Quantum Mechanics

Lecture #3: Ch. 4: Three-dimensional problems

Fa Wang[1]

[1]International Center for Quantum Materials, School of Physics, Peking University, Beijing 100871, China

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Outline

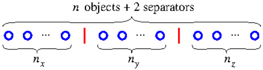
Goals and Requirements: Lecture #3

- This lecture deals with non-relativistic particle in 3D static central potential, $\hat{H} = \frac{\hat{\boldsymbol{p}}^2}{2m} + V(r)$.
- The goal of this lecture is for you to become familiar with the following items:
  - separation of variable in Cartesian coordinates for $V(\boldsymbol{r}) = V_x(x) + V_y(y) + V_z(z)$
  - separation of variable in polar coordinates for central potential $V(r)$
  - radial equation for central potential, asymptotic behavior of radial wave function
  - orbital angular momentum operators: ladder operators, eigenvalues and eigenstates
  - the basic concept of spin-1/2, Pauli matrices
  - the idea about "addition of angular momentum": Clebsch-Gordon theorem
  - basic picture of "spherical wave"
- By the end of this lecture, you should master the following skills:
  - writing down radial equation for central potential problems
  - using ladder operators to do calculations about angular momentum, in particular,
  - solving addition of two angular momentum (C.-G. coefficients)
  - solving problems about spin-1/2 (2×2 matrices)
- "Side remark"s are NOT required.
- References:

  D.J. Griffiths, *Introduction to Quantum Mechanics*, Chapter 4.

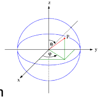
Eigenvalue problem in 3D Cartesian coordinates

- $\hat{H} = \frac{\hat{\boldsymbol{p}}^2}{2m} + V(\hat{x}, \hat{y}, \hat{z})$, $\hat{\boldsymbol{p}}^2 = \hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2$, $[\hat{r}_a, \hat{p}_b] = \mathrm{i}\hbar\delta_{a,b}$ for $a, b = x, y, z$. Then $\hat{H}\psi(x, y, z) = [-\frac{\hbar^2}{2m}\nabla^2 + V(x, y, z)]\psi(x, y, z)$, $\nabla^2 = \partial_x^2 + \partial_y^2 + \partial_z^2$ is Laplacian operator.
  - If $V(x, y, z) = V_x(x) + V_y(y) + V_z(z)$, separation of variables for x, y, z can be used, $\hat{H} = \hat{H}_x + \hat{H}_y + \hat{H}_z$, $\hat{H}_a = -\frac{\hbar^2}{2m}\partial_a^2 + V_a(r_a)$ for $a = x, y, z$, solve three 1D eigenvalue problems $\hat{H}_a\psi_a(r_a) = E_a \cdot \psi_a(r_a)$, then the 3D eigenstates are $\psi(x, y, z) = \psi_x(x) \cdot \psi_y(y) \cdot \psi_z(z)$, with eigenvalue $E = E_x + E_y + E_z$.
  - Example: free particle, $V(x, y, z) = 0$, eigenstates are 3D planewaves labeled by momentum eigenvalue $\boldsymbol{p}$, $\psi_{\boldsymbol{p}}(\boldsymbol{r}) = \frac{e^{\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{r}/\hbar}}{(2\pi\hbar)^{3/2}} = \frac{e^{\mathrm{i}p_x x/\hbar}}{\sqrt{2\pi\hbar}} \frac{e^{\mathrm{i}p_y y/\hbar}}{\sqrt{2\pi\hbar}} \frac{e^{\mathrm{i}p_z z/\hbar}}{\sqrt{2\pi\hbar}}$, with eigenvalues $E_{\boldsymbol{p}} = \frac{\boldsymbol{p}^2}{2m} = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$, and orthonormal condition $\langle\psi_{\boldsymbol{p}}|\psi_{\boldsymbol{p}'}\rangle = \delta(\boldsymbol{p} - \boldsymbol{p}') = \delta(p_x - p_x') \cdot \delta(p_y - p_y') \cdot \delta(p_z - p_z')$ (3D Dirac δ-function). Note: these eigenstates are highly degenerate (except for $E = 0$), E is independent of the direction of $\boldsymbol{p}$.
  - Example: 3D harmonic oscillator, $V(x, y, z) = \frac{m\omega^2\boldsymbol{r}^2}{2} = \frac{m\omega^2x^2}{2} + \frac{m\omega^2y^2}{2} + \frac{m\omega^2z^2}{2}$, eigenstates are products of 1D harmonic oscillator eigenstates $\psi_{n_a}(r_a)$, labeled by $n_a = 0, 1, \ldots$ for $a = x, y, z$, $\psi_{n_x,n_y,n_z}(x, y, z) = \psi_{n_x}(x) \cdot \psi_{n_y}(y) \cdot \psi_{n_z}(z)$, with total energy $E_{n_x,n_y,n_z} = \hbar\omega \cdot (n_x + n_y + n_z + \frac{3}{2})$. Note: degeneracy is the number of combinations (n_x, n_y, n_z) with the same $n = n_x + n_y + n_z$, which is $\binom{n+2}{2} = \frac{(n+2)(n+1)}{2}$ [see schematic picture below, choose positions of 2 "separators" in $(n + 2)$ slots].



Polar coordinates for central potentials

- $\hat{H} = \frac{\hat{\boldsymbol{p}}^2}{2m} + V(r)$, the "central potential" $V(r)$ depends on radius $r = \sqrt{x^2 + y^2 + z^2}$ only.
  - Reminder: 3D polar coordinates (r, θ, ϕ).
    Label the position by *radius* r, *polar angle* θ, and *azimuth angle* ϕ (see picture on the right).
    NOTE: $r \geq 0$; $0 \leq \theta \leq \pi$; $\phi + 2\pi$ and ϕ label the same point, so usually $0 \leq \phi \leq 2\pi$.
    Relation to Cartesian coordinates: $x = r \sin\theta \cos\phi$, $y = r \sin\theta \sin\phi$, $z = r \cos\theta$.
    Laplacian operator: $\nabla^2 = \frac{1}{r^2}\partial_r(r^2\partial_r) + \frac{1}{r^2 \sin\theta}\partial_\theta(\sin\theta\partial_\theta) + \frac{1}{r^2\sin^2\theta}\partial_\phi^2$.



  - Separation of radial and angular parts of wave function: assume $\psi(r,\theta,\phi) = R(r)\cdot Y(\theta,\phi)$, from $[-\frac{\hbar^2}{2m}\nabla^2 + V(r)]\psi = E\cdot\psi$, divide both sides by $\frac{\hbar^2}{2mr^2}\psi$, separate terms depending on r and on θ, ϕ,
    $\frac{1}{R(r)}\cdot[\partial_r(r^2\partial_r) - (V(r)-E)\cdot\frac{2mr^2}{\hbar^2}]R(r) = -\frac{1}{Y(\theta,\phi)}\cdot[\frac{1}{\sin\theta}\partial_\theta(\sin\theta\partial_\theta) + \frac{1}{\sin^2\theta}\partial_\phi^2)]Y(\theta,\phi)$,
    this must equal to a constant, denoted by $\ell(\ell+1)$ and $\ell = 0, 1, \ldots$ (see [4.1][4.1]).

