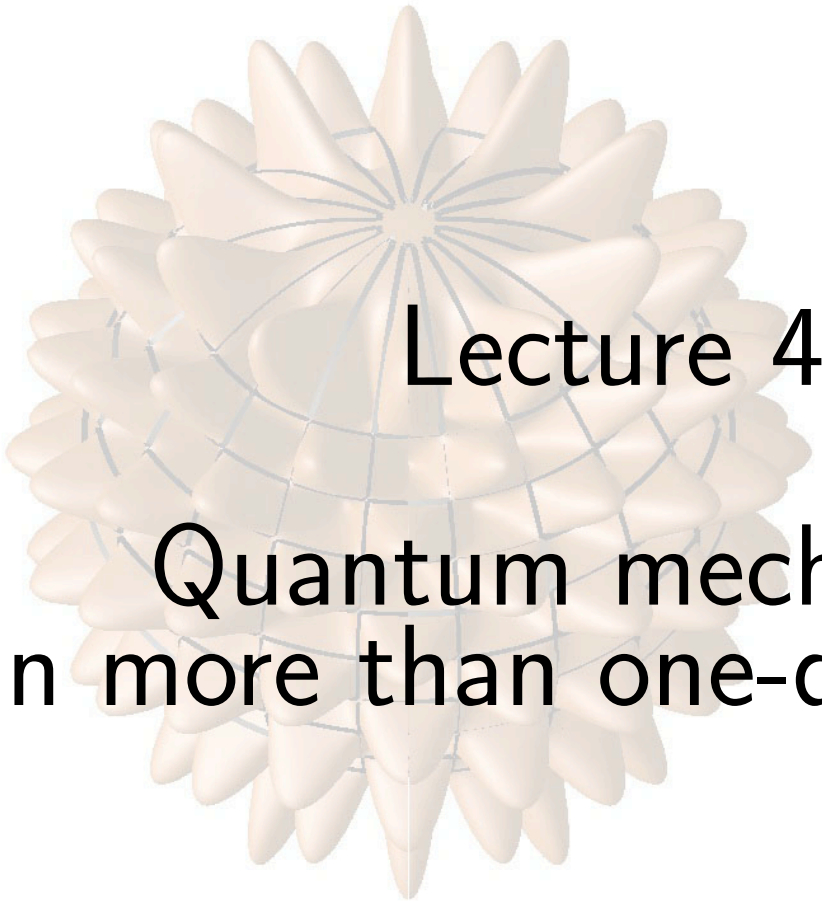

Lecture 4

Quantum mechanics in more than one-dimension

Background

- Previously, we have addressed quantum mechanics of 1d systems and explored bound and unbound (scattering) states.
- Although general concepts carry over to higher dimension, without symmetry, states of the Schrödinger operator are often inaccessible.
- In such situations, we must exploit **approximation methods** to address properties of the states $\Rightarrow$ **perturbation theory.**
- However, when degree of symmetry is high, the quantum mechanics can often be reduced to a tractable "low-dimensional" theory.

Here we address three-dimensional problems involving a **central potential** (e.g. an atom) where the system has full rotational symmetry.

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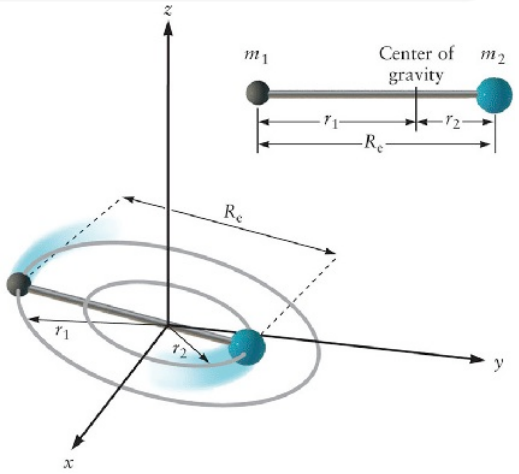
- In such situations, we must exploit **approximation methods** to address properties of the states $\Rightarrow$ **perturbation theory.**
- However, when degree of symmetry is high, the quantum mechanics can often be reduced to a tractable "low-dimensional" theory.

Here we address three-dimensional problems involving a **central potential** (e.g. an atom) where the system has full rotational symmetry.

Rigid diatomic molecule

Consider quantum mechanics of a rigid diatomic molecule with nuclear masses m_1 and m_2, and *fixed* bond length, r.



- Since molecule is rigid, coordinates specified by centre of mass

$$\mathbf{R} = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2}$$

and orientation, $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$ (with $|\mathbf{r}| = r$).

- With total mass $M = m_1 + m_2$, and moment of inertia, $I = \mu r^2$, where $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$ is reduced mass,

$$\hat{H} = \frac{\hat{\mathbf{P}}^2}{2M} + \frac{\hat{\mathbf{L}}^2}{2I}$$

with $\hat{\mathbf{P}} = -i\hbar\nabla_{\mathbf{R}}$ and $\hat{\mathbf{L}} = \mathbf{r} \times \hat{\mathbf{p}}$ is **internal angular momentum**.

