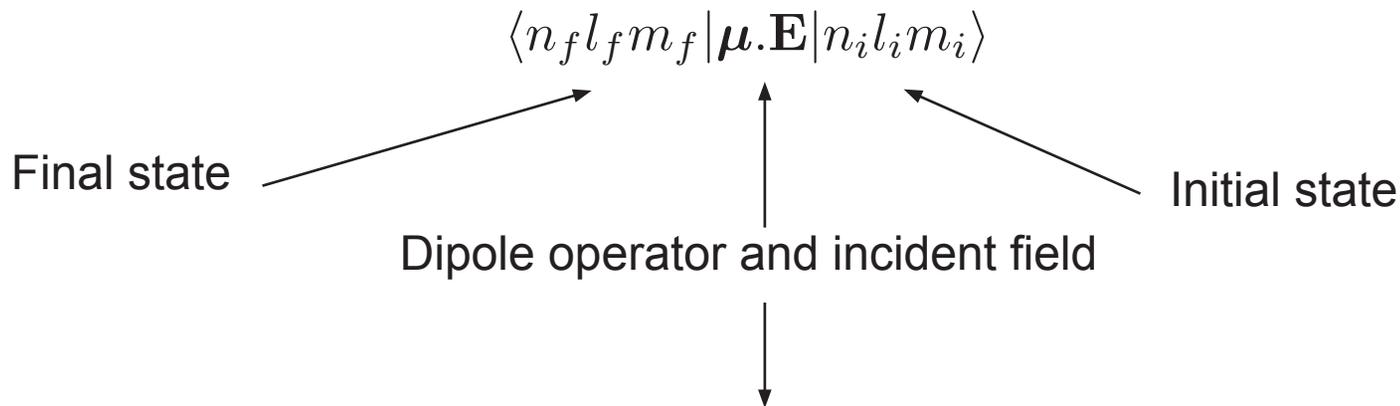
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Following discussions after the session, here's a little more on alignment...

Note that the final written notes I am preparing will present this a little more thoroughly.

## **Atomic case**

Consider an electronic dipole transition (spin neglected). The transition probability is given by the dipole matrix element:



We can write the dipole operator and radiation field in spherical basis functions:

$$\boldsymbol{\mu} = -e\mathbf{r} = \sum_q \mu_q$$

$$\mathbf{E} = E\hat{\mathbf{e}} = E \sum_q e_q$$

$$\begin{aligned} \mu_0 &= er_z \\ \mu_{\pm 1} &= \mp \frac{e}{\sqrt{2}}(r_x \pm ir_y) \end{aligned}$$

$$\begin{aligned} e_0 &= e_z \\ e_{\pm} &= \mp \frac{1}{\sqrt{2}}(e_x \pm ie_y) \end{aligned}$$

# addendum - alignment

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The dot product now becomes:

$$\boldsymbol{\mu} \cdot \mathbf{E} = E(\boldsymbol{\mu} \cdot \hat{\mathbf{e}}) = E \sum_q (-1)^q \mu_q e_{-q}$$

This is the most general form of the equations, for specific cases it can be shown that:

$$\begin{aligned} q=0 \\ \boldsymbol{\mu} \cdot \mathbf{E} &= eEr \sqrt{\frac{4\pi}{3}} Y_{1,0}(\theta, \phi) \\ \\ q=+/-1 \\ \boldsymbol{\mu} \cdot \mathbf{E} &= \mp eEr \sqrt{\frac{4\pi}{3}} Y_{1,\pm 1}(\theta, \phi) \end{aligned}$$

Hence we end up with spherical harmonics again!

In this spherical basis  $q=0$  is the case for linearly polarized light (along the z-axis) while  $q=+/-1$  represents circularly polarized light. In the case where the sample is isotropic (unpolarized) before interaction we can always choose the z-axis to coincide with the laser polarization.