- Angular wave function: *spherical harmonics* $Y_\ell^m(\theta,\phi)$.
  - $\ell = 0, 1, 2, \ldots$ is "azimuthal quantum number", or "orbital angular momentum quantum number"; $m = -\ell, -\ell+1, \ldots, \ell$ is "magnetic quantum number".
  - $Y_\ell^m = \epsilon\sqrt{\frac{2\ell+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}\,e^{\mathrm{i}m\phi}P_\ell^m(\cos\theta)$; $\epsilon = +1$ for $m \geq 0$; $= (-1)^m$ for $m < 0$;
    $P_\ell^m(x) = (1-x^2)^{|m|/2}(\frac{\mathrm{d}}{\mathrm{d}x})^{|m|}P_\ell(x)$ is *associated Legendre polynomial*;
    $P_\ell(x) = \frac{1}{2^\ell \ell!}(\frac{\mathrm{d}}{\mathrm{d}x})^\ell[(x^2-1)^\ell]$ is *Legendre polynomial*.
  - $\int_0^\pi \sin\theta \mathrm{d}\theta \int_0^{2\pi}\mathrm{d}\phi\,[Y_\ell^m(\theta,\phi)]^* Y_{\ell'}^{m'}(\theta,\phi) = \delta_{\ell,\ell'}\delta_{m,m'}$.
    $-[\frac{1}{\sin\theta}\partial_\theta(\sin\theta\partial_\theta) + \frac{1}{\sin^2\theta}\partial_\phi^2)]Y_\ell^m(\theta,\phi) = \ell(\ell+1)\cdot Y_\ell^m(\theta,\phi)$.
    Note: the other solution to the angular eigenvalue problem (2nd order differential equation) is not a smooth function (diverges) at $\theta = 0$ or π.

Polar coordinates for central potentials (cont'd)

- Radial equation: $[-\frac{\hbar^2}{2m}\frac{1}{r^2}\partial_r(r^2\partial_r) + V(r) + \frac{\hbar^2\ell(\ell+1)}{2mr^2}]R(r) = E\cdot R(r)$. Define $u(r) = r\cdot R(r)$, then $[-\frac{\hbar^2}{2m}\partial_r^2 + V(r) + \frac{\hbar^2\ell(\ell+1)}{2mr^2}]u(r) = E\cdot u(r)$.
  This looks like a 1D eigenvalue problem, with following differences:
  (i) in addition to $V(r)$, there is a "centrifugal potential" $\frac{\hbar^2\ell(\ell+1)}{2mr^2}$;
  (ii) the problem is defined for $r \geq 0$ region, and $u(r) \sim r^{\ell+1}$ as $r \to 0$.
  - Argument for the $r \to 0$ behavior: as $r \to 0$, centrifugal potential dominates, $(-\partial_r^2 + \frac{\ell(\ell+1)}{r^2})u \sim 0$, then $u \sim r^{\ell+1}$ or $u \sim r^{-\ell}$, normalizable ψ requires that $\int_0^\infty |u(r)|^2\,\mathrm{d}r < \infty$, then it must be $u \sim r^{\ell+1}$ namely $R(r) \sim r^\ell$. This argument does not seem to work for $\ell = 0$ case, but the conclusion is still valid there.
  - For given ℓ, m quantum numbers, there will be a sequence of energy eigenvalues, labeled by some "principal quantum number", usually denoted by n for discrete bound states or k for continuous scattering states.
  - Note that the radial equation does not depend on m quantum number. So $E_{n\ell m} = E_{n\ell}$, $\psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)Y_\ell^m(\theta,\phi)$, and this energy level is $(2\ell+1)$-fold degenerate (for $m = -\ell,\ldots,\ell$).

- Example: free particle, $V(r) = 0$.
  - Continuous $E_k = \frac{\hbar^2k^2}{2m} \geq 0$ states, labeled by wavevector k. The solutions to radial equation are *spherical Bessel functions* $R_{k\ell}(r) \propto j_\ell(kr)$. The entire wave function $\psi_{k\ell m} \propto j_\ell(kr)Y_\ell^m(\theta,\phi)$ are "spherical waves".
  - Spherical Bessel function $j_\ell(x) = (-x)^\ell(\frac{1}{x}\frac{\mathrm{d}}{\mathrm{d}x})^\ell(\frac{\sin x}{x})$.
    When $x \to 0$, $j_\ell(x) \sim x^\ell$; when $x \to \infty$, $j_\ell(x) \sim \frac{\sin(x-\frac{\ell\pi}{2})}{x}$.
  - Spherical Neumann function $n_\ell(x) = -(-x)^\ell(\frac{1}{x}\frac{\mathrm{d}}{\mathrm{d}x})^\ell(\frac{\cos x}{x})$, is the other solution to the radial equation.
    When $x \to 0$, $n_\ell(x) \sim x^{-\ell-1}$; when $x \to \infty$, $n_\ell(x) \sim -\frac{\cos(x-\frac{\ell\pi}{2})}{x}$.

Finite spherical well potential

- $V(r) = \begin{cases} -V_0, & r < a; \\ 0, & r > a. \end{cases}$ (Problem 4.9 in textbook).
  - Bound states energy E must have $-V_0 < E < 0$. Define $k = \frac{\sqrt{2m(E+V_0)}}{\hbar}$ and $\kappa = \frac{\sqrt{-2mE}}{\hbar}$.
  - s-wave($\ell = 0$) case: the eigenstate should be $u(r) = r \cdot R(r) = \begin{cases} A \cdot \sin(kr), & r < a; \\ B \cdot \exp(-\kappa r), & r > a. \end{cases}$
    This is exactly the "odd solutions" to the 1D finite square well potential defined for $|x| < a$.
    Therefore, if $\frac{a\sqrt{2mV_0}}{\hbar} < \frac{\pi}{2}$, there will be no s-wave bound state for 3D spherical potential.
  - Side remark: the generic eigenstate should be $R_{k\ell}(r) = \begin{cases} A \cdot j_\ell(kr), & r < a; \\ B \cdot h_\ell^{(1)}(\mathrm{i}\kappa r), & r > a; \end{cases}$.
    Here $h_\ell^{(1)}(x) = j_\ell(x) + \mathrm{i} n_\ell(x) = -\mathrm{i}(-x)^\ell (\frac{1}{x}\frac{\mathrm{d}}{\mathrm{d}x})^\ell (\frac{e^{\mathrm{i}x}}{x})$, is the "spherical Hankel function of the first kind".
    When $x \to \infty$, $h_\ell^{(1)}(x) \sim (-\mathrm{i})^{\ell+1}\frac{e^{\mathrm{i}x}}{x}$, so $h_\ell^{(1)}(\mathrm{i}\kappa r) \sim \frac{e^{-\kappa r}}{\kappa r}$ as $r \to \infty$.
    - The boundary condition at a, that R and $\frac{\mathrm{d}R}{\mathrm{d}r}$ are both continuous, determines k,κ and thus E.
    - Consider the threshold case when the nth bound state first appears while increasing V_0. Then $E_{n\ell} = 0$, $\kappa = +0$, so $B = 0$, $j_\ell(ka) = 0$, namely ka is a positive root of j_ℓ for this threshold case.
    - Denote the nth positive root of $j_\ell(x)$ by $\beta_{n\ell}$ (see textbook Figure 4.2). If
      $\beta_{n\ell} \le \frac{a\sqrt{2mV_0}}{\hbar} < \beta_{(n+1)\ell}$, then there will be n bound states in ℓ channel.
    - $\beta_{1,\ell} \ge \beta_{1,0} = \frac{\pi}{2}$, so if there is no bound state in $\ell = 0$ channel, there will be no bound state at all.
  - The above qualitative feature is true for other 3D potential wells:
    if the 3D potential well is too "shallow", there will be no bound state.

