The Mathematics of Quantum Physics 1

A guide

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Of course, I have *not* written this entirely by myself; there is a lot of GenAI in here. However, I do promise that I have gone through the entire material, modified most sentences, cut it down to only the relevant parts, and added relevant cross-references from the textbook and the worksheets :)

Topic	Problems	Sections
Formalism, measurement	W4.1, W4.2, W4.5; 3.7, 3.14, 3.16, 3.18, 3.37	1 to 13, 18
3D equation, hydrogen	W4.3, W4.4, W4.6; 4.1, 4.9, 4.53	17, 19, 20
Angular momentum, spin	W5.1, W5.2, W5.3; A.28, 4.22, 4.30	8, 14, 15, 16
Adding angular momenta	W5.4, W5.5; 4.32, 4.34, 4.37, 4.38	21, 22
Identical particles	5.5, 5.6, 5.7, 5.17, 5.18	23
Finite well, barriers	2.29, 2.30, 2.33, 2.34, 2.35, 2.48	24, 25

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Part 0. Basic stuff

Matrices, determinants, linear systems

Matrix times vector

$$(Av)_i = \sum_j A_{ij} v_j.$$

Run along row i and down the vector, multiplying pairs and adding. Column j of A is the image of the j-th basis vector.

Example T.1

$$\begin{pmatrix} 2 & -1 \\ 0 & 3 \end{pmatrix} \begin{pmatrix} 4 \\ 5 \end{pmatrix} = \begin{pmatrix} 3 \\ 15 \end{pmatrix}, \qquad \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 1 \\ i \end{pmatrix} = \begin{pmatrix} -i^2 \\ i \end{pmatrix} = \begin{pmatrix} 1 \\ i \end{pmatrix}.$$

The second vector came back unchanged: an eigenvector with eigenvalue 1.

Matrix times matrix

$$(AB)_{ik} = \sum_j A_{ij} B_{jk}, \qquad (m \times n)(n \times p) = (m \times p).$$

Example T.2

$$A = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad B = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \qquad AB = \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix}, \qquad BA = \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix} = -AB.$$

Matrix multiplication does not commute. These two are σ_x and σ_y, and this failure to commute is the uncertainty principle.

The identity I has ones on the diagonal. The transpose swaps rows and columns. The adjoint $A^\dagger$ transposes and conjugates:

$$A = \begin{pmatrix} 1 & 2+i \\ 0 & -3i \end{pmatrix} \implies A^\dagger = \begin{pmatrix} 1 & 0 \\ 2-i & 3i \end{pmatrix}.$$

Determinants

$$\det \begin{pmatrix} a & b \\ c & d \end{pmatrix} = ad - bc, \qquad \det \begin{pmatrix} a & b & c \\ d & e & f \\ g & h & i \end{pmatrix} = a \begin{vmatrix} e & f \\ h & i \end{vmatrix} - b \begin{vmatrix} d & f \\ g & i \end{vmatrix} + c \begin{vmatrix} d & e \\ g & h \end{vmatrix}.$$

Each minor is what is left after deleting that coefficient's row and column; the signs alternate as $\begin{pmatrix} + & - & + \\ - & + & - \\ + & - & + \end{pmatrix}$. Expand along whichever row or column has the most zeros.

Example T.3

$$\det \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} = -1 \begin{vmatrix} 1 & 1 \\ 0 & 0 \end{vmatrix} = 0.$$

Three properties:

- $\det(AB) = \det A \det B$ and $\det(A^\mathsf{T}) = \det A$;
- $\det A \neq 0$ iff A is invertible;

- $\det A = 0$ iff $Av = 0$ has a solution with $v \neq 0$.

The third gives the characteristic equation: if A were invertible, $Av = 0$ would force $v = A^{-1}0 = 0$. An eigenvector is a non-zero solution of $(A - \lambda I)v = 0$, so $\det(A - \lambda I)$ must vanish.

The trace is $\operatorname{Tr} A = \sum_i A_{ii}$, and $\operatorname{Tr}(AB) = \operatorname{Tr}(BA)$ even when $AB \neq BA$.

Homogeneous systems

Solving $(A - \lambda I)v = 0$ with λ already known: the determinant is zero by construction, so the rows repeat information and the solution is a direction, not a vector.