# addendum - alignment

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The dipole matrix element now becomes

$$\langle n_f l_f m_f | \boldsymbol{\mu} \cdot \mathbf{E} | n_i l_i m_i \rangle = (-1)^q e E \sqrt{\frac{4\pi}{3}} \langle n_f l_f m_f | r Y_{1,q}(\theta, \phi) | n_i l_i m_i \rangle$$

The eigenstates in radial and angular parts:  $|nlm\rangle = \chi_{nl}(r) Y_{lm}(\theta, \phi)$

Hence,

$$\langle n_f l_f m_f | \boldsymbol{\mu} \cdot \mathbf{E} | n_i l_i m_i \rangle = (-1)^q e E \underbrace{\sqrt{\frac{4\pi}{3}} \langle \chi_{n_f l_f}(r) | r | \chi_{n_i l_i}(r) \rangle}_{\text{Radial part}} \underbrace{\langle Y_{l_f m_f}(\theta, \phi) | Y_{1,q}(\theta, \phi) | Y_{l_i m_i}(\theta, \phi) \rangle}_{\text{Angular part}}$$

We can deal with the angular part analytically using standard angular momentum algebra. This will give the relative transition intensity for different  $m$ , and hence alignment information.

# addendum - alignment

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The angular part of the dipole matrix element gives:

$$\begin{aligned}\langle Y_{l_f m_f}(\theta, \phi) | Y_{1,q}(\theta, \phi) | Y_{l_i m_i}(\theta, \phi) \rangle &= \iint Y_{l_f m_f}^* Y_{1,q} Y_{l_i m_i} \sin \theta d\theta d\phi \\ &= \iint (-1)^{m_f} Y_{l_f -m_f} Y_{1,q} Y_{l_i m_i} \sin \theta d\theta d\phi \\ &= (-1)^{m_f} \left[ \frac{3(2l_i + 1)(2l_f + 1)}{4\pi} \right]^{1/2} \begin{pmatrix} l_i & 1 & l_f \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_i & 1 & l_f \\ m_i & q & -m_f \end{pmatrix}\end{aligned}$$

If we're only interested in alignment (polarization) of the final state for some given transition then we just need to consider the final term here:

$$\rho_{m_f, m_f} \propto \sum_{m_i} \begin{pmatrix} l_i & 1 & l_f \\ m_i & q & -m_f \end{pmatrix}^2$$

Density matrix describes populations of  $m_f$  levels.

Sum over initial state  $m_i$  levels. Here we assume these levels are equally populated.

# addendum - alignment

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This looks very similar to the first case shown in the main talk, except generalized for any  $q$ . In the atomic case this shows alignment is independent of the transition, assuming that only a single transition is excited (i.e. we don't need to know about the weighting of different  $n, l$  in the radial part of the dipole matrix element).

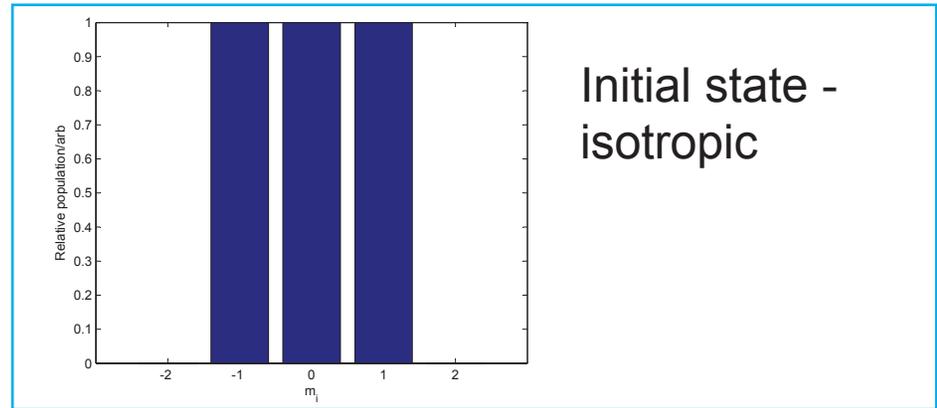
This follows from general symmetry considerations - before the laser field there is no quantization axis, so all  $m_l$  are degenerate and isotropic (no polarization of sample). For linearly polarized light  $q=0$  and the alignment is then just induced by the cosine term ( $Y_{10}$ ) from the dipole, so we always get a final result which looks like  $\cos^2$  for any allowed transition.

For circularly polarized light  $q=\pm 1$  (note also that the z-axis is conventionally taken to be the propagation axis in this case, while propagation axis is in the xy plane for linearly polarized case).