3D harmonic oscillator: polar coodinates

- $V(r) = \frac{m\omega^2}{2} r^2$, the radial equation is $[-\frac{\hbar^2}{2m}\partial_r^2 + \frac{m\omega^2}{2} r^2 + \frac{\hbar^2 \ell(\ell+1)}{2mr^2}]u(r) = E \cdot u(r)$.
  - Define $\xi = \sqrt{\frac{m\omega}{\hbar}} r$, $\lambda = \frac{2E}{\hbar\omega}$, then $[-\frac{\mathrm{d}^2}{\mathrm{d}\xi^2} + \xi^2 + \frac{\ell(\ell+1)}{\xi^2}]u = \lambda \cdot u$.
  - From previous discussion [2.2], $u \sim \xi^{\ell+1}$ as $\xi \to 0$, and similar to 1D case $u \sim e^{-\xi^2/2}$ as $\xi \to \infty$.
  - Define $u(\xi) = \xi^{\ell+1} e^{-\xi^2/2} \rho(\xi)$, then $[-\frac{\mathrm{d}^2}{\mathrm{d}\xi^2} + 2(\xi - \frac{\ell+1}{\xi})\frac{\mathrm{d}}{\mathrm{d}\xi} + (2\ell + 3 - \lambda)]\rho = 0$.
  - Assume $\rho(\xi) = \sum_{j=0}^{\infty} c_j \xi^j$, note that $c_0 \neq 0$, the recursion relation is $c_{j+2} = \frac{(2j+2\ell+3-\lambda)}{(j+2)(j+2\ell+3)} c_j$.
  - Similar to 1D, series of ρ must be truncated, otherwise $\rho \sim e^{\xi^2}$ contradicts with normalizable assumption. Here the difference to 1D case is that: the truncation order j ($c_j \neq 0$ but all $c_{j'} = 0$ for $j' > j$) must be an even integer $j = 2k$ ($k = 0, 1, \ldots$), because $c_0 \neq 0$; and all odd j terms must vanish.
  - Define $n = \ell + 2k$, then $E_{n\ell m} = E_n = \hbar\omega \cdot (n + \frac{3}{2})$. Here $n = 0, 1, \ldots$.
  - For given energy level E_n (given n), the ℓ can be $n, n-2, n-4, \ldots$, and each choice of ℓ corresponds to $(2\ell+1)$-fold degeneracy from $m = -\ell, \ldots, \ell$. So the total degeneracy is $\sum_{k=0}^{\lfloor n/2 \rfloor} [2(n-2k)+1]$
    $= \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}[(t^{2n+1} + t^{2n-1} + t^{2n-3} + \cdots + t) + (t^{2n+1} - t^{2n-1} + t^{2n-3} - \cdots + (-1)^n t)]\Big|_{t=1}$
    $= \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}[t \cdot \frac{t^{2n+2}-1}{t^2-1} + t \cdot \frac{t^{2n+2}+(-1)^n}{t^2+1}]\Big|_{t=1} = \frac{(n+2)(n+1)}{2}$.
  - Side remark: the degeneracy is higher than $(2\ell+1)$, due to $SU(3)$ symmetry of the 3D harmonic oscillator which is larger than $SO(3)$ spatial rotation symmetry of generic central potential problem. There are more conserved quantities than the orbital angular momentum, and the trajectories of classical isotropic 3D harmonic oscillator are closed loops.

Bound states for "hydrogen atom" (textbook Section 4.2)

- $V(r) = -\frac{\mathrm{e}^2}{4\pi\epsilon_0}\frac{1}{r}$. NOTE: the e here is "elementary charge" $\approx 1.602\times 10^{-19}$(Coulomb), not to be confused with the "base of natural logarithms" $e = 2.71828\ldots$; ϵ_0 is the absolute dielectric constant of vacuum. They always appear in combination $\frac{\mathrm{e}^2}{\epsilon_0}$ here.
  - Bound states have $E < 0$, define $\kappa = \frac{\sqrt{-2mE}}{\hbar}$, $\rho = \kappa r$, $\rho_0 = \frac{\mathrm{e}^2}{2\pi\epsilon_0}\cdot\frac{m}{\hbar^2\kappa}$. Then the radial equation for $u = r\cdot R(r)$ becomes $[-\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} + (1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2})]u = 0$.
  - The asymptotic behavior for u is: $u \sim \rho^{\ell+1}$ as $\rho\to 0$; and $u\sim e^{-\rho}$ as $\rho\to\infty$.
  - Define $u(\rho) = \rho^{\ell+1}e^{-\rho}\cdot v(\rho)$, then $\{-\rho\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} + 2(\ell+1-\rho)\frac{\mathrm{d}}{\mathrm{d}\rho} + [\rho_0 - 2(\ell+1)]\}v = 0$.
  - Assume $v(\rho) = \sum_{j=0}^{\infty} c_j\rho^j$, note that $c_0 \neq 0$, recursion relation is $c_{j+1} = \frac{2(j+\ell+1)-\rho_0}{(j+1)(j+2\ell+2)}c_j$.
  - Series of v must be truncated, otherwise $v\sim e^{2\rho}$ contradicts with normalizable assumption. If $c_j\neq 0$ but $c_{j'} = 0$ for $j' > j$, then $2(j+\ell+1) = \rho_0$, define $n = j+\ell+1$, then $E_{n\ell m} = E_n = -[\frac{m}{2\hbar^2}(\frac{\mathrm{e}^2}{4\pi\epsilon_0})^2]\frac{1}{n^2} = \frac{E_1}{n^2}$.
    Here $E_1 = -\frac{m}{2\hbar^2}(\frac{\mathrm{e}^2}{4\pi\epsilon_0})^2 = -\frac{\hbar^2}{2m}(\frac{1}{a})^2 = -\frac{1}{2}\frac{\mathrm{e}^2}{4\pi\epsilon_0}\frac{1}{a} \approx -13.6\mathrm{eV}$(electron-Volt), is the *Rydberg constant*.
  - *Bohr radius* $a = \frac{4\pi\epsilon_0}{\mathrm{e}^2}\frac{\hbar^2}{m} \approx 0.529$Å. Here Å(ångström) is 10^{-10}(metre).
  - Ground state is non-degenerate, $\psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi a^3}}e^{-r/a}$. For generic $\psi_{n\ell m}$, see textbook Section 4.2.
  - n is "principal quantum number", and $n = 1, 2, \ldots$.
    For given n, the ℓ can be $0, 1, \ldots, (n-1)$. So the total degeneracy is $\sum_{\ell=0}^{n-1}(2\ell+1) = n^2$.
  - Side remark: the degeneracy is higher than $(2\ell+1)$, due to $SO(4)$ symmetry of the $\frac{1}{r}$ potential problem. There are more conserved quantities (Laplace-Runge-Lenz vector), and classical trajectories are closed loops (Kepler's laws).