Rigid diatomic molecule

$$\hat{H} = \frac{\hat{\mathbf{P}}^2}{2M} + \frac{\hat{\mathbf{L}}^2}{2I}$$

- Since internal and centre of mass degrees of freedom separate, wavefunction can be factorized as $\psi(\mathbf{r}, \mathbf{R}) = e^{i\mathbf{K}\cdot\mathbf{R}} Y(\mathbf{r})$.
- Internal component of wavefunction, $Y(\mathbf{r})$, describes quantum "particle moving on a sphere" with $r = |\mathbf{r}|$ constant – a **rigid rotor**,

$$\hat{H}_{\mathrm{rot}} = \frac{\hat{\mathbf{L}}^2}{2I}$$

- Eigenstates of rotor are states of angular momentum operator, $\hat{\mathbf{L}}^2$.
- Indeed, in *any* quantum mechanical system involving a radial potential, angular momentum is conserved, i.e. $[\hat{H}, \hat{\mathbf{L}}] = 0$ and angular component of wavefunction indexed by states of $\hat{\mathbf{L}}^2$.

Angular momentum: commutation relations

To explore quantum rotor model, $\hat{H}_{\rm rot}$, we must therefore address properties of the angular momentum operator.

- Following the usual quantization procedure, the angular momentum operator defined by $\hat{\mathbf{L}} = \mathbf{r} \times \hat{\mathbf{p}}$ where $[\hat{p}_i, r_j] = -i\hbar\delta_{ij}$.
- Using this relation, one may show that components of angular momentum operators obey **commutation relations**,

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

e.g. $[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$

ϵ_{ijk} is antisymmetric tensor (Levi-Civita symbol) $\epsilon_{123} = 1 = -\epsilon_{213}$ (together with all permutations) while other components are zero.

Angular momentum: eigenvalues

- Since angular momentum, $\hat{\mathbf{L}}$ is a *vector* quantity, it may be defined by magnitude, $\hat{\mathbf{L}}^2$, and direction.
- As components of $\hat{\mathbf{L}}$ are mutually non-commuting, a common set of eigenstates for any two can not be constructed.
- They do, however, commute with $\hat{\mathbf{L}}^2$ (exercise) – therefore, we will seek eigenbasis of $\hat{\mathbf{L}}^2$ and *one* direction, say $\hat{L}_z$,

$$\hat{\mathbf{L}}^2|a,b\rangle = a|a,b\rangle, \qquad \hat{L}_z|a,b\rangle = b|a,b\rangle$$

- To find states $|a,b\rangle$, we could turn to coordinate basis and express $\hat{\mathbf{L}}^2$ and $\hat{L}_z$ as differential operators – however, before doing so, we can learn much using operator formalism (cf. harmonic oscillator).

Angular momentum: raising and lowering operators

$$\hat{\mathbf{L}}^2|a,b\rangle = a|a,b\rangle, \qquad \hat{L}_z|a,b\rangle = b|a,b\rangle$$

- Let us then define operators $\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y$
- Since $[\hat{\mathbf{L}}^2, \hat{L}_i] = 0$, $\hat{\mathbf{L}}^2(\hat{L}_\pm|a,b\rangle) = \hat{L}_\pm\hat{\mathbf{L}}^2|a,b\rangle = a(\hat{L}_\pm|a,b\rangle)$,
  i.e. $\hat{L}_\pm|a,b\rangle$ is also eigenstate of $\hat{\mathbf{L}}^2$ with eigenvalue a.
- From commutation relations, $[\hat{L}_i, \hat{L}_j] = i\hbar\,\epsilon_{ijk}\hat{L}_k$, we have

$$[\hat{L}_z, \hat{L}_\pm] = [\hat{L}_z, \hat{L}_x \pm i\hat{L}_y] = i\hbar(\hat{L}_y \mp i\hat{L}_x) = \pm\hbar(\hat{L}_x \pm i\hat{L}_y) = \pm\hbar\hat{L}_\pm$$

- Therefore, while $\hat{L}_\pm$ conserve eigenvalue a, they do effect projection,

$$\hat{L}_z\hat{L}_\pm|a,b\rangle = \hat{L}_\pm\hat{L}_z|a,b\rangle + [\hat{L}_z, \hat{L}_\pm]|a,b\rangle = (b \pm \hbar)\hat{L}_\pm|a,b\rangle$$

$\therefore$ if $\hat{L}_z|a,b\rangle = b|a,b\rangle$, $\hat{L}_\pm|a,b\rangle$ is either zero, or an eigenstate of $\hat{L}_z$ with eigenvalue $b \pm \hbar$, i.e. $\hat{L}_\pm|a,b\rangle = C_\pm(a,b)|a,b\pm\hbar\rangle$

