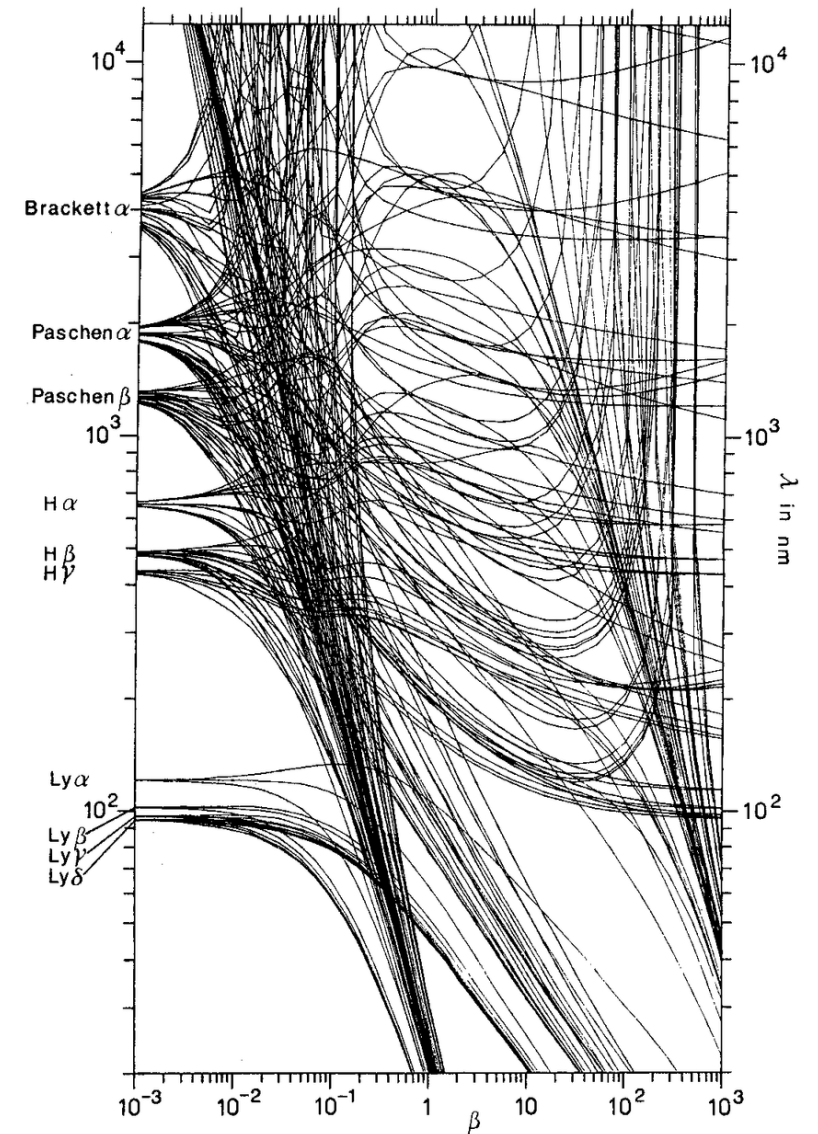


# Today in Physics 237: rotational symmetry and degeneracy

- Rotational symmetry and angular momentum conservation
- Degeneracy
- Selection rules for scalar operators
- Reduced matrix elements

Calculations to guide the experimental determination of rotational degeneracy in H.



# Rotation about a single axis

- Just as translations are generated by linear momentum, rotations are generated by angular momentum:

$$\hat{T}(a) = e^{-ia\hat{p}/\hbar} \quad , \quad \hat{R}_z(\varphi) = e^{-i\varphi\hat{L}_z/\hbar} \quad .$$