Orbital angular momentum operators

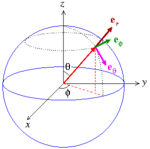
- Orbital angular momentum $\hat{\boldsymbol{L}} = \hat{\boldsymbol{r}} \times \hat{\boldsymbol{p}}$, namely $\hat{L}_a = \epsilon_{abc}\hat{r}_b\hat{p}_c$.
  - Here we have used the "Einstein summation convention" for implicit summation over repeated "dummy" indices (indicated by blue color). So $\epsilon_{abc}\hat{r}_b\hat{p}_c$ actually means $\sum_b\sum_c \epsilon_{abc}\hat{r}_b\hat{p}_c$.
  - Levi-Civita symbol $\epsilon_{abc} = \begin{cases} +1, & abc = xyz, yzx, zxy; \\ -1, & abc = zyx, xzy, yxz; \\ 0, & \text{otherwise.} \end{cases}$
    It is totally anti-symmetric: $\epsilon_{abc} = -\epsilon_{acb} = -\epsilon_{bac} = -\epsilon_{cba} = \epsilon_{bca} = \epsilon_{cab}$.
    Useful identity: $\epsilon_{abc}\epsilon_{afg} = \delta_{bf}\delta_{cg} - \delta_{bg}\delta_{cf}$.
  - $\hat{L}_a$ are all hermitian operators (observables). Note that $\hat{r}_b\hat{p}_c = \hat{p}_c\hat{r}_b$ for $b \neq c$.
  - $[\hat{L}_a, \hat{r}_b] = \mathrm{i}\hbar\epsilon_{abc}\hat{r}_c$, $[\hat{L}_a, \hat{p}_b] = \mathrm{i}\hbar\epsilon_{abc}\hat{p}_c$, $[\hat{L}_a, \hat{L}_b] = \mathrm{i}\hbar\epsilon_{abc}\hat{L}_c$. The last one is also written as $\hat{\boldsymbol{L}} \times \hat{\boldsymbol{L}} = \mathrm{i}\hbar\hat{\boldsymbol{L}}$.
    Proof: $[\hat{L}_a, \hat{p}_b] = [\epsilon_{acd}\hat{r}_c\hat{p}_d, \hat{p}_b] = \epsilon_{acd}(\hat{r}_c[\hat{p}_d, \hat{p}_b] + [\hat{r}_c, \hat{p}_b]\hat{p}_d) = 0 + \epsilon_{acd}(\mathrm{i}\hbar\delta_{cb})\hat{p}_d = \mathrm{i}\hbar\epsilon_{abd}\hat{p}_d$.
    $[\hat{L}_a, \hat{r}_b] = [\epsilon_{acd}\hat{r}_c\hat{p}_d, \hat{r}_b] = \epsilon_{acd}(\hat{r}_c[\hat{p}_d, \hat{r}_b] + [\hat{r}_c, \hat{r}_b]\hat{p}_d) = \epsilon_{acd}\hat{r}_c(-\mathrm{i}\hbar\delta_{db}) + 0 = -\mathrm{i}\hbar\epsilon_{acb}\hat{r}_c = \mathrm{i}\hbar\epsilon_{abc}\hat{r}_c$.
    $[\hat{L}_a, \hat{L}_b] = [\hat{L}_a, \epsilon_{bcd}\hat{r}_c\hat{p}_d] = \epsilon_{bcd}([\hat{L}_a, \hat{r}_c]\hat{p}_d + \hat{r}_c[\hat{L}_a, \hat{p}_d]) = \mathrm{i}\hbar\epsilon_{bcd}(\epsilon_{acf}\hat{r}_f\hat{p}_d + \hat{r}_c\epsilon_{adg}\hat{p}_g)$
    $= \mathrm{i}\hbar[(\delta_{ba}\delta_{df} - \delta_{bf}\delta_{da})\hat{r}_f\hat{p}_d - (\delta_{ba}\delta_{cg} - \delta_{bg}\delta_{ca})\hat{r}_c\hat{p}_g] = \mathrm{i}\hbar(-\hat{r}_b\hat{p}_a + \hat{r}_a\hat{p}_b)$; and
    $\mathrm{i}\hbar\epsilon_{abc}\hat{L}_c = \mathrm{i}\hbar\epsilon_{abc}\epsilon_{cdf}\hat{r}_d\hat{p}_f = \mathrm{i}\hbar(\delta_{ad}\delta_{bf} - \delta_{af}\delta_{bd})\hat{r}_d\hat{p}_f = \mathrm{i}\hbar(\hat{r}_a\hat{p}_b - \hat{r}_b\hat{p}_a)$.
  - Side remark: angular momentum operators are generators of (spatial) rotation. A "vector" operator $\hat{\boldsymbol{A}}$ should satisfy $[\hat{L}_a, \hat{A}_b] = \mathrm{i}\hbar\epsilon_{abc}\hat{A}_c$, and then $e^{-\mathrm{i}\theta\boldsymbol{n}\cdot\hat{\boldsymbol{L}}/\hbar}\hat{\boldsymbol{A}}e^{\mathrm{i}\theta\boldsymbol{n}\cdot\hat{\boldsymbol{L}}/\hbar} = \hat{\boldsymbol{A}} \cdot R_{\boldsymbol{n}}(\theta)$, where $R_{\boldsymbol{n}}(\theta)$ is the $SO(3)$ matrix for rotation around $\boldsymbol{n}$ axis ($|\boldsymbol{n}| = 1$) by angle θ.
- $\hat{\boldsymbol{L}}^2 \equiv \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$. Then $[\hat{\boldsymbol{L}}^2, \hat{L}_a] = 0$.
  - Proof: $[\hat{\boldsymbol{L}}^2, \hat{L}_a] = [\hat{L}_b\hat{L}_b, \hat{L}_a] = \hat{L}_b \cdot \mathrm{i}\hbar\epsilon_{bac}\hat{L}_c + \mathrm{i}\hbar\epsilon_{bac}\hat{L}_c \cdot \hat{L}_b = \mathrm{i}\hbar(\epsilon_{bac} + \epsilon_{cab})\hat{L}_b\hat{L}_c$ (exchange names of dummy indices $b \leftrightarrow c$ in the 2nd term) $= 0$ (anti-symmetry of ϵ-symbol).
  - Side remark: similarly, $[\hat{\boldsymbol{A}}^2, \hat{L}_a] = 0$ for "vector" operator $\hat{\boldsymbol{A}}$ (see Side remark above).