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Angular momentum: raising and lowering operators

$$\hat{L}_\pm |a, b\rangle = C_\pm(a, b)|a, b \pm \hbar\rangle$$

- To fix normalization, $\langle a, b|a, b\rangle = 1$, noting that $\hat{L}_\pm^\dagger = \hat{L}_\mp$,

$$\left|\left|\hat{L}_\pm |a, b\rangle\right|\right|^2 \equiv \langle a, b|\hat{L}_\pm^\dagger \hat{L}_\pm |a, b\rangle = \langle a, b|\hat{L}_\mp \hat{L}_\pm |a, b\rangle$$

- Then, since $\hat{L}_\mp \hat{L}_\pm = \hat{L}_x^2 + \hat{L}_y^2 \pm i[\hat{L}_x, \hat{L}_y] = \hat{\mathbf{L}}^2 - \hat{L}_z^2 \mp \hbar \hat{L}_z$,

$$\left|\left|\hat{L}_\pm |a, b\rangle\right|\right|^2 = \langle a, b|(\hat{\mathbf{L}}^2 - \hat{L}_z^2 \mp \hbar \hat{L}_z)|a, b\rangle = a - b^2 \mp \hbar b \geq 0$$

- Since $a \geq 0$ and b is real, must have $b_{\min} \leq b \leq b_{\max}$,

$$\langle a, b_{\max}|\hat{L}_+^\dagger \hat{L}_+ |a, b_{\max}\rangle = a - b_{\max}^2 - \hbar b_{\max} = 0$$
$$\langle a, b_{\min}|\hat{L}_-^\dagger \hat{L}_- |a, b_{\min}\rangle = a - b_{\min}^2 + \hbar b_{\min} = 0$$

i.e. $a = b_{\max}(b_{\max} + \hbar)$ and $b_{\min} = -b_{\max}$.

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Angular momentum: raising and lowering operators

$$a = b_{\max}(b_{\max} + \hbar) \text{ and } b_{\min} = -b_{\max}$$

- For given a, $b_{\max}$ and $b_{\min}$ determined uniquely – cannot be two states with the same a but different b annihilated by $\hat{L}_+$.
- If we keep operating on $|a, b_{\min}\rangle$ with $\hat{L}_+$, we generate a sequence of states with $\hat{L}_z$ eigenvalues $b_{\min} + \hbar$, $b_{\min} + 2\hbar$, $b_{\min} + 3\hbar$, $\cdots$.
- Only way for series to terminate is for $b_{\max} = b_{\min} + n\hbar$ with n integer, i.e. $b_{\max}$ is either integer or half odd integer $\times\hbar$.

Angular momentum: eigenvalues

- Eigenvalues of $\hat{L}_z$ form ladder, with eigenvalue $b = m\hbar$ and $m_{\max} = \ell = -m_{\min}$.

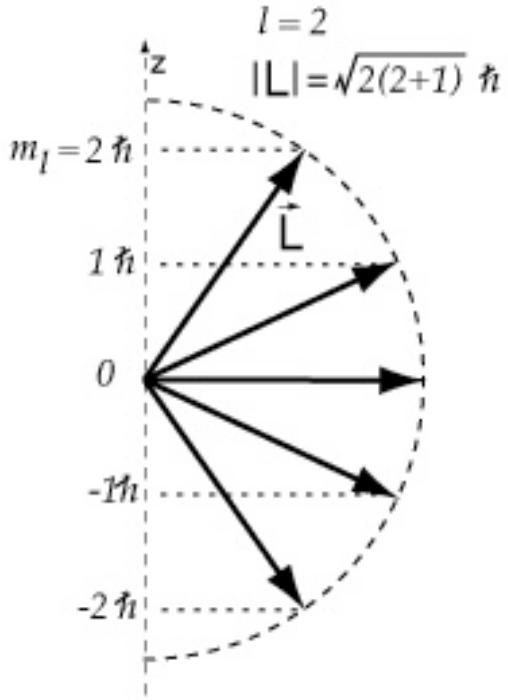
  m known as **magnetic quantum number**.

- Eigenvalues of $\hat{\mathbf{L}}^2$ are $a = \ell(\ell+1)\hbar^2$.

$$\hat{\mathbf{L}}^2|\ell, m\rangle = \ell(\ell+1)\hbar^2|\ell, m\rangle$$

$$\hat{L}_z|\ell, m\rangle = m\hbar|\ell, m\rangle$$

- Both ℓ and m are integer or half odd integers, but spacing of ladder of m always unity.