Example T.4

$$\begin{pmatrix} 2 & -2 \\ -1 & 1 \end{pmatrix} v = 0, \qquad \det = 2 - 2 = 0.$$

Row 1 gives $v_1 = v_2$; row 2 repeats it. Take $v = \binom{1}{1}$, normalise to $\frac{1}{\sqrt{2}}\binom{1}{1}$.

Example T.5

$$\begin{pmatrix} -1 & 1 & 0 \\ 1 & -1 & 1 \\ 0 & 1 & -1 \end{pmatrix} v = 0.$$

Rows 1 and 3 give $v_1 = v_2 = v_3$; row 2 then reads $v_1 = 0$, so $v = 0$. Here $\det = 1 \neq 0$ and there is nothing to find. If you get $v = 0$ while looking for an eigenvector, it means the eigenvalue is wrong.

Scaling

$\binom{1}{1}$, $\binom{2}{2}$ and $\frac{i}{\sqrt{2}}\binom{1}{1}$ are the same state, and normalising fixes the length.

Part I. States

1 Vector spaces

Definition

A complex vector space is a set whose elements can be added and multiplied by complex numbers, staying inside the set, with

$$u+v=v+u, \quad (u+v)+w=u+(v+w), \quad v+0=v, \quad v+(-v)=0,$$

$$c(u+v)=cu+cv, \quad (c+d)v=cv+dv, \quad c(dv)=(cd)v, \quad 1v=v.$$

Note that there is no mention (yet) of lengths, angles, arrows. Anything closed under addition and scaling qualifies. You could make a vector space out of cows if you wanted as long as you define what cow+cow is and so on.

Example 1.1

(a) $\mathbb{R}^3$, arrows added tip to tail.
(b) $\mathbb{C}^2$, columns of two complex numbers. This is spin $\frac{1}{2}$ and the double well of W4.1.
(c) Complex functions on $[0,L]$, with $(f+g)(x):=f(x)+g(x)$ and $(cf)(x):=cf(x)$. Each axiom holds at each x separately. A wave function is an element of a vector space in the same sense that $(1,2,3)$ is.

A vector in $\mathbb{C}^3$ is a list indexed by $i\in\{1,2,3\}$; a function on $[0,L]$ is a list indexed by $x\in[0,L]$:

finite dimensional	functions
label i	label x
component v_i	value $\psi(x)$
$\sum_i$	$\int \mathrm{d}x$
δ_{ij}	$\delta(x-x')$

Naturally, every formula below remains true under this translation.

1.1 Complex numbers

For $z=a+ib$: $z^*=a-ib$ and $z^*z=a^2+b^2=|z|^2\geq 0$. Also $(zw)^*=z^*w^*$, $1/i=-i$, and z is real iff $z^*=z$. The phase $e^{i\theta}=\cos\theta+i\sin\theta$ has modulus one.

2 Inner products

In $\mathbb{R}^3$, $u\cdot v=\sum u_iv_i$ gives $v\cdot v=|v|^2$ and $u\cdot v=0$ for perpendicular vectors. Copied naively into $\mathbb{C}^2$ it breaks: for $v=\binom{1}{i}$,

$$v_1v_1+v_2v_2=1+i^2=0,$$

a non-zero vector of zero length. Conjugating the first factor gives $|1|^2+|i|^2=2$. This is why we use complex conjugates: we want $|\psi|^2$ real and positive, which is exactly what a probability needs!

Definition

An inner product assigns $\langle\psi\,|\,\phi\rangle\in\mathbb{C}$ to each ordered pair, with

(i) $\langle\phi\,|\,\psi\rangle=\langle\psi\,|\,\phi\rangle^*$;

(ii) $\langle\psi\,|\,a\phi_1+b\phi_2\rangle=a\langle\psi\,|\,\phi_1\rangle+b\langle\psi\,|\,\phi_2\rangle$;

(iii) $\langle\psi\,|\,\psi\rangle \geq 0$, zero only for $\psi = 0$.