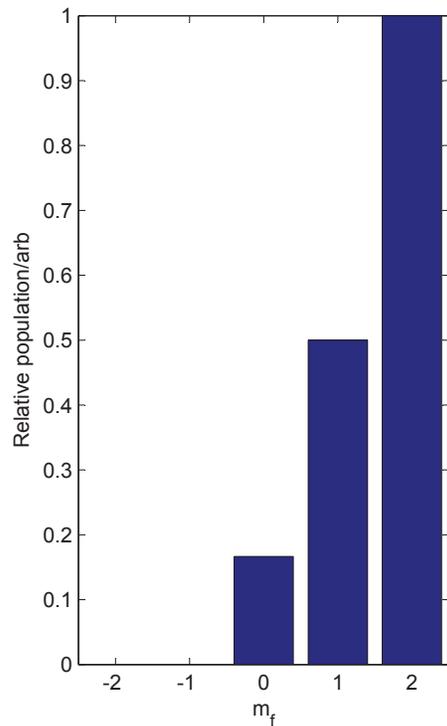
In this case the polarization is purely electronic - it is the  $l$  vector which is aligned or polarized by the excitation.

# addendum - alignment

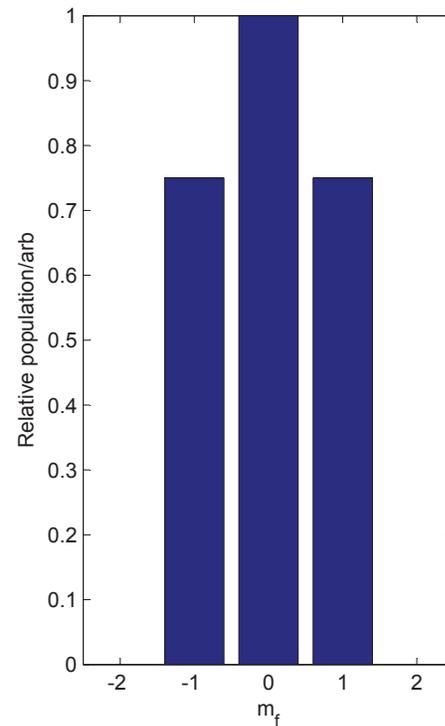
Example:  $p \rightarrow d$  transition



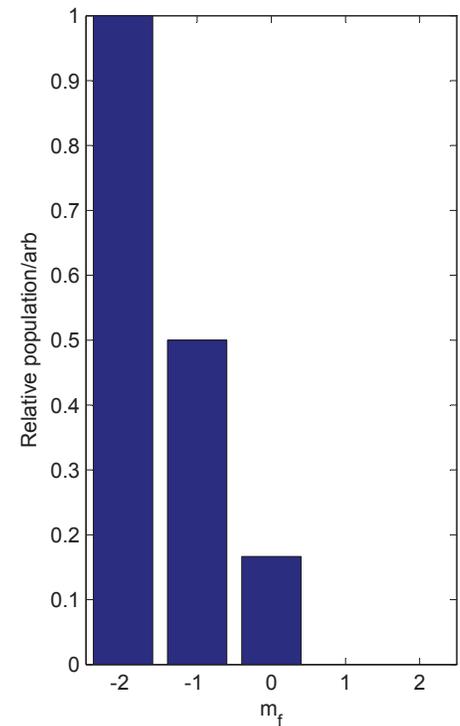
$q = -1$



$q = 0$



$q = 1$



# addendum - alignment

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## **Molecular case**

Very similar to the atomic case, except we now also have quantization along the molecular axis, i.e. we can define a molecular frame (MF) which is distinct from the lab frame (LF).

Recall for the atomic case we had:

$$\boldsymbol{\mu} \cdot \mathbf{E} = E(\boldsymbol{\mu} \cdot \hat{\mathbf{e}}) = E \sum_q (-1)^q \mu_q e_{-q}$$

In the LF we can write something equivalent:

$$E(\boldsymbol{\mu} \cdot \hat{\mathbf{e}}) = E \sum_p (-1)^p \mu_p e_{-p}$$

  $p$  are the spherical basis vectors in the LF.