Angular momentum: raising and lowering operators

$$\hat{\mathbf{L}}^2|\ell, m\rangle = \ell(\ell+1)\hbar^2|\ell, m\rangle, \qquad \hat{L}_z|\ell, m\rangle = m\hbar|\ell, m\rangle$$

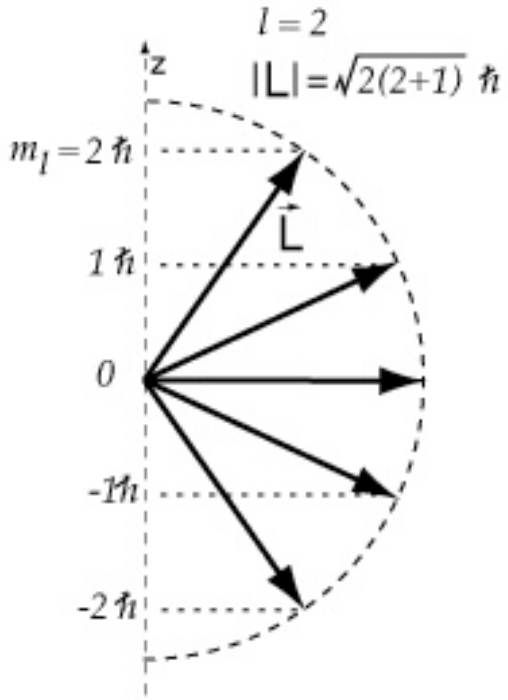
- Finally, making use of identity,

$$\left|\left|\hat{L}_\pm|\ell, m\rangle\right|\right|^2 = \langle\ell, m|\left(\hat{\mathbf{L}}^2 - \hat{L}_z^2 \pm \hbar\hat{L}_z\right)|\ell, m\rangle$$

we find that

$$\hat{L}_+|\ell, m\rangle = \sqrt{\ell(\ell+1) - m(m+1)}\hbar|l, m+1\rangle$$

$$\hat{L}_-|\ell, m\rangle = \sqrt{\ell(\ell+1) - m(m-1)}\hbar|l, m-1\rangle$$



Representation of the angular momentum states

Although we can use an operator-based formalism to construct eigenvalues of $\hat{\mathbf{L}}^2$ and $\hat{L}_z$ it is sometimes useful to have coordinate representation of states, $Y_{\ell m}(\theta, \phi) = \langle \theta, \phi | \ell, m \rangle$.

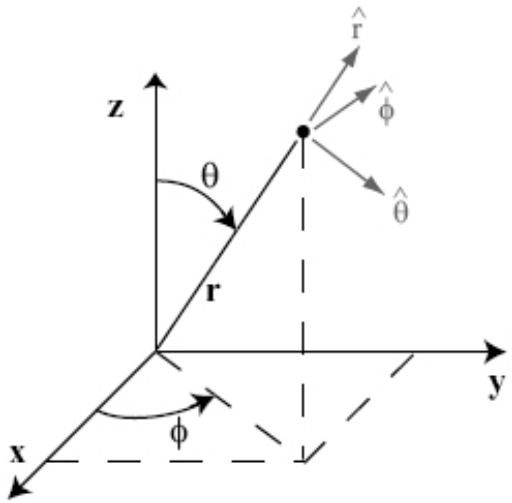
- Using the expression for the gradient operator in spherical polars,

$$\nabla = \hat{\mathbf{e}}_r \partial_r + \hat{\mathbf{e}}_\theta \frac{1}{r} \partial_\theta + \hat{\mathbf{e}}_\phi \frac{1}{r \sin\theta} \partial_\phi$$

with $\hat{\mathbf{L}} = -i\hbar \mathbf{r} \times \nabla$, a little algebra shows,

$$\hat{L}_z = -i\hbar \partial_\phi, \quad \hat{L}_\pm = \hbar e^{\pm i\phi} \left(\pm \partial_\theta + i \cot\theta \partial_\phi \right)$$

$$\hat{\mathbf{L}}^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \partial_\theta (\sin\theta \partial_\theta) + \frac{1}{\sin^2\theta} \partial_\phi^2 \right]$$



Representation of the angular momentum states

$$\hat{L}_z = -i\hbar\partial_\phi, \qquad \hat{L}_\pm = \hbar e^{\pm i\phi}\left(\pm\partial_\theta + i\cot\theta\partial_\phi\right)$$

- Beginning with $\hat{L}_z = -i\hbar\partial_\phi$,

$$-i\hbar\partial_\phi Y_{\ell m}(\theta,\phi) = m\hbar Y_{\ell m}(\theta,\phi)$$

since equation is separable, we have the solution

$$Y_{\ell m}(\theta,\phi) = F(\theta)e^{im\phi}$$

with $-\ell \leq m \leq \ell$.

- N.B. if ℓ (and therefore m) integer, continuity of wavefunction, $Y_{\ell m}(\theta,\phi+2\pi) = Y_{\ell m}(\theta,\phi)$, is assured.

[Not so if ℓ is half-integer.]