- Check with a very small rotation  $\delta$ , so that a first-order approximation applies:  $\hat{R}_z \cong 1 - \frac{i\delta}{\hbar}\hat{L}_z$ , so

$$\hat{x}' = \hat{R}_z^\dagger \hat{x} \hat{R}_z \cong \left(1 + \frac{i\delta}{\hbar}\hat{L}_z\right) \hat{x} \left(1 - \frac{i\delta}{\hbar}\hat{L}_z\right) = \hat{x} + \frac{i\delta}{\hbar}\hat{L}_z\hat{x} - \frac{i\delta}{\hbar}\hat{x}\hat{L}_z + \frac{\delta^2}{\hbar^2}\hat{L}_z\hat{x}\hat{L}_z \cong \hat{x} + \frac{i\delta}{\hbar}[\hat{L}_z, \hat{x}] = \hat{x} - \delta\hat{y} \quad ,$$

second order

using the commutator you calculated in G&S problem 4.22 ([assignment 9](#)). Similarly  $\hat{y}' = \hat{R}_z^\dagger \hat{y} \hat{R}_z \cong \hat{y} + \delta\hat{x}$  ,  
 $\hat{z}' = \hat{R}_z^\dagger \hat{z} \hat{R}_z = \hat{z}$  .

- Or, all together,

$$\begin{bmatrix} \hat{x}' \\ \hat{y}' \\ \hat{z}' \end{bmatrix} \cong \begin{bmatrix} 1 & -\delta & 0 \\ \delta & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \hat{x} \\ \hat{y} \\ \hat{z} \end{bmatrix}$$

Recall that, for first order in  $\delta$ ,  
 $\cos\delta \cong 1$  and  $\sin\delta \cong \delta$ ,  
 so this *is* the usual form for  
 the rotation matrix (c.f. [Lecture 9](#))

# Rotation in 3-D

- As  $\hat{R}_z(\varphi) = e^{-i\varphi\hat{L}_z/\hbar} = e^{-i\varphi\hat{\mathbf{z}}\cdot\hat{\mathbf{L}}/\hbar}$ , we see that a rotation about any unit vector  $\hat{\mathbf{n}}$  would be, unsurprisingly,  $\hat{R}_{\hat{\mathbf{n}}}(\varphi) = e^{-i\varphi\hat{\mathbf{n}}\cdot\hat{\mathbf{L}}/\hbar}$ .
- Any operator which transforms the same way under rotations as the position operator  $\hat{\mathbf{r}}$  is also a vector operator. For infinitesimal rotations, the transformation of a vector operator  $\hat{\mathbf{V}}$  would follow from a commutation relation with  $\hat{\mathbf{L}}$ ; in Cartesian components with  $x, y, z = 1, 2, 3$ ,

$$[\hat{L}_i, \hat{V}_j] = i\hbar\epsilon_{ijk}\hat{V}_k$$

## 3-D Levi-Civita tensor

$\epsilon_{ijk} = 1$  if  $ijk = 123$  or  $231$  or  $312$ ;  $-1$  if  $ijk = 321$  or  $213$  or  $132$ ;  $0$  otherwise

- Summary:

	Parity	Rotation	Examples
Vector $\hat{\mathbf{V}}$	$\{\hat{\Pi}, \hat{V}_i\} = \hat{\Pi}\hat{V}_i + \hat{V}_i\hat{\Pi} = 0$	$[\hat{L}_i, \hat{V}_j] = i\hbar\epsilon_{ijk}\hat{V}_k$	$\hat{\mathbf{r}}, \hat{\mathbf{p}}$
Pseudovector $\hat{\mathbf{V}}$	$[\hat{\Pi}, \hat{V}_i] = 0$	$[\hat{L}_i, \hat{V}_j] = i\hbar\epsilon_{ijk}\hat{V}_k$	$\hat{\mathbf{L}}$ ; cross product of two vectors
Scalar $\hat{f}$	$[\hat{\Pi}, \hat{f}] = 0$	$[\hat{L}_i, \hat{f}] = 0$	$\hat{\mathbf{r}} \cdot \hat{\mathbf{r}}$
Pseudoscalar $\hat{f}$	$\{\hat{\Pi}, \hat{f}\} = 0$	$[\hat{L}_i, \hat{f}] = 0$	Scalar triple product of three vectors