Generally we want to describe the incident radiation in the LF, but the transition dipole moments in the MF... we can allow for this by introducing a frame rotation:

$$E(\boldsymbol{\mu} \cdot \hat{\mathbf{e}}) = E \sum_{p,q} (-1)^p e_{-p} D_{pq}^{1*}(\phi, \theta, \chi) \mu_q$$

# addendum - alignment

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We also need different basis states for angular momentum as we now have two projection terms to consider.

$$|\alpha j k m\rangle = \left[ \frac{2j+1}{8\pi^2} \right]^{1/2} \Phi_\alpha(r) D_{mk}^{j*}(\phi, \theta, \chi)$$

This collects all other quantum numbers required

$j k m$  are general angular momentum quantum numbers - see later!

Radial wavefunction.

Angular wavefunction.

# addendum - alignment

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Proceeding as before the angular part of the dipole matrix element is now given by:

$$\begin{aligned} \langle j_f k_f m_f | D_{pq}^{1*}(\phi, \theta, \chi) | j_i k_i m_i \rangle &= \frac{\sqrt{(2j_i + 1)(2j_f + 1)}}{8\pi^2} \iint D_{m_f k_f}^{j_f*} D_{pq}^{1*} D_{m_i k_i}^{j_i} \sin \theta d\theta d\phi \\ &= \sqrt{(2j_i + 1)(2j_f + 1)} \begin{pmatrix} j_i & 1 & j_f \\ m_i & -p & -m_f \end{pmatrix} \begin{pmatrix} j_i & 1 & j_f \\ k_i & -q & -k_f \end{pmatrix} \end{aligned}$$

This looks very similar to the atomic case shown before, except we now have terms in  $k, q$  - the MF part of the transition.

# addendum - alignment

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The density matrix is now given by:

$$\rho_{m_f m_f} \propto \left| \sum_{m_i} \begin{pmatrix} j_i & 1 & j_f \\ m_i & -p & -m_f \end{pmatrix} \right|^2$$



Defined for specific LF polarization  $p$ .

Again this assumes that transitions pertaining to different states (different  $\alpha$ ) are not mixed - in that case we would also need to know something about the relative transition intensities given by the radial part of the transition matrix elements.

The MF part in general does not affect the LF alignment, except for removing transitions which are not allowed, e.g. for  $j_i=j_f=0$  we can't also have  $k_i=k_f=0$ .

# addendum - alignment

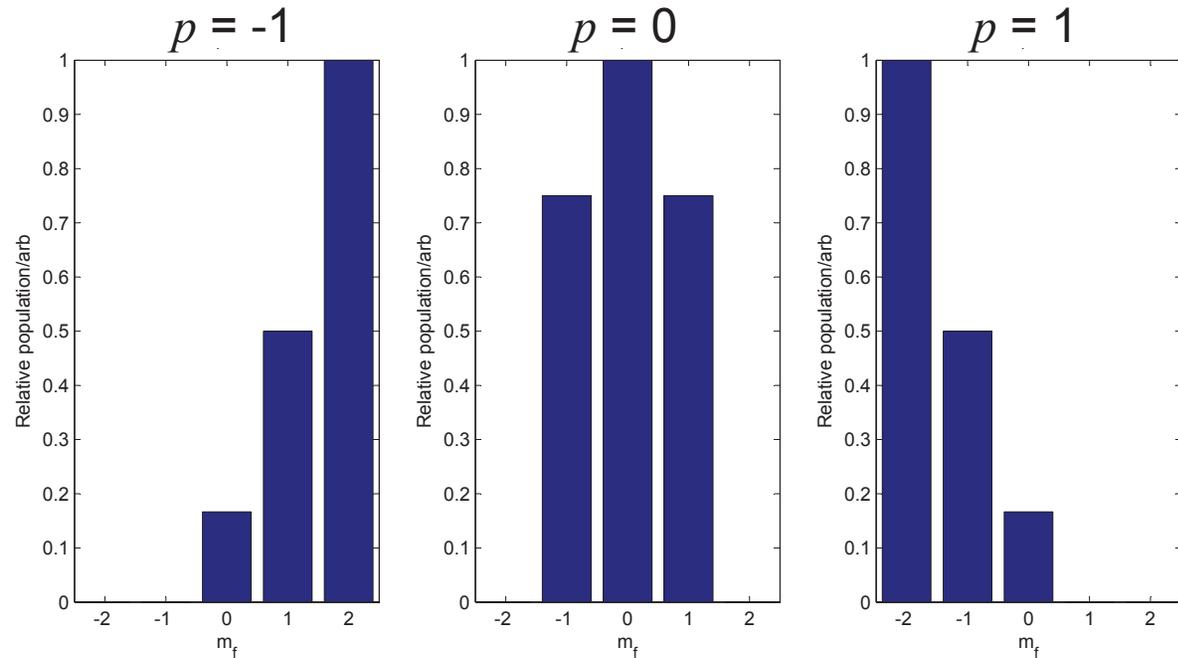
Examples...