Representation of the angular momentum states

$$Y_{\ell m}(\theta,\phi) = F(\theta)e^{im\phi}, \qquad \hat{L}_{\pm} = \hbar e^{\pm i\phi}\left(\pm\partial_\theta + i\cot\theta\partial_\phi\right)$$

- (Drawing analogy with procedure to find HO states) to find $F(\theta)$, consider state of maximal m, $|\ell,\ell\rangle$, for which $\hat{L}_+|\ell,\ell\rangle = 0$.
- Making use of coordinate representation of raising operator

$$0 = \langle\theta,\phi|\hat{L}_+|\ell,\ell\rangle = \hbar e^{i\phi}\left(\partial_\theta + i\cot\theta\partial_\phi\right)Y_{\ell\ell}(\theta,\phi)$$
$$= \hbar e^{i(\ell+1)\phi}\left(\partial_\theta - \ell\cot\theta\right)F(\theta)$$

  i.e. $\partial_\theta F(\theta) = \ell\cot\theta F(\theta)$ with the solution $F(\theta) = C\sin^\ell\theta$.
- The 2ℓ states with values of m lower than ℓ generated by repeated application of $\hat{L}_-$ on $|\ell,\ell\rangle$.

$$Y_{\ell m}(\theta,\phi) = C\underbrace{\left(-\partial_\theta + i\cot\theta\partial_\phi\right)}_{\hat{L}_-}{}^{\ell-m}\left[\sin^\ell\theta e^{i\ell\phi}\right]$$

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Representation of the angular momentum states

- Eigenfunctions of $\hat{\mathbf{L}}^2$ are known as **spherical harmonics**,

$$Y_{\ell m}(\theta,\phi) = (-1)^{m+|m|}\left[\frac{2\ell+1}{4\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}\right]^{1/2} P_\ell^{|m|}(\cos\theta)e^{im\phi}$$

where the functions $P_\ell^m(\xi) = \frac{(1-\xi^2)^{m/2}}{2^\ell \ell!}\frac{d^{m+\ell}}{d\xi^{m+\ell}}(\xi^2-1)^\ell$ are known as **associated Legendre polynomials**.

- I see no reason why you should ever memorize these functions!

$$Y_{00} = 1$$
$$Y_{10} = \cos\theta, \qquad Y_{11} = e^{i\phi}\sin\theta$$
$$Y_{20} = 3\cos^2\theta - 1, \quad Y_{21} = e^{i\phi}\sin\theta\cos\theta, \quad Y_{22} = e^{2i\phi}\sin^2\theta$$

- States with $\ell = 0, 1, 2, 3, \ldots$ are known as $s, p, d, f, \ldots$-orbitals.
- Note symmetries: $Y_{\ell,-m} = (-1)^m Y_{\ell m}^*$ and $\hat{P}Y_{\ell m} = (-1)^\ell Y_{\ell m}$.

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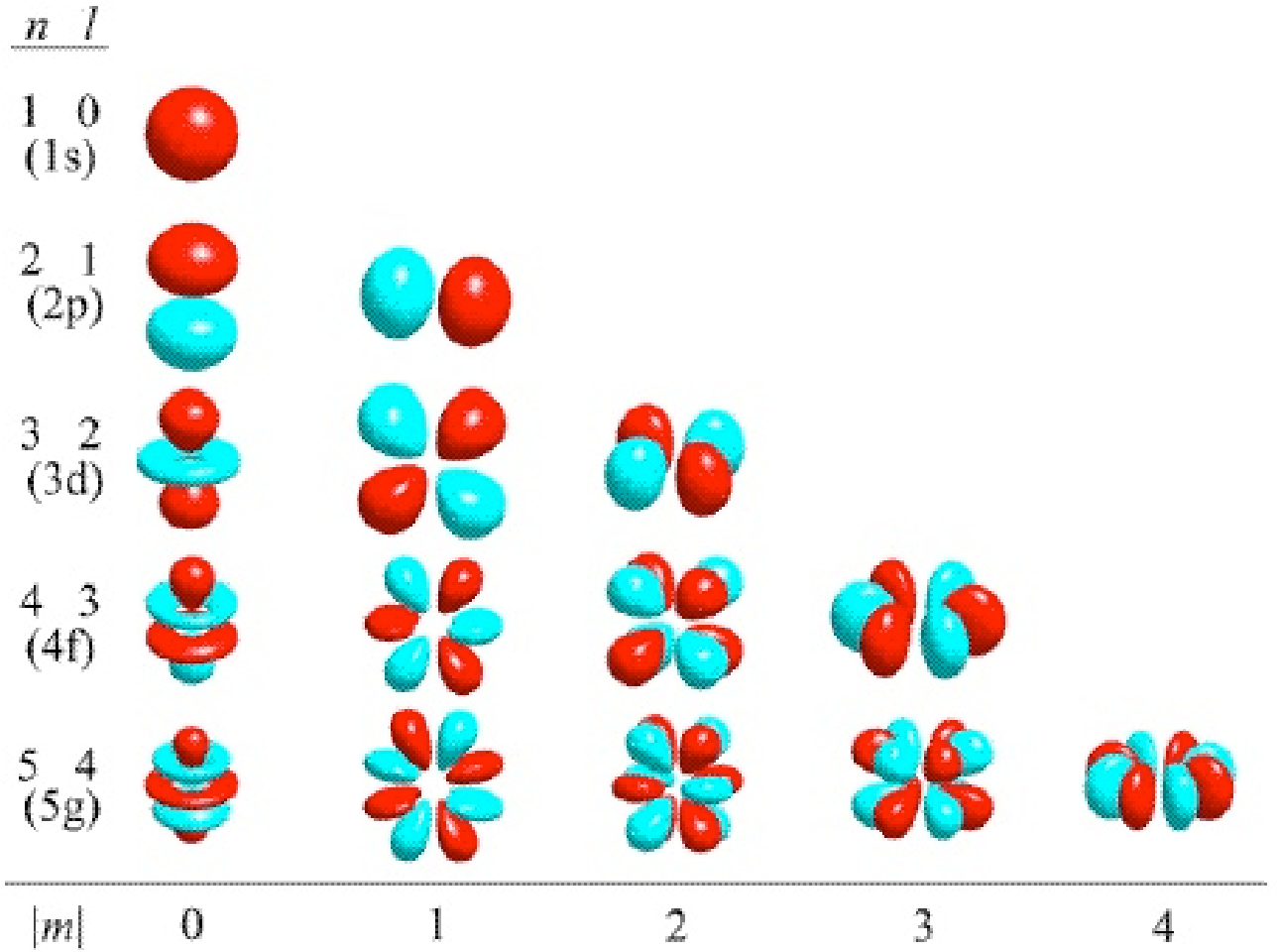
  where the functions $P_\ell^m(\xi) = \frac{(1-\xi^2)^{m/2}}{2^\ell \ell!}\frac{d^{m+\ell}}{d\xi^{m+\ell}}(\xi^2-1)^\ell$ are known as **associated Legendre polynomials**.