Orbital angular momentum: eigenvalues and eigenstates

- Ladder operators: $\hat{L}_\pm \equiv \hat{L}_x \pm \mathrm{i}\hat{L}_y$.
  - $(\hat{L}_\pm)^\dagger = \hat{L}_\mp$, $[\hat{\boldsymbol{L}}^2, \hat{L}_\pm] = 0$, $[\hat{L}_z, \hat{L}_\pm] = \pm\hbar\hat{L}_\pm$, $[\hat{L}_-, \hat{L}_+] = -2\hbar\hat{L}_z$. Exercise: check these.
  - $\hat{\boldsymbol{L}}^2 = \hat{L}_-\hat{L}_+ + \hat{L}_z(\hat{L}_z + \hbar) = \hat{L}_+\hat{L}_- + \hat{L}_z(\hat{L}_z - \hbar)$. Exercise: check these.
- Eigenstates of $\hat{\boldsymbol{L}}^2$ and $\hat{L}_z$ are labeled as $|\ell, m\rangle$; $\ell = 0, 1, \ldots$; $m = -\ell, (-\ell+1), \ldots, \ell$.
  $\hat{\boldsymbol{L}}^2|\ell, m\rangle = \hbar^2\ell(\ell+1)|\ell, m\rangle$, $\hat{L}_z|\ell, m\rangle = m\hbar|\ell, m\rangle$, and
  $\hat{L}_\pm|\ell, m\rangle = \hbar\sqrt{(\ell\mp m)(\ell\pm m+1)}|\ell, m\pm 1\rangle$ (under Condon-Shortley convention).
  - Derivation (textbook Section 4.3): denote eigenstate $|\hat{\boldsymbol{L}}^2 = \alpha\hbar^2, \hat{L}_z = m\hbar\rangle$ as $|\alpha; m\rangle$ here. From $[\hat{\boldsymbol{L}}^2, \hat{L}_\pm] = 0$ and $[\hat{L}_z, \hat{L}_\pm] = \pm\hbar\hat{L}_\pm$, we have $\hat{L}_\pm|\alpha; m\rangle \propto |\alpha; m\pm 1\rangle$ or vanishes. So for given α, the allowed m values form a "ladder" $(\ldots, m-1, m, m+1, \ldots)$. Note that $\hat{L}_\mp\hat{L}_\pm$ are positive semi-definite, $\langle\alpha; m|\hat{L}_\mp\hat{L}_\pm|\alpha; m\rangle = (\hat{L}_\pm|\alpha; m\rangle, \hat{L}_\pm|\alpha; m\rangle) \geq 0$. Use $\hat{L}_\mp\hat{L}_\pm = \hat{\boldsymbol{L}}^2 - \hat{L}_z(\hat{L}_z \pm \hbar)$, we have $\alpha \geq m(m\pm 1)$. So $\frac{1}{2} - \sqrt{\alpha + \frac{1}{4}} \leq m \leq -\frac{1}{2} + \sqrt{\alpha + \frac{1}{4}}$. So the "ladder" of m must be truncated, and is of the form $(m_{\text{min}}, m_{\text{min}}+1, \ldots, m_{\text{max}}-1, m_{\text{max}})$. Then $\hat{L}_-|\alpha; m_{\text{min}}\rangle = 0$ and $\hat{L}_+|\alpha; m_{\text{max}}\rangle = 0$, otherwise we would have $m = m_{\text{min}} - 1$ or $m = m_{\text{max}} + 1$ states. Then $\alpha\hbar^2 = \hat{\boldsymbol{L}}^2|\alpha; m_{\text{min}}\rangle = [\hat{L}_+\hat{L}_- + \hat{L}_z(\hat{L}_z - \hbar)]|\alpha; m_{\text{min}}\rangle = 0 + m_{\text{min}}(m_{\text{min}} - 1)\hbar^2$, so $\alpha = m_{\text{min}}(m_{\text{min}} - 1)$, and similarly $\alpha = m_{\text{max}}(m_{\text{max}} + 1)$. Since $m_{\text{min}} \leq m_{\text{max}}$, we must have $m_{\text{min}} = \frac{1}{2} - \sqrt{\alpha + \frac{1}{4}}$, and $m_{\text{max}} = -\frac{1}{2} + \sqrt{\alpha + \frac{1}{4}} = -m_{\text{min}} \equiv \ell$. So $\alpha = \ell(\ell+1)$, m can be $-\ell, -\ell+1, \ldots, \ell$. And $m_{\text{max}} - m_{\text{min}} = 2\ell$ is a non-negative integer. Hereafter we denote $|\alpha; m\rangle$ as $|\ell, m\rangle$.
  - This only demands that $2\ell = 0, 1, \ldots$. See next page for the reason why $\ell = 0, 1, \ldots$.
  - $(\hat{L}_\pm|\ell, m\rangle, \hat{L}_\pm|\ell, m\rangle) = \langle\ell, m|\hat{L}_\mp\hat{L}_\pm|\ell, m\rangle = \langle\ell, m|\hat{\boldsymbol{L}}^2 - \hat{L}_z(\hat{L}_z \pm \hbar)|\ell, m\rangle$
    $= \hbar^2(\ell(\ell+1) - m(m\pm 1)) = \hbar^2(\ell\mp m)(\ell\pm m+1)$,
    this determines $\hat{L}_\pm$ matrix elements up to a phase factor (fixed by Condon-Shortley convention).

Orbital angular momentum: polar coordinates

- Rewrite $\hat{\boldsymbol{L}}$ in terms of polar coordinates
  - define local orthonormal basis vectors along r, θ, ϕ directions,
    $\boldsymbol{e}_r = \frac{\boldsymbol{r}}{r} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$, $\boldsymbol{e}_\phi = \frac{\boldsymbol{e}_z \times \boldsymbol{e}_r}{|\boldsymbol{e}_z \times \boldsymbol{e}_r|} = (-\sin\phi, \cos\phi, 0)$,
    $\boldsymbol{e}_\theta = \boldsymbol{e}_\phi \times \boldsymbol{e}_r = (\cos\theta\cos\phi, \cos\theta\sin\phi, -\sin\theta)$.
    Then $\nabla = \boldsymbol{e}_r\partial_r + \boldsymbol{e}_\theta \frac{1}{r}\partial_\theta + \boldsymbol{e}_\phi \frac{1}{r\sin\theta}\partial_\phi$.
    $\hat{\boldsymbol{L}} = -\mathrm{i}\hbar \cdot r\boldsymbol{e}_r \times \nabla = -\mathrm{i}\hbar \cdot (\boldsymbol{e}_\phi\partial_\theta - \boldsymbol{e}_\theta \frac{1}{\sin\theta}\partial_\phi)$
    $= -\mathrm{i}\hbar \cdot (-\sin\phi\partial_\theta - \cos\phi\cot\theta\partial_\phi, \cos\phi\partial_\theta - \sin\phi\cot\theta\partial_\phi, \partial_\phi)$
  - NOTE: the above formula of ∇ is for the "gradient", you cannot use it alone to rewrite Laplacian $\nabla^2 = \mathrm{div}\,\mathrm{grad}$.



- $\hat{L}_z = -\mathrm{i}\hbar\frac{\partial}{\partial\phi}$, $\hat{L}_\pm = \pm\hbar e^{\pm\mathrm{i}\phi}(\frac{\partial}{\partial\theta} \pm \mathrm{i}\cot\theta\frac{\partial}{\partial\phi})$. Note that $\hat{\boldsymbol{L}}$ does not depend on radius r.
  - From $\hat{L}_z|\ell, m\rangle = m\hbar|\ell, m\rangle$, the corresponding wave function is $f(r,\theta)e^{\mathrm{i}m\phi}$. Note that (r,θ,ϕ) and $(r,\theta,\phi+2\pi)$ are the same point, the wave function should be single-valued, $\psi(r,\theta,\phi) = \psi(r,\theta,\phi+2\pi)$ (for more rigorous argument, see textbook Problem 4.57), then m and thus ℓ must be integer.
- $\hat{\boldsymbol{L}}^2 = -[\frac{1}{\sin\theta}\partial_\theta(\sin\theta\partial_\theta) + \frac{1}{\sin^2\theta}\partial_\phi^2]$.
- Central potential Hamiltonian $\hat{H} = \frac{\hat{\boldsymbol{p}}^2}{2m} + V(r) = -\frac{\hbar^2}{2m}\frac{1}{r^2}\partial_r(r^2\partial_r) + \frac{\hat{\boldsymbol{L}}^2}{2mr^2} + V(r)$, has spatial rotation symmetry, $[\hat{H}, \hat{\boldsymbol{L}}^2] = 0$, $[\hat{H}, \hat{L}_a] = 0$. So we can have eigenstates of $\hat{H}$ and $\hat{\boldsymbol{L}}^2$ and $\hat{L}_z$, $|\hat{H} = E_{n\ell m}, \hat{\boldsymbol{L}}^2 = \hbar^2\ell(\ell+1), \hat{L}_z = m\hbar\rangle$, usually denoted as $\psi_{n\ell m}$.
- Orbital angular momentum eigenstates $|\ell, m\rangle$ corresponds to wave function $R(r)Y_\ell^m(\theta,\phi)$ where $R(r)$ is an arbitrary function.