(i) and (ii) together give conjugate linearity in the first slot:

$$\langle a\psi\,|\,\phi\rangle = \langle\phi\,|\,a\psi\rangle^* = a\langle\phi\,|\,\psi\rangle^* = a^*\langle\psi\,|\,\phi\rangle.$$

Where the star goes

$$\langle\psi\,|\,c\phi\rangle = c\langle\psi\,|\,\phi\rangle, \qquad \langle c\psi\,|\,\phi\rangle = c^*\langle\psi\,|\,\phi\rangle.$$

Physics convention puts the conjugate in the first slot, and mathematicians do the opposite. It would seem like only one of them is using the logical side of their brain but hey who am I to judge.

The three useful ones:

$$\langle u\,|\,v\rangle = \sum_i u_i^* v_i, \qquad \langle f\,|\,g\rangle = \int_a^b f^* g\,\mathrm{d}x, \qquad \langle f\,|\,g\rangle = \int_{-\infty}^{\infty} f^* g\,\mathrm{d}x.$$

Example 2.1

On $[0,1]$, $f = x$ and $g = e^{i\pi x}$. By parts with $v = e^{i\pi x}/(i\pi)$,

$$\langle f\,|\,g\rangle = \int_0^1 x e^{i\pi x}\mathrm{d}x = \frac{e^{i\pi}}{i\pi} - \left[\frac{e^{i\pi x}}{(i\pi)^2}\right]_0^1 = \frac{-1}{i\pi} - \frac{2}{\pi^2} = \frac{i}{\pi} - \frac{2}{\pi^2},$$

using $e^{i\pi} = -1$ and $-1/i = i$. Conjugate symmetry predicts $\langle g\,|\,f\rangle = -\frac{2}{\pi^2} - \frac{i}{\pi}$.

2.1 Norm

$\|\psi\| = \sqrt{\langle\psi\,|\,\psi\rangle}$, and for a wave function $\|\psi\|^2 = \int |\psi|^2 \mathrm{d}x$ is the total probability. Normalised means $\|\psi\| = 1$.

Example 2.2

$\psi = Ax(L - x)$ on $[0, L]$:

$$1 = A^2 \int_0^L (L^2x^2 - 2Lx^3 + x^4)\mathrm{d}x = A^2 L^5 \left(\tfrac{1}{3} - \tfrac{1}{2} + \tfrac{1}{5}\right) = \frac{A^2 L^5}{30}, \qquad A = \sqrt{\frac{30}{L^5}}.$$

Phase

$\langle e^{i\theta}\psi\,|\,e^{i\theta}\psi\rangle = e^{-i\theta}e^{i\theta}\langle\psi\,|\,\psi\rangle$, so an overall phase is invisible. A relative phase between two terms of a superposition, however, is not invisible, and that gives us interference:)

3 Hilbert space

Definition

A Hilbert space is a complex vector space with an inner product that is *complete*: every sequence whose terms get arbitrarily close to each other converges inside the space.

The rationals fail completeness: $1, 1.4, 1.41, 1.414, \dots$ closes up on $\sqrt{2}$, which is not rational. Completeness is what lets you write $|\psi\rangle = \sum_n c_n |n\rangle$ with infinitely many terms and know the sum is still a state.

The three commonly used Hilbert spaces we've seen so far are: $\mathbb{C}^2$ for spin $\frac{1}{2}$ and for the double well; $\mathbb{C}^3$ for the $l = 1$ states; and $L^2(a, b)$, the functions with $\int |\psi|^2 < \infty$, for wave mechanics.

A note on 'complete'

Guys please don't get confused between the two times you've heard 'complete'. A complete *space* has convergent Cauchy sequences. A complete *set* of vectors spans the vector space, $\sum_n |n\rangle\langle n| = I$. The set $\{\phi_2, \phi_4, \dots\}$ in the infinite well is orthonormal and badly incomplete.

Aside

Von Neumann coined "Hilbert space" in 1929 while axiomatising quantum mechanics. The L^2 norm itself predates quantum mechanics by two decades and came out of integral equations. So what I'm trying to say is that maths did it first yk

4 Bases and components

Orthonormal means

$$\langle e_m \,|\, e_n \rangle = \delta_{mn} = \begin{cases} 1, & m = n \\ 0, & m \neq n \end{cases}$$

with δ_{mn} the Kronecker delta. A basis also satisfies $\psi = \sum_n c_n e_n$, and the c_n are the components.