- As an example of the first few (unnormalized) spherical harmonics:

$$\begin{aligned} Y_{00} &= 1 \\ Y_{10} &= \cos\theta, & Y_{11} &= e^{i\phi}\sin\theta \\ Y_{20} &= 3\cos^2\theta - 1, & Y_{21} &= e^{i\phi}\sin\theta\cos\theta, & Y_{22} &= e^{2i\phi}\sin^2\theta \end{aligned}$$

- States with $\ell = 0, 1, 2, 3,\ldots$ are known as $s, p, d, f,\ldots$-orbitals.
- Note symmetries: $Y_{\ell,-m} = (-1)^m Y_{\ell m}^*$ and $\hat{P}Y_{\ell m} = (-1)^\ell Y_{\ell m}$.

Representation of the angular momentum states



radial coordinate fixed by $|\mathrm{Re}\, Y_{\ell m}(\theta, \phi)|$ and colours indicate relative sign of real part.

Rigid rotor model

- After this lengthy digression, we return to problem of quantum mechanical rotor Hamiltonian and the rigid diatomic molecule.
- Eigenstates of the Hamiltonian,

$$\hat{H} = \frac{\hat{\mathbf{P}}^2}{2M} + \frac{\hat{\mathbf{L}}^2}{2I}$$

given by $\psi(\mathbf{R}, \mathbf{r}) = e^{i\mathbf{K}\cdot\mathbf{R}} Y_{\ell,m}(\theta, \phi)$ with eigenvalues

$$E_{\mathbf{K},\ell} = \frac{\hbar^2 \mathbf{K}^2}{2M} + \frac{\hbar^2}{2I}\ell(\ell+1)$$

where, for each set of quantum numbers $(\mathbf{K}, \ell)$, there is a $2\ell + 1$-fold degeneracy.

- With this background, we now turn to general problem of 3d system with centrally symmetric potential, $V(r)$ (e.g. atomic hydrogen).

The central potential

- When central force field is entirely radial, the Hamiltonian for the relative coordinate is given by

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + V(r)$$

- Using the identity,

$$\hat{\mathbf{L}}^2 = (\mathbf{r} \times \hat{\mathbf{p}})^2 = r_i \hat{p}_j r_i \hat{p}_j - r_i \hat{p}_j r_j \hat{p}_i = r^2 \hat{\mathbf{p}}^2 - (\mathbf{r} \cdot \hat{\mathbf{p}})^2 + i\hbar(\mathbf{r} \cdot \hat{\mathbf{p}})$$

with $\mathbf{r} \cdot \hat{\mathbf{p}} = -i\hbar \mathbf{r} \cdot \nabla = -i\hbar r \partial_r$, find $\hat{\mathbf{p}}^2 = \frac{\hat{\mathbf{L}}^2}{r^2} - \frac{\hbar^2}{r^2}\left[(r\partial_r)^2 + r\partial_r\right]$

- Noting that $(r\partial_r)^2 + r\partial_r = r^2\partial_r^2 + 2r\partial_r$, we obtain the Schrödinger equation,

$$\left[-\frac{\hbar^2}{2m}\left(\partial_r^2 + \frac{2}{r}\partial_r\right) + V(r) + \frac{\hat{\mathbf{L}}^2}{2mr^2}\right]\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