# Continuous rotations and angular momentum conservation

- A **central** potential  $V(\mathbf{r}) = V(r)$  ([Lecture 14](#), p. 7), independent of the angular coordinates  $\vartheta$  and  $\varphi$ , is a scalar.
- And  $\hat{p}^2 = \hat{\mathbf{p}} \cdot \hat{\mathbf{p}} = -\hbar^2 \nabla^2$  is a scalar because  $\hat{\mathbf{p}}$  is a vector.
- In this case the Hamiltonian  $\hat{H} = -\hbar^2 \nabla^2 / 2m + V(r)$  is a scalar, and commutes with a rotation by any angle about any axis:  $[\hat{H}, \hat{R}_{\hat{n}}(\varphi)] = 0$ .
- This includes infinitesimal rotation,  $\hat{R}_{\hat{n}}(\delta) \cong 1 - \frac{i\delta}{\hbar} \hat{\mathbf{n}} \cdot \hat{\mathbf{L}}$ , and therefore continuous rather than discrete angular displacement. Therefore  $[\hat{H}, \hat{\mathbf{L}}] = 0$ : this Hamiltonian commutes with all three components of  $\mathbf{L}$ , and thus with  $\hat{L}^2$ .
- And if  $\hat{\mathbf{L}}$  has no explicit time dependence (i.e. if  $\partial \hat{\mathbf{L}} / \partial t = 0$ ) then, according to the generalized Ehrenfest theorem ([Lecture 11](#), p.5),

$$\frac{d}{dt} \langle \mathbf{L} \rangle = \frac{i}{\hbar} \langle [\hat{H}, \hat{\mathbf{L}}] \rangle = 0 \quad ; \quad \text{also} \quad \frac{d}{dt} \langle L_x \rangle = \frac{d}{dt} \langle L_y \rangle = \frac{d}{dt} \langle L_z \rangle = 0 \quad , \quad \text{Angular momentum is conserved}$$

precisely as in classical mechanics, via Noether's First Theorem.

# Continuous rotations and angular momentum conservation (cont'd)

- Since this Hamiltonian commutes with  $\hat{L}^2$  and all three components of  $\hat{\mathbf{L}}$ , the three observables  $\hat{H}$ ,  $\hat{L}^2$  and  $\hat{L}_z$  comprise a complete set of compatible observables.
  - We noticed this to be true for the spherical quantum well and the hydrogen atom, but now we have demonstrated that they would be a complete set for any central potential.
  - And the same quantum numbers would suffice to specify a bound state, in any central potential problem:

$$\hat{H}\psi_{n\ell m} = E_n\psi_{n\ell m}$$

$$\hat{L}^2\psi_{n\ell m} = \ell(\ell+1)\hbar^2\psi_{n\ell m}$$

$$\hat{L}_z\psi_{n\ell m} = m\hbar\psi_{n\ell m}$$

# Symmetry and degeneracy

- Now we have three cases of symmetry involving operators which commute with the Hamiltonian: translation, parity, and rotation.
- Symmetry leads to states which share the same energy eigenvalue. For if  $[\hat{H}, \hat{Q}] = 0$ , and  $\hat{Q}$  transforms state  $\psi$  into  $\psi'$ , then

$$\hat{H}|\psi'_n\rangle = \hat{H}(\hat{Q}|\psi_n\rangle) = \hat{Q}\hat{H}|\psi_n\rangle = \hat{Q}E_n|\psi_n\rangle = E_n\hat{Q}|\psi_n\rangle = E_n|\psi'_n\rangle \quad ;$$

states  $\psi$  and  $\psi'$  share the same  $E_n$ . If  $\psi$  and  $\psi'$  are different, orthogonal states, this makes them **degenerate**.