$$j_i = 1, k_i = 0$$

$$\Delta j = 1$$

$$\Delta k = 0, \pm 1$$

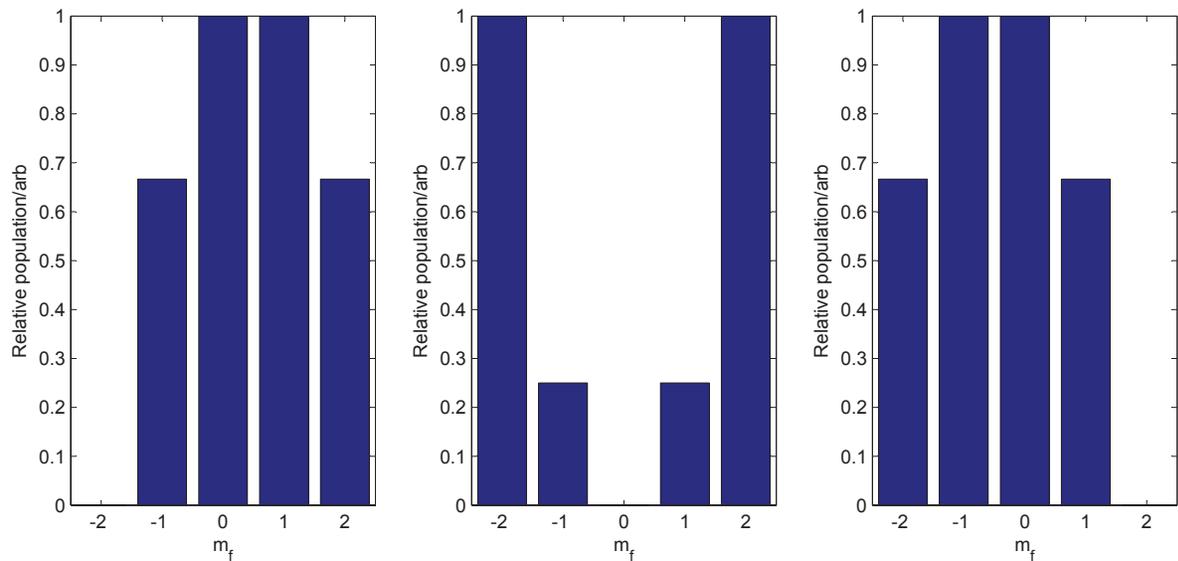
(i.e. alignment not affected by  $k$ )