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- From separability, $\psi(\mathbf{r})=R(r)Y_{\ell,m}(\theta,\phi)$, where

$$\left[-\frac{\hbar^2}{2m}\left(\partial_r^2+\frac{2}{r}\partial_r\right)+\frac{\hbar^2}{2mr^2}\ell(\ell+1)+V(r)\right]R(r)=ER(r)$$

- Finally, setting $R(r)=u(r)/r$, obtain "one-dimensional" equation

$$\left[-\frac{\hbar^2\partial_r^2}{2m}+V_{\text{eff}}(r)\right]u(r)=Eu(r),\quad V_{\text{eff}}(r)=\frac{\hbar^2}{2mr^2}\ell(\ell+1)+V(r)$$

with boundary condition $u(0)=0$, and normalization,

$$\int d^3r\,|\psi(\mathbf{r})|^2=\int_0^\infty r^2dr\,|R(r)|^2=\int_0^\infty dr\,|u(r)|^2=1$$

- So, for bound state, $\lim_{r\to\infty}|u(r)|\leq\frac{a}{r^{1/2+\epsilon}}$ with $\epsilon>0$.

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The central potential: bound states

$$\left[-\frac{\hbar^2\partial_r^2}{2m} + V_{\text{eff}}(r)\right] u(r) = Eu(r), \quad V_{\text{eff}}(r) = \frac{\hbar^2}{2mr^2}\ell(\ell+1) + V(r)$$

- Since $u(0) = 0$, we may "map" Hamiltonian from half-line to full with the condition that we admit only antisymmetric wavefunctions.

- Existence of bound states can then be related back to the one-dimensional case:

  Previously, we have seen that a (symmetric) attractive potential always leads to a bound state in one-dimension. However, odd parity states become bound only at a critical strength of interaction.

  So, for a general attractive potential $V(r)$, the existence of a bound state is not guaranteed even for $\ell = 0$.

Atomic hydrogen

$$\left[-\frac{\hbar^2\partial_r^2}{2m}+V_{\text{eff}}(r)\right]u(r)=u(r),\qquad V_{\text{eff}}(r)=\frac{\hbar^2}{2mr^2}\ell(\ell+1)+V(r)$$

- The hydrogen atom consists of an electron bound to a proton by the Coulomb potential,

$$V(r)=-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$$

  and, strictly speaking, m denotes the reduced mass (generalization to nuclear charge Ze follows straightforwardly).

- Since we are interested in finding bound states of proton-electron system, we are looking for solutions with $E<0$.

- Here we sketch the methodology in outline – for details, refer back to IB.

Atomic hydrogen

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- To simplify equation, set $\rho = \kappa r$, where $\hbar\kappa = \sqrt{-2mE}$

$$\partial_\rho^2 u(\rho) = \left(1 - \frac{2\nu}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right) u(\rho), \qquad 2\nu = \frac{e^2}{4\pi\epsilon}\frac{\kappa}{E}$$

- At large separations, $\partial_\rho^2 u(\rho) \simeq u(\rho)$ and $u(\rho) \simeq e^{-\rho}$.
- Near origin, dominant term for small ρ is centrifugal component,

$$\partial_\rho^2 u(\rho) \simeq \frac{\ell(\ell+1)}{\rho^2} u(\rho)$$

for which $u(\rho) \sim \rho^{\ell+1}$.

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Atomic hydrogen

- Finally, defining $u(\rho) = e^{-\rho}\rho^{\ell+1}w(\rho)$, equation for $w(\rho)$ reveals that $\nu = \frac{e^2}{4\pi\epsilon_0}\frac{\kappa}{2E}$ must take integer values, n – **principal quantum number**, i.e.

$$E_n = -\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{m}{2\hbar^2}\frac{1}{n^2} \equiv -\frac{1}{n^2}\mathrm{Ry}$$

- Therefore, $\rho = \kappa_n r$, where $\kappa_n = \sqrt{-2mE_n} = \frac{e^2}{4\pi\epsilon_0}\frac{m}{\hbar^2}\frac{1}{n} = \frac{1}{a_0 n}$, with

$$a_0 = \frac{4\pi\epsilon_0}{e^2}\frac{\hbar^2}{m} = 0.529 \times 10^{-10}\,\mathrm{m}$$

the atomic **Bohr radius**.

- Formally, the set of functions $w_{n\ell}(\rho) = L^{2\ell+1}_{n-\ell-1}(2\rho)$ are known as **associated Laguerre polynomials** $L^k_p(z)$.