Example 4.1

Two orthonormal bases of $\mathbb{C}^2$:

$$e_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix},\ e_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}; \qquad f_1 = \tfrac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix},\ f_2 = \tfrac{1}{\sqrt{2}} \begin{pmatrix} -1 \\ 1 \end{pmatrix}.$$

For the second, $\langle f_1 \,|\, f_1 \rangle = \frac{1}{2}(1+1) = 1$ and $\langle f_1 \,|\, f_2 \rangle = \frac{1}{2}(-1+1) = 0$. The $1/\sqrt{2}$ is only for the length.

These two we've seen several times: as $\{|\phi_L\rangle, |\phi_R\rangle\}$ and $\{|\phi_g\rangle, |\phi_e\rangle\}$ in W4.1, and as the eigenvectors of $\hat{S}_z$ and $\hat{S}_x$ for spin.

4.1 The projection trick

Projection

For orthonormal $\{e_n\}$ and $\psi = \sum_n c_n e_n$,

$$\boxed{c_m = \langle e_m \,|\, \psi \rangle}$$

$$\langle e_m \,|\, \psi \rangle = \Big\langle e_m \Big| \sum_n c_n e_n \Big\rangle \overset{(1)}{=} \sum_n c_n \langle e_m \,|\, e_n \rangle \overset{(2)}{=} \sum_n c_n \delta_{mn} \overset{(3)}{=} c_m.$$

(1) linearity in the second slot, so the constants come out unconjugated. (2) orthonormality. (3) every term with $n \neq m$ is multiplied by zero; one survives.

Example 4.2

$\psi = (2,\, 3i,\, -1)^{\mathsf{T}}$ in the standard basis of $\mathbb{C}^3$:

$$\langle e_2 \,|\, \psi \rangle = 0^* \cdot 2 + 1^* \cdot 3i + 0^* \cdot (-1) = 3i = c_2.$$

Example 4.3

$\psi = \binom{3}{5}$ in the two bases of Example 4.1. In the first, $c_1 = 3$, $c_2 = 5$. In the second,

$$c_1' = \tfrac{1}{\sqrt{2}}(3+5) = 4\sqrt{2}, \qquad c_2' = \tfrac{1}{\sqrt{2}}(-3+5) = \sqrt{2},$$

and $4\sqrt{2} \cdot \frac{1}{\sqrt{2}}\binom{1}{1} + \sqrt{2} \cdot \frac{1}{\sqrt{2}}\binom{-1}{1} = \binom{4}{4} + \binom{-1}{1} = \binom{3}{5}$.

4.2 For functions

$$\langle \phi_m \,|\, \phi_n \rangle = \int_0^L \phi_m^* \phi_n \mathrm{d}x = \delta_{mn}, \qquad \boxed{c_n = \int_0^L \phi_n(x)^*\, \psi(x)\, \mathrm{d}x}$$

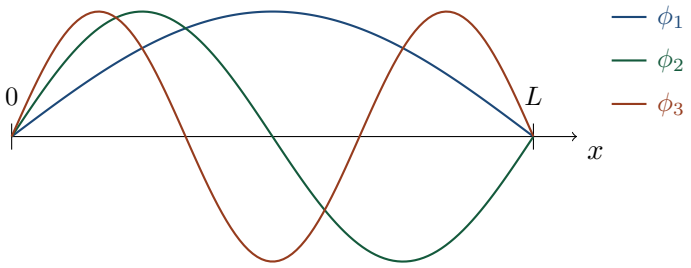
This is simultaneously the Fourier coefficient formula and the formula for expanding a state in energy eigenstates.