$$j_i = 2, k_i = 1$$

$$\Delta j = 0$$

$$\Delta k = 0, \pm 1$$



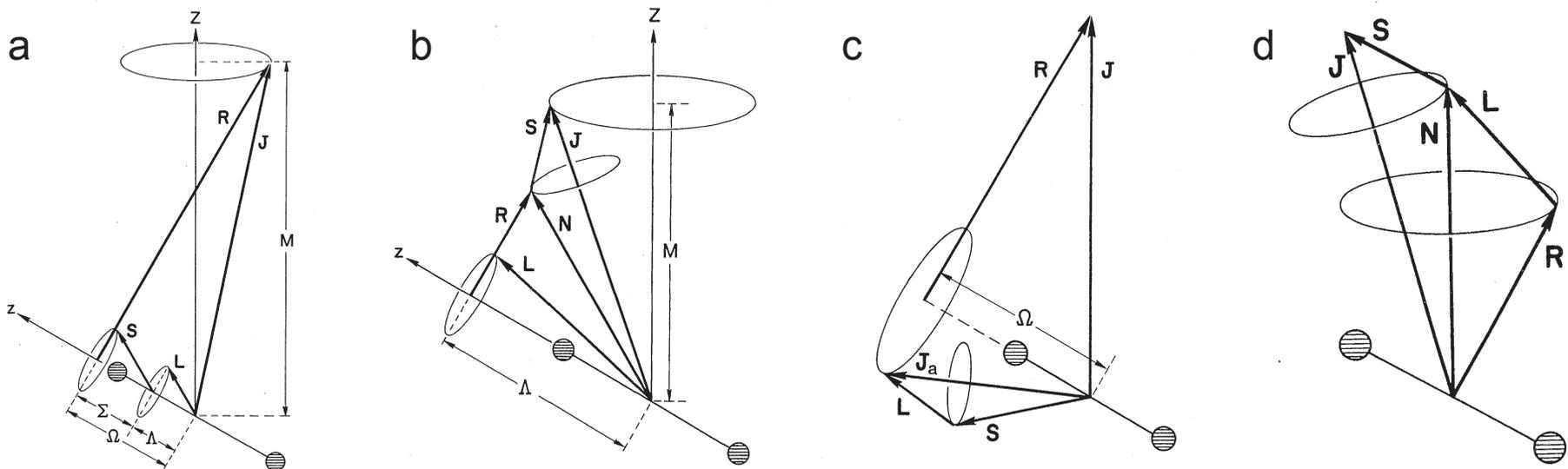
The important thing here is  $\Delta j$ , this chooses whether we prepare  $j_f$  parallel or perpendicular to the lab frame, i.e. couple to low or high  $m_i$  - we can just consider this as vector addition.

# addendum - alignment

What does alignment mean in this case? In the atomic case we only have electronic angular momentum (orbital + spin, although we often ignore the latter, similarly nuclear spin is ignored), so alignment of angular momentum can only mean alignment of electronic angular momentum.

In the molecular case we can have electronic, rotational and even vibrational contributions to the total angular momentum. Exactly how these components relate to  $j$  will depend on the coupling of these factors, hence will depend on which Hund's case is most appropriate.

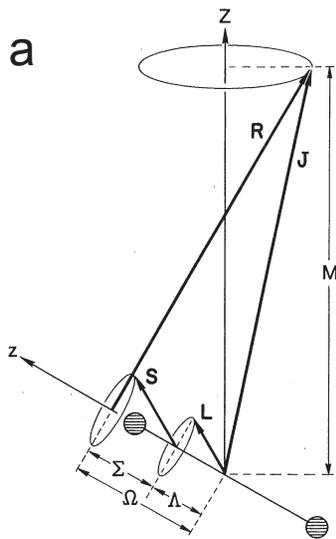
## Hund's cases a - d



Reproduced from Zare, Angular Momentum

# addendum - alignment

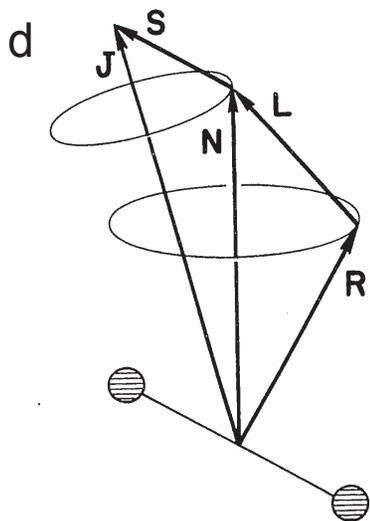
The clearest (!) cases are (a) and (d)...



Here  $j$  is the coupling between rotational angular momentum and electronic angular momentum projected onto the molecular axis, hence  $J = R + \Omega$  (using Zare's notation,  $\Omega$  is equivalent to  $k$  as previously used).

For a singlet state  $\Omega = 0$  hence  $J = R$  and we align purely rotational angular momentum - the plane of rotation of the molecule is confined in the vector picture.

More generally we have  $\Omega \neq 0$  so we align both electronic and rotational angular momentum to some degree. Because  $L$  is coupled to the internuclear axis aligning this axis is equivalent to aligning  $L$ .



Here  $j$  is the coupling between rotational angular momentum and the total electronic angular momentum, hence  $J = R + L + S$ .

In this case the electronic angular momentum is not tied to the internuclear axis (e.g. we have a Rydberg state). This means that there are no longer 'parallel' and 'perpendicular' transitions defined in the MF. If we make an electronic transition we align  $L$ , but not the molecular axis; if we make a rotational transition we change  $R$  but don't affect  $L$ .