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Atomic hydrogen

- Translating back from ρ to r,

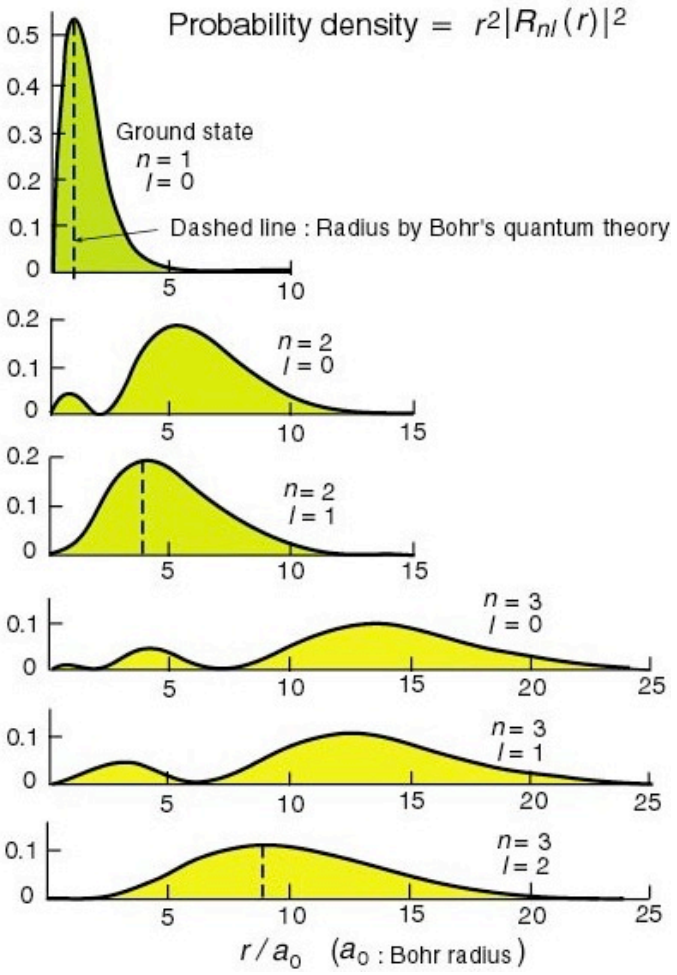
$$R_{n\ell}(r) = Ne^{-Zr/na_0}\left(\frac{Zr}{na_0}\right)^{\ell} L^{2\ell+1}_{n-\ell-1}(2Zr/na_0)$$

For principal quantum number n, and $\ell = n-1$, $R_{n,n-1} \propto r^{n-1}\, e^{-Zr/na_0}$.

$$R_{10} = 2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-Zr/a_0}$$

$$R_{21} = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$

$$R_{20} = \frac{1}{\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(1-\frac{1}{2}\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$



Atomic hydrogen

- But why the high degeneracy? Since $[\hat{H}, \hat{\mathbf{L}}] = 0$, we expect that states of given ℓ have a $2\ell + 1$-fold degeneracy.
- Instead, we find that each principal quantum number n has an n^2-fold degeneracy, i.e. for given n, all allowed ℓ-states degenerate.
- As a rule, **degeneracies are never accidental** but always reflect some symmetry – which we must have missed(!)
- In fact, one may show that the (Runge-Lenz) vector operator

$$\hat{\mathbf{R}} = \frac{1}{2m}(\hat{\mathbf{p}} \times \hat{\mathbf{L}} - \hat{\mathbf{L}} \times \hat{\mathbf{p}}) - \frac{e^2}{4\pi\epsilon_0}\frac{\mathbf{r}}{r}$$

  is also conserved by the Hamiltonian dynamics, $[\hat{H}, \hat{\mathbf{R}}] = 0$.
- From this operator, we can identify generators for the complete degenerate subspace (cf. $\hat{L}_\pm$) – a piece of mathematical physics (happily) beyond the scope of these lectures.

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Summary

- For problems involving a central potential,

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + V(r)$$

  Hamiltonian is invariant under spatial rotations, $\hat{U} = e^{-\frac{i}{\hbar}\theta \mathbf{e}_n \cdot \hat{\mathbf{L}}}$.

- This invariance implies that the states separate into degenerate multiplets $|\ell, m\rangle$ with fixed by angular momentum ℓ.

$$\hat{\mathbf{L}}^2|\ell, m\rangle = \ell(\ell+1)\hbar^2|\ell, m\rangle, \qquad \hat{L}_z|\ell, m\rangle = m\hbar|\ell, m\rangle$$

- The $2\ell + 1$ states within each multiplet are generated by the action of the angular momentum raising and lowering operators,

$$\hat{L}_\pm|\ell, m\rangle = \sqrt{\ell(\ell+1) - m(m\pm 1)}\hbar|l, m\pm 1\rangle$$

Summary

- In the case of atomic hydrogen,

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r}$$

an additional symmetry leads to degeneracy of states of given principal quantum number, n,

$$E_n = -\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{m}{2\hbar^2}\frac{1}{n^2} \equiv -\frac{1}{n^2}\mathrm{Ry}$$

- The extent of the wavefunction is characterized by the Bohr radius,

$$a_0 = \frac{4\pi\epsilon_0}{e^2}\frac{\hbar^2}{m} = 0.529 \times 10^{-10}\,\mathrm{m}$$