Spin-1/2

- "Spin"s are angular momentum associated with internal degrees of freedom, usually cannot be described by $\psi(\boldsymbol{r})$-type orbital wave function. So their "ℓ" quantum number (usually S) can be half-odd-integers. Spin angular momentum operators $\hat{\boldsymbol{S}}$ still satisfy $[\hat{S}_a, \hat{S}_b] = \mathbb{i}\hbar\epsilon_{abc}\hat{S}_c$. Most fundamental fermions (*e.g.* electrons) have spin $S = 1/2$.
- Spin-1/2 is a 2-dim'l Hilbert space with basis $|S=\frac{1}{2}, S_z = \pm\frac{1}{2}\rangle$ (denoted by $|\uparrow\rangle, |\downarrow\rangle$ hereafter). Conversely, 2-dim'l Hilbert spaces are usually viewed as pseudo-spin-1/2.
  - Under the $|\uparrow\rangle, |\downarrow\rangle$ basis, $\hat{S}_a = \frac{\hbar}{2}\sigma_a$, where σ_a are 2×2 hermitian traceless Pauli matrices, $a = x, y, z$.
  - $\hat{S}_+|\downarrow\rangle = \hbar|\uparrow\rangle$, $\hat{S}_-|\uparrow\rangle = \hbar|\downarrow\rangle$.
- About Pauli matrices:
  - $\sigma_x \equiv \sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$, $\sigma_y \equiv \sigma_2 = \begin{pmatrix} 0 & -\mathbb{i} \\ \mathbb{i} & 0 \end{pmatrix}$, $\sigma_z \equiv \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$, $\sigma_0 = \mathbb{1}_{2\times 2} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$.
  - $\mathrm{Tr}(\sigma_i\sigma_j) = 2\delta_{ij}$, $i, j = 0, 1, 2, 3$.
    Any 2×2 matrix M is a linear combination of Pauli matrices, $M = \sum_{i=0}^{3}\sigma_i \mathrm{Tr}(\sigma_i M)/2$.
  - $\sigma_a\sigma_b = \mathbb{i}\epsilon_{abc}\sigma_c + \delta_{ab}\sigma_0$, $a, b, c = x, y, z$. So $[\sigma_a, \sigma_b] = 2\mathbb{i}\epsilon_{abc}\sigma_c$, $\{\sigma_a, \sigma_b\} = 2\delta_{ab}\sigma_0$.
  - If $M = \boldsymbol{n}\cdot\boldsymbol{\sigma} \equiv \sum_{a=1}^{3} n_a\sigma_a$, then $\mathrm{Tr}(M) = 0$, $M^2 = n_a\sigma_a \cdot n_b\sigma_b = \frac{1}{2}(n_a n_b \sigma_a\sigma_b + n_b n_a \sigma_b\sigma_a)$ $= \frac{1}{2}n_a n_b\{\sigma_a, \sigma_b\} = n_a n_a \sigma_0 = |\boldsymbol{n}|^2\cdot\sigma_0$. So the eigenvalues of M are $\pm|\boldsymbol{n}| = \pm\sqrt{n_x^2 + n_y^2 + n_z^2}$.
  - textbook Problem 4.30: for $\boldsymbol{n} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$, eigenvectors of $\boldsymbol{n}\cdot\boldsymbol{\sigma}$ are (up to phase factors) $\begin{pmatrix} e^{-\mathbb{i}\phi}\cos\frac{\theta}{2} \\ \sin\frac{\theta}{2} \end{pmatrix}$ for eigenvalue $+|\boldsymbol{n}|$; and $\begin{pmatrix} -\sin\frac{\theta}{2} \\ e^{\mathbb{i}\phi}\cos\frac{\theta}{2} \end{pmatrix}$ for eigenvalue $-|\boldsymbol{n}|$
  - textbook Problem 4.56(e): $\exp(\mathbb{i}\phi\boldsymbol{n}\cdot\boldsymbol{\sigma}) = \cos(\phi)\sigma_0 + \mathbb{i}\sin(\phi)\boldsymbol{n}\cdot\boldsymbol{\sigma}$, here $|\boldsymbol{n}| = 1$.

Spin-1/2 (cont'd)

- Generic spin-1/2 states: $|\psi\rangle = \psi_\uparrow|\uparrow\rangle + \psi_\downarrow|\downarrow\rangle$, or $\begin{pmatrix}\psi_\uparrow\\ \psi_\downarrow\end{pmatrix}$, $\langle\psi|\psi\rangle = |\psi_\uparrow|^2 + |\psi_\downarrow|^2 = 1$.
  - The expectation value of spin operator is a fixed-length vector, $\langle\psi|\hat{\boldsymbol{S}}|\psi\rangle = \frac{\hbar}{2}\boldsymbol{n}$, $\boldsymbol{n} = \langle\psi|\boldsymbol{\sigma}|\psi\rangle$, $|\boldsymbol{n}| = 1$. Check: use the identity $\sum_{a=x,y,z}(\sigma_a)_{\alpha\beta}(\sigma_b)_{\gamma\rho} = 2\delta_{\alpha\rho}\delta_{\beta\gamma} - \delta_{\alpha\beta}\delta_{\gamma\rho}$ $(\alpha,\beta,\gamma,\rho = 1,2$ or $\uparrow,\downarrow$, this is related to "orthogonality theorem" in group representation theory), $n_a = \langle\psi|\sigma_a|\psi\rangle = \psi^*_\alpha(\sigma_a)_{\alpha\beta}\psi_\beta$, then $\boldsymbol{n}\cdot\boldsymbol{n} = n_a n_a = \psi^*_\alpha(\sigma_a)_{\alpha\beta}\psi_\beta\cdot\psi^*_\gamma(\sigma_a)_{\gamma\rho}\psi_\rho = (2\delta_{\alpha\rho}\delta_{\beta\gamma} - \delta_{\alpha\beta}\delta_{\gamma\rho})\psi^*_\alpha\psi_\beta\psi^*_\gamma\psi_\rho = (\langle\psi|\psi\rangle)^2 = 1$.
  - Conversely, given this $\boldsymbol{n}$, $|\psi\rangle$ is the eigenstate $|\boldsymbol{n}\cdot\hat{\boldsymbol{S}} = +\frac{\hbar}{2}\rangle$ (see the eigenvectors of $\boldsymbol{n}\cdot\boldsymbol{\sigma}$ in previous page).
  - Side remark: This kind of "fully polarized" states $|\boldsymbol{n}\cdot\hat{\boldsymbol{S}} = +\hbar S\rangle$ are "spin coherent states". Generic spin-1/2 states are spin coherent states, but generic higher spin $(S > \frac{1}{2})$ states may not be spin coherent states.
  - Side remark: The spin-1/2 states have "1-to-1" (up to overall complex phase factor of $|\psi\rangle$) correspondence to the $\boldsymbol{n}$ vectors, which form the "Bloch sphere" $\mathbb{S}^2$. Although naively the states $|\psi\rangle$ form a 3-sphere $\mathbb{S}^3$, because $(\mathrm{Re}\psi_\uparrow)^2 + (\mathrm{Im}\psi_\uparrow)^2 + (\mathrm{Re}\psi_\downarrow)^2 + (\mathrm{Im}\psi_\downarrow)^2 = 1$. This is actually the "Hopf map" $\mathbb{S}^3 \to \mathbb{S}^2$.
  - Side remark: $|\psi\rangle$ as a function of $\boldsymbol{n}$ cannot be continuous everywhere. Take *e.g.* $|\psi\rangle = \begin{pmatrix} e^{-\mathrm{i}\phi}\cos\frac{\theta}{2}\\ \sin\frac{\theta}{2}\end{pmatrix}$ for $\boldsymbol{n} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$, then it is discontinuous at "north pole" $\theta = 0$, $\lim_{\theta\to 0}|\psi\rangle = \begin{pmatrix} e^{-\mathrm{i}\phi}\\ 0\end{pmatrix}$ depends on ϕ. Multiplying $|\psi\rangle$ by any phase factor function $e^{\mathrm{i}f(\theta,\phi)}$ will not eliminate discontinuity.