- If  $\hat{Q}$  is the only symmetry operator for which  $[\hat{H}, \hat{Q}] = 0$ , then  $\psi$  and  $\psi'$  could be the *same* state, part of the two common complete set of eigenstates which can be chosen if  $[\hat{H}, \hat{Q}] = 0$ .
- But suppose there are two operators,  $\hat{Q}$  and  $\hat{\Lambda}$ , which commute with the Hamiltonian but not with each other. Then there cannot be a complete set of states which are all eigenstates of all three operators  $\hat{H}$ ,  $\hat{Q}$  and  $\hat{\Lambda}$ .

# Rotational degeneracy

Example (G&S 6.3): Consider a system with a central potential, states  $\psi_{n\ell m}$  and their energy eigenvalues  $E_n$ . Use the fact that the Hamiltonian for a central potential commutes with any component of  $\hat{L}$ , and therefore also with  $\hat{L}_{\pm}$ , to show that  $\psi_{n\ell m\pm 1}$  are degenerate with  $\psi_{n\ell m}$ .

- Since  $[\hat{H}, \hat{L}_{\pm}] = 0$ ,
 
$$\hat{H}\hat{L}_{\pm}\psi_{n\ell m} = \hat{H}\hbar\sqrt{\ell(\ell+1)-m(m\pm 1)}\psi_{n\ell m\pm 1}$$

$$= \hat{L}_{\pm}\hat{H}\psi_{n\ell m} = E_n\hat{L}_{\pm}\psi_{n\ell m} = E_n\hbar\sqrt{\ell(\ell+1)-m(m\pm 1)}\psi_{n\ell m\pm 1} \quad ;$$

$$\hat{H}\psi_{n\ell m\pm 1} = E_n\psi_{n\ell m\pm 1} \quad , \quad \text{to compare with } \hat{H}\psi_{n\ell m} = E_n\psi_{n\ell m} \quad , \quad \text{q.e.d.}$$

- This explains a  $2\ell + 1$ –fold degeneracy, due to the spherical harmonics, and common to all central potentials.
- Each state of hydrogen has a total degeneracy of  $n^2 > 2\ell + 1$ . The balance is accounted for by conservation of the **Laplace-Runge-Lenz vector**,  $\hat{M} = (\hat{p} \times \hat{L} - \hat{L} \times \hat{p})/2m - e^2\mathbf{r}/r$ , an extra symmetry of some central potentials including  $1/r$ .
- This is demonstrated in G&S problem 6.34, on assignment Never.

# Translation symmetry and parity degeneracy

G&S problem 6.18: Consider the free quantum in one dimension:  $\hat{H} = \hat{p}^2/2m$ . This Hamiltonian commutes with both the translation and the inversion operators.

- Show that translation and inversion don't commute.
- Because of the translational symmetry, we know that the eigenstates of  $\hat{H}$  can be chosen to be simultaneously eigenstates of momentum,  $f_p$ . Show that the parity operator turns  $f_p(x)$  into  $f_p(-x)$ ; these two states must have the same energy.
- Alternatively, because of the inversion symmetry we know that the eigenstates of  $\hat{H}$  can be chosen to be simultaneously eigenstates of parity, namely

$$\frac{1}{\sqrt{\pi\hbar}} \cos\left(\frac{px}{\hbar}\right) \quad \text{and} \quad \frac{1}{\sqrt{\pi\hbar}} \sin\left(\frac{px}{\hbar}\right) .$$

Show that the translation operator mixes these two states together; they therefore must be degenerate.

## Translation symmetry and parity degeneracy (continued)

a.  $[\hat{p}, \hat{T}(a)]f_p(x) = \hat{p}\hat{T}(a)f_p(x) - \hat{T}(a)\hat{p}f_p(x) = \hat{p}f_p(x-a) - \hat{T}f_p(-x) = f_p(-x-a) - f_p(-[x-a])$   
 $= f_p(-x-a) - f_p(-x+a) \neq 0$  ; they don't commute.

b. As we saw long time ago, the (nonnormalizable) time-independent free-quantum solutions are of the form

$$f_p(x) = \frac{e^{ipx}}{\sqrt{2\pi\hbar}} \quad \hat{p}f_p(x) = \hat{p}\frac{e^{ipx}}{\sqrt{2\pi\hbar}} = \frac{e^{-ipx}}{\sqrt{2\pi\hbar}} = f_p(-x) .$$