Example 4.4

$\phi_n = \sqrt{2/L}\sin(n\pi x/L)$. These are real, so

$$\langle \phi_m \,|\, \phi_n \rangle = \frac{2}{L}\int_0^L \sin\frac{m\pi x}{L}\sin\frac{n\pi x}{L}\mathrm{d}x = \frac{1}{L}\int_0^L \left[\cos\frac{(m-n)\pi x}{L} - \cos\frac{(m+n)\pi x}{L}\right]\mathrm{d}x.$$

For integer $k \neq 0$, $\int_0^L \cos(k\pi x/L)\mathrm{d}x = \frac{L}{k\pi}\sin(k\pi) = 0$. Since $m+n \geq 2$ the second term always dies; the first dies unless $m = n$, where the integrand is 1 and the integral is L. So $\langle \phi_m \,|\, \phi_n \rangle = \delta_{mn}$, and the prefactor $\sqrt{2/L}$ was chosen to make it 1 rather than $L/2$.



Example 4.5

Expand the normalised $\psi = \sqrt{30/L^5}\, x(L-x)$ in the basis above. With $a = n\pi/L$ and the standard antiderivatives

$$\int x\sin(ax)\mathrm{d}x = \frac{\sin ax}{a^2} - \frac{x\cos ax}{a}, \qquad \int x^2\sin(ax)\mathrm{d}x = \frac{2x\sin ax}{a^2} - \left(\frac{x^2}{a} - \frac{2}{a^3}\right)\cos ax,$$

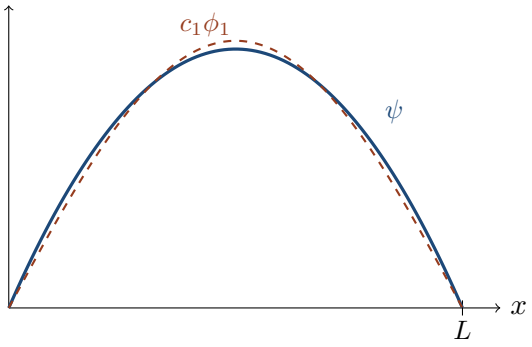
evaluated at $x = L$ where $\sin(n\pi) = 0$ and $\cos(n\pi) = (-1)^n$,

$$\int_0^L x(L-x)\sin(ax)\mathrm{d}x = \frac{2}{a^3}\left(1-(-1)^n\right) = \begin{cases} 4L^3/(n^3\pi^3), & n \text{ odd} \\ 0, & n \text{ even} \end{cases}$$

the L^2/a terms having cancelled. So for odd n,

$$c_n = \sqrt{\frac{60}{L^6}} \cdot \frac{4L^3}{n^3\pi^3} = \frac{8\sqrt{15}}{(n\pi)^3}.$$

$c_1 \approx 0.9993$, so an energy measurement returns the ground state value 99.85% of the time: the parabola and the first sine are nearly the same shape.



5 Change of basis

Put the new basis vectors of Example 4.1 in the columns of a matrix:

$$R = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} = \begin{pmatrix} \cos 45^\circ & -\sin 45^\circ \\ \sin 45^\circ & \cos 45^\circ \end{pmatrix}.$$

The two orthonormal bases are related by a rotation of the axes. Orthonormal columns give $R^\mathsf{T} R = I$ and $\det R = 1$.

A complex matrix with $U^\dagger U = I$ is **unitary**, and

$$\langle U\psi \,|\, U\phi\rangle = \langle \psi \,|\, U^\dagger U\phi\rangle = \langle \psi \,|\, \phi\rangle.$$

Overlaps, and hence all probabilities, are unchanged by a change of basis.

Example 5.1

$$R^\mathsf{T}\begin{pmatrix} 3 \\ 5 \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}\begin{pmatrix} 3 \\ 5 \end{pmatrix} = \begin{pmatrix} 4\sqrt{2} \\ \sqrt{2} \end{pmatrix},$$

matching Example 4.3. The entries of R^T are the overlaps $\langle f_m \,|\, e_n\rangle$: the projection trick as a matrix.

Matrix of an operator

$$A_{mn} = \langle m \,|\, \hat{A} \,|\, n\rangle, \qquad A' = U^\dagger A U \text{ under a change of basis.}$$

Eigenvalues, trace and determinant are unchanged. Matrix entries belong to the operator *and* the basis; eigenvalues belong to the operator.

Example 5.2

$\hat{A} = \left(\begin{smallmatrix} 0 & 1 \\ 1 & 0 \end{smallmatrix}\right)$ in basis (a). In basis (b),

$$R^{\mathsf{T}} A R = \frac{1}{2}\begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

An operator is diagonal in the basis of its own eigenvectors.