Spin-1/2 (cont'd)

- Larmor precession (textbook Example 4.3):
  - Consider a position-fixed spin-1/2 particle (electron) in a static magnetic field $\boldsymbol{B} = (0, 0, B_0)$ along z direction. The Hamiltonian is $\hat{H} = -\boldsymbol{B} \cdot \hat{\boldsymbol{M}}$ where $\hat{\boldsymbol{M}} = \gamma \hat{\boldsymbol{S}}$ is the magnetic moment, γ is "gyromagnetic ratio".
  - Side remark: $\gamma = \frac{\text{magnetic moment}}{\text{angular momentum}} = g \cdot \frac{\mathrm{e}}{2m} = g\frac{\mu_B}{\hbar}$. Here e is elementary charge, m is (electron) mass, $\mu_B \equiv \frac{\mathrm{e}\hbar}{2m}$ is "Bohr magneton", g is dimensionless Landé g-factor. For orbital angular momentum, $g = 1$ [consider a particle moving on a circle of radius r with speed v, orbital angular momentum $L = mvr$, magnetic moment $M = \text{(electric current)} \cdot \text{(area)} = \frac{\mathrm{e}}{2\pi r/v} \cdot \pi r^2 = \frac{\mathrm{e}vr}{2} = \frac{\mathrm{e}}{2m} \cdot L$]; for electron spin, $g \approx 2$.
  - $\mathrm{i}\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle$. So here $|\psi(t)\rangle = \exp(\mathrm{i}B_0\gamma\frac{1}{2}\sigma_z \cdot t)|\psi(0)\rangle = \begin{pmatrix} e^{\mathrm{i}B_0\gamma t/2}\psi_\uparrow(0) \\ e^{-\mathrm{i}B_0\gamma t/2}\psi_\downarrow(0) \end{pmatrix}$.

    $\langle\psi(t)|\hat{\boldsymbol{S}}|\psi(t)\rangle = \langle\psi(0)|\hat{\boldsymbol{S}}|\psi(0)\rangle \cdot \begin{pmatrix} \cos(B_0\gamma t) & -\sin(B_0\gamma t) & 0 \\ \sin(B_0\gamma t) & \cos(B_0\gamma t) & 0 \\ 0 & 0 & 1 \end{pmatrix}$, precesses around the field direction.

    Exercise: check this result.
  - By Heisenberg equations of motion, $\frac{\mathrm{d}}{\mathrm{d}t}\langle\hat{S}_a\rangle = \frac{\mathrm{i}}{\hbar}\langle[\hat{H}, \hat{S}_a]\rangle = \frac{\mathrm{i}}{\hbar}\langle[-\gamma B_b\hat{S}_b, \hat{S}_a]\rangle = \gamma B_b\epsilon_{bac}\langle\hat{S}_c\rangle$, namely $\frac{\mathrm{d}}{\mathrm{d}t}\langle\hat{\boldsymbol{S}}\rangle = \gamma\langle\hat{\boldsymbol{S}}\rangle \times \boldsymbol{B}$, $\frac{\mathrm{d}}{\mathrm{d}t}$(angular momentum) = (torque).
- Spinor wave function: $\begin{pmatrix} \psi_\uparrow(\boldsymbol{r}) \\ \psi_\downarrow(\boldsymbol{r}) \end{pmatrix}$, for both position and spin state of a spin-1/2 particle.
  - Normalization: $\langle\psi|\psi\rangle \equiv \int[|\psi_\uparrow(\boldsymbol{r})|^2 + |\psi_\downarrow(\boldsymbol{r})|^2]\,\mathrm{d}^3\boldsymbol{r} = 1$.
  - Statistical interpretation: $|\psi_\uparrow(\boldsymbol{r})|^2$ is the probability density to have a spin $\uparrow$ ($S_z = +\frac{\hbar}{2}$) particle at $\boldsymbol{r}$; . . . .
  - Basis: $\begin{pmatrix} R_{n\ell}(r)Y_\ell^m(\theta,\phi) \\ 0 \end{pmatrix}$ and $\begin{pmatrix} 0 \\ R_{n\ell}(r)Y_\ell^m(\theta,\phi) \end{pmatrix}$, or $|\psi_{n\ell m}\rangle|\uparrow\rangle$ and $|\psi_{n\ell m}\rangle|\downarrow\rangle$.
  - Operators: $O(\hat{\boldsymbol{r}}, \hat{\boldsymbol{p}})|\psi\rangle \equiv \begin{pmatrix} O(\hat{\boldsymbol{r}}, \hat{\boldsymbol{p}})\psi_\uparrow(\boldsymbol{r}) \\ O(\hat{\boldsymbol{r}}, \hat{\boldsymbol{p}})\psi_\downarrow(\boldsymbol{r}) \end{pmatrix}$; action of spin operators are just matrix-vector multiplication.