$f_p(\pm x)$  have the **same energy**, differing only in direction of travel once the  $e^{-i\omega t}$  factor is included.

c. Yeah, they're mixed:

$$\hat{T} \frac{1}{\sqrt{\pi\hbar}} \cos\left(\frac{px}{\hbar}\right) = \frac{1}{\sqrt{\pi\hbar}} \cos\left(\frac{p[x-a]}{\hbar}\right) = \frac{1}{\sqrt{\pi\hbar}} \left[ \cos\left(\frac{px}{\hbar}\right) \cos\left(\frac{pa}{\hbar}\right) + \sin\left(\frac{px}{\hbar}\right) \sin\left(\frac{pa}{\hbar}\right) \right] ,$$

$$\hat{T} \frac{1}{\sqrt{\pi\hbar}} \sin\left(\frac{px}{\hbar}\right) = \frac{1}{\sqrt{\pi\hbar}} \sin\left(\frac{p[x-a]}{\hbar}\right) = \frac{1}{\sqrt{\pi\hbar}} \left[ \sin\left(\frac{px}{\hbar}\right) \cos\left(\frac{pa}{\hbar}\right) - \cos\left(\frac{px}{\hbar}\right) \sin\left(\frac{pa}{\hbar}\right) \right] .$$

# Selection rules for scalar operators

A scalar operator is one for which  $[\hat{L}, \hat{f}] = 0$ :  $[\hat{L}_z, \hat{f}] = 0$  ,  $[\hat{L}_\pm, \hat{f}] = 0$  ,  $[\hat{L}^2, \hat{f}] = 0$  (page 3).

- As we did for parity, we can find selection rules for scalar operators by considering their matrix elements between eigenstates of  $\hat{L}_z$  and  $\hat{L}^2$ ,  $|n\ell m\rangle$  and  $|n'\ell'm'\rangle$ , which of course have definite angular momentum.  $\hat{L}_z = (\hat{L}_z)^\dagger$ , so

$$\langle n'\ell'm' | [\hat{L}_z, \hat{f}] | n\ell m \rangle = 0 \Rightarrow \langle n'\ell'm' | \hat{L}_z \hat{f} | n\ell m \rangle - \langle n'\ell'm' | \hat{f} \hat{L}_z | n\ell m \rangle = (m' - m) \langle n'\ell'm' | \hat{f} | n\ell m \rangle = 0 .$$

$$[\hat{L}_z, \hat{f}] = 0 \quad , \quad [\hat{L}_\pm, \hat{f}] = 0 \quad , \quad [\hat{L}^2, \hat{f}] = 0 .$$

- Similarly,

$$\langle n'\ell'm' | [\hat{L}^2, \hat{f}] | n\ell m \rangle = 0 \Rightarrow \langle n'\ell'm' | \hat{L}^2 \hat{f} | n\ell m \rangle - \langle n'\ell'm' | \hat{f} \hat{L}^2 | n\ell m \rangle = \hbar^2 [\ell'(\ell'+1) - \ell(\ell+1)] \langle n'\ell'm' | \hat{f} | n\ell m \rangle = 0 .$$

- So the selection rules for quantum transitions mediated by a scalar operator include  $\Delta\ell = 0, \Delta m = 0$ . Now for the ladder operators:

$$\langle n'\ell'm' | [\hat{L}_\pm, \hat{f}] | n\ell m \rangle = 0 \Rightarrow \langle n'\ell'm' | \hat{L}_\pm \hat{f} | n\ell m \rangle - \langle n'\ell'm' | \hat{f} \hat{L}_\pm | n\ell m \rangle = 0 .$$

## Selection rules for scalar operators (continued)

- Noting that the ladder operators are each other's Hermitian conjugate, and as we found in [Lecture 21](#) (see also G&S problem 4.21 on [assignment #9](#)):

$$\langle n'\ell'm' | \hat{L}_{\pm} \hat{f} | n\ell m \rangle = \hbar \sqrt{\ell'(\ell'+1) - m'(m' \mp 1)} \langle n'\ell'm' \mp 1 | \hat{f} | n\ell m \rangle = \delta_{\ell'\ell} \delta_{m' \mp 1, m} \quad ,$$

$$\langle n'\ell'm' | \hat{f} \hat{L}_{\pm} | n\ell m \rangle = \hbar \sqrt{\ell(\ell+1) - m(m \pm 1)} \langle n'\ell'm' | \hat{f} | n\ell m \pm 1 \rangle = \delta_{\ell'\ell} \delta_{m', m \pm 1} \quad .$$

- These terms are both zero unless  $\ell' = \ell$  and  $m' = m \pm 1$ . When both of these are true, the square-root factors are equal, and the last expression on page 10 becomes

$$\langle n'\ell m | \hat{f} | n\ell m \rangle = \langle n'\ell m \pm 1 | \hat{f} | n\ell m \pm 1 \rangle \quad .$$

That is, the **matrix elements of a scalar operator are independent of  $m$** . And since they are, we can write

$$\langle n'\ell'm' | \hat{f} | n\ell m \rangle = \delta_{\ell'\ell} \delta_{m'm} \langle n'\ell | \hat{f} | n\ell \rangle \quad ,$$

## Selection rules for scalar operators (continued)

- This new symbol  $\langle n'\ell' | \hat{f} | n\ell \rangle$  is called a **reduced matrix element**.
  - At this point it is just a notation indicating that the integrals which would be involved in the calculation of  $\langle n'\ell'm' | \hat{f} | n\ell m \rangle$  are independent of  $m$  and are zero unless  $\ell' = \ell$  and  $m' = m$ . But we'll give them more to do in a little while.

G&S example 6.4: (a) Find  $\langle r^2 \rangle$  for all four of the degenerate  $n = 2$  states of a hydrogen atom.

- First  $\ell = 1$ , of which there are three,  $m = 1, 0$ , and  $-1$ :  $\langle 211 | \hat{r}^2 | 211 \rangle = \langle 210 | \hat{r}^2 | 210 \rangle = \langle 21-1 | \hat{r}^2 | 21-1 \rangle = \langle 21 | \hat{r}^2 | 21 \rangle$  .
- To calculate the reduced matrix element just pick any of the normal matrix elements:

$$\begin{aligned} \langle 21 | \hat{r}^2 | 21 \rangle &= \langle 210 | \hat{r}^2 | 210 \rangle = \int r^2 |\psi_{210}|^2 d\tau \\ &= \int_0^\infty r^4 |R_{21}(r)|^2 dr \int_0^{2\pi} \int_0^\pi |Y_1^0(\vartheta, \varphi)|^2 \sin\vartheta d\vartheta d\varphi = \int_0^\infty r^4 \frac{1}{24a^3} \frac{r^2}{a^2} e^{-r/a} dr = \frac{a^2}{24} \int_0^\infty u^6 e^{-u} du = \frac{6!a^2}{24} = 30a^2 \end{aligned}$$

1 (Normalized)

## Selection rules for scalar operators (continued)

- The other one is  $\ell = 0$ :  $\langle 20 | \hat{r}^2 | 20 \rangle = \langle 200 | \hat{r}^2 | 200 \rangle = \int r^2 |\psi_{200}|^2 d\tau$

$$= \int_0^{\infty} r^4 |R_{20}(r)|^2 dr \int_0^{\pi} \int_0^{2\pi} |Y_0^0(\vartheta, \varphi)|^2 \sin\vartheta d\vartheta d\varphi$$

1 (Normalized)

$$= \int_0^{\infty} r^4 \frac{1}{2a^3} \left( 1 - \frac{1}{2} \frac{r^2}{a^2} \right) e^{-r/a} dr = 42a^2 \quad .$$

- The angular integrals didn't have much to do this time, and a slick theorem will do away with them altogether next time.