Addition of angular momentum

- Addition of two angular momentum:
  - two Hilbert spaces $\mathcal{H}_{J_1}$ and $\mathcal{H}_{J_2}$ (for two independent degrees of freedom, *e.g.* orbital and spin state of an electron), with complete orthonormal basis $|J_1, m_1\rangle$ and $|J_2, m_2\rangle$ respectively, $m_i = -J_i, -J_i + 1, \ldots, J_i$.
  - the tensor product Hilbert space $\mathcal{H}_{J_1} \otimes \mathcal{H}_{J_2}$ (for describing both degrees of freedom), has $(2J_1 + 1)(2J_2 + 1)$ basis $|J_1, m_1\rangle|J_2, m_2\rangle$, also written as $|J_1, m_1; J_2, m_2\rangle$.
  - angular momentum operators $\hat{\boldsymbol{J}}_i$ in $\mathcal{H}_{J_i}$ are extended to $\mathcal{H}_{J_1} \otimes \mathcal{H}_{J_2}$ as $\hat{\boldsymbol{J}}_1 \otimes \hat{\mathbb{1}}$ and $\hat{\mathbb{1}} \otimes \hat{\boldsymbol{J}}_2$, then $[\hat{J}_{i,a}, \hat{J}_{j,b}] = \delta_{ij} \mathrm{i}\hbar\epsilon_{abc}\hat{J}_{i,c}$.
  - total angular momentum $\hat{\boldsymbol{J}} = \hat{\boldsymbol{J}}_1 + \hat{\boldsymbol{J}}_2 \equiv \hat{\boldsymbol{J}}_1 \otimes \hat{\mathbb{1}} + \hat{\mathbb{1}} \otimes \hat{\boldsymbol{J}}_2$, then $[\hat{J}_a, \hat{J}_b] = \mathrm{i}\hbar\epsilon_{abc}\hat{J}_c$. There should be eigenstates of $\hat{\boldsymbol{J}}^2$ and $\hat{J}_z$, $|J, m\rangle$, in $\mathcal{H}_{J_1} \otimes \mathcal{H}_{J_2}$.
- Clebsch-Gordon theorem: roughly speaking, total J quantum number can be $|J_1 - J_2|$, $|J_1 - J_2| + 1, \ldots, J_1 + J_2$, and each choice of J [$(2J + 1)$-multiplet] appears only once. The tensor product Hilbert space $\mathcal{H}_{J_1} \otimes \mathcal{H}_{J_2}$ can be decomposed into a direct sum $\mathcal{H}_{|J_1 - J_2|} \oplus \mathcal{H}_{|J_1 - J_2|+1} \oplus \cdots \oplus \mathcal{H}_{J_1+J_2}$.
  - Consistency check: dimensions match, $(2J_1 + 1)(2J_2 + 1) = \sum_{J=|J_1-J_2|}^{J_1+J_2}(2J + 1)$.
- Clebsch-Gordon(C.-G.) coefficients: $\langle J_1, m_1; J_2, m_2|J, m\rangle$, or $C_{J_1\,J_2\,J}^{m_1 m_2 m}$.
  - C.-G. coefficients form the unitary matrix for changing between $|J, m\rangle$ and $|J_1, m_1; J_2, m_2\rangle$ basis.
    $|J, m\rangle = \sum_{m_1}\sum_{m_2} |J_1, m_1; J_2, m_2\rangle\langle J_1, m_1; J_2, m_2|J, m\rangle$,
    $|J_1, m_1; J_2, m_2\rangle = \sum_J \sum_m |J, m\rangle\langle J, m|J_1, m_1; J_2, m_2\rangle$.
  - Selection rule for $\hat{J}_z$: nonzero C.-G. coefficients must have $m_1 + m_2 = m$.
    Proof: consider $\langle J_1, m_1; J_2, m_2|\hat{J}_z|J, m\rangle$, note that $\hat{J}_z = \hat{J}_{1,z} + \hat{J}_{2,z}$.

Addition of angular momentum (cont'd)

- Computing C.-G. coefficients (use $C^{m_1,m_2,m}_{J_1,\,J_2,\,\ J}$ symbol here):
  - For a given J, first consider the highest $m = J$ state, $|J, J\rangle = \sum_{m_1} C^{m_1,(J-m_1),J}_{J_1,J_2,\ J} |J_1, m_1; J_2, J - m_1\rangle$.
    Use $0 = \hat{J}_+|J, J\rangle = (\hat{J}_{1,+} + \hat{J}_{2,+}) \sum_{m_1} C^{m_1,(J-m_1),J}_{J_1,J_2,\ J} |J_1, m_1; J_2, J - m_1\rangle$
    $= \hbar \sum_{m_1} C^{m_1,(J-m_1),J}_{J_1,J_2,\ J} (\sqrt{(J_1 - m_1)(J_1 + m_1 + 1)}|J_1, m_1 + 1; J_2, J - m_1\rangle$
    $+\sqrt{(J_2 - J + m_1)(J_2 + J - m_1 + 1)}|J_1, m_1; J_2, J - m_1 + 1\rangle)$.
    The coefficient for $|J_1, m_1 + 1; J_2, J - m_1\rangle$ in the final result must vanish,
    $C^{m_1,(J-m_1),J}_{J_1,J_2,\ J}\sqrt{(J_1 - m_1)(J_1 + m_1 + 1)} + C^{m_1+1,(J-m_1-1),J}_{J_1,J_2,\ J}\sqrt{(J_2 - J + m_1 + 1)(J_2 + J - m_1)} = 0$.
    This fixes the ratio between all $C^{m_1,(J-m_1),J}_{J_1,J_2,\ J}$, together with normalization $\sum_{m_1} |C^{m_1,(J-m_1),J}_{J_1,J_2,\ J}|^2 = 1$,
    this solves all $C^{m_1,(J-m_1),J}_{J_1,J_2,\ J}$ up to overall phase factor.
  - Once we have solved highest $m = J$ state, other $|J, m\rangle$ states can be obtained by repeated application of lowering operator $\hat{J}_- = \hat{J}_{1,-} + \hat{J}_{2,-}$ on $|J, J\rangle$.
  - Example: two spin-1/2s, $J_1 = J_2 = \frac{1}{2}$, $m_1, m_2 =\uparrow, \downarrow$, and denote $|J_1, m_1; J_2, m_2\rangle$ just be $|m_1; m_2\rangle$.
    Total $J = 1$ (spin triplet):
    $|J = 1, m = 1\rangle = |\uparrow;\uparrow\rangle$ (only this term according to selection rule);
    $|J = 1, m = 0\rangle = \frac{\hat{J}_-}{\hbar\sqrt{2}}|J = 1, m = 1\rangle = \frac{\hat{J}_{1,-}+\hat{J}_{2,-}}{\hbar\sqrt{2}}|\uparrow;\uparrow\rangle = \frac{1}{\sqrt{2}}(|\downarrow;\uparrow\rangle + |\uparrow;\downarrow\rangle)$;
    $|J = 1, m = -1\rangle = |\downarrow;\downarrow\rangle$.
    Total $J = 0$ (spin singlet):
    $C^{\downarrow,\uparrow,0}_{\frac{1}{2},\frac{1}{2},0}\sqrt{(\frac{1}{2} - (-\frac{1}{2}))(\frac{1}{2} + (-\frac{1}{2}) + 1)} + C^{\uparrow,\downarrow,0}_{\frac{1}{2},\frac{1}{2},0}\sqrt{(\frac{1}{2} - 0 + (-\frac{1}{2}) + 1)(\frac{1}{2} + 0 - (-\frac{1}{2}))} = 0$, so we can choose $C^{\downarrow,\uparrow,0}_{\frac{1}{2},\frac{1}{2},0} = -C^{\uparrow,\downarrow,0}_{\frac{1}{2},\frac{1}{2},0} = \frac{1}{\sqrt{2}}$, spin singlet state $|J = 0, m = 0\rangle = \frac{1}{\sqrt{2}}(|\downarrow;\uparrow\rangle - |\uparrow;\downarrow\rangle)$.