6 Bras

Definition

A dual vector is a map $f : V \to \mathbb{C}$ that eats a vector and returns one number, and is linear:

$$f(au + bv) = af(u) + bf(v).$$

These maps form a vector space themselves, the dual space V^*.

A dual vector is a 'procedure', not a thing sitting in space.

Example 6.1

On $\mathbb{C}^2$ define $f(v) := 2v_1 + 3v_2$. It returns a number: $f\binom{1}{4} = 14$. It is linear:

$$f(au + bv) = 2(au_1 + bv_1) + 3(au_2 + bv_2) = af(u) + bf(v).$$

And it is a row times a column,

$$f(v) = \begin{pmatrix} 2 & 3 \end{pmatrix}\begin{pmatrix} v_1 \\ v_2 \end{pmatrix},$$

with $(1 \times 2)(2 \times 1) = 1 \times 1$. As you know, Kets are columns, Bras are rows (wait do we have to capitalize this stuff).

Setting $w = \binom{2}{3}$ gives $\langle w \,|\, v\rangle = 2^* v_1 + 3^* v_2 = f(v)$, so f is "take the overlap with w". That is general.

Riesz

Every dual vector on a Hilbert space is $\langle w \,|\, \cdot\rangle$ for a unique w. So $\mathcal{H}^*$ is a copy of $\mathcal{H}$! We have one map per vector, which is why bras can be labelled by kets.

Dirac notation

$|\psi\rangle$ is the state, a column. $\langle\psi|$ is the map "overlap me with what comes next", a row. Together they give a number, $\langle\psi||\phi\rangle = \langle\psi \,|\, \phi\rangle$.
Ket to bra: transpose and conjugate every entry. For functions, $\langle f|$ is the instruction $g \mapsto \int f^* g \, \mathrm{d}x$, not a function.

Example 6.2

$|\psi\rangle = \binom{1+i}{2}$, $|\phi\rangle = \binom{i}{1}$, so $\langle\psi| = (1 - i \;\; 2)$.

$$\langle\psi \,|\, \phi\rangle = (1-i)i + 2 = i - i^2 + 2 = 3 + i, \qquad \langle\phi \,|\, \psi\rangle = (-i)(1+i) + 2 = 3 - i = \langle\psi \,|\, \phi\rangle^*.$$

Feeding $|\psi\rangle$ to its own bra,

$$\langle\psi\,|\,\psi\rangle = (1-i)(1+i) + 4 = 2 + 4 = 6, \qquad \|\psi\| = \sqrt{6}.$$

Real and positive. Without the conjugate it would have been $(1+i)^2 + 4 = 4 + 2i$.

Example 6.3

The bra of $c|\psi\rangle$ is $c^*\langle\psi|$. With $c = 2i$,

$$2i|\psi\rangle = \begin{pmatrix} 2i-2 \\ 4i \end{pmatrix} \implies \begin{pmatrix} -2i-2 & -4i \end{pmatrix} = -2i\begin{pmatrix} 1-i & 2 \end{pmatrix} = (2i)^*\langle\psi|.$$

Why keep them apart

In $\langle\psi\,|\,\hat{A}\,|\,\phi\rangle$ the operator acts rightwards on the ket, and the result is fed to the map $\langle\psi|$. Scalars come out unstarred from the right and starred from the left. Row times column is a number; column times row, $|n\rangle\langle n|$, is a matrix.

Part II. Operators

7 Operators and matrices

An operator maps $\mathcal{H} \to \mathcal{H}$: it eats a vector and returns a vector. Linear means $\hat{A}(a|u\rangle + b|v\rangle) = a\hat{A}|u\rangle + b\hat{A}|v\rangle$. All operators here are linear.

Example 7.1

$\hat{A} = \left(\begin{smallmatrix} 0 & 1 \\ 1 & 0 \end{smallmatrix}\right)$ swaps components. $\hat{x}\psi(x) = x\psi(x)$. $\hat{p}\psi = -i\hbar\, \mathrm{d}\psi/\mathrm{d}x$. The double-well Hamiltonian $\hat{H} = \left(\begin{smallmatrix} E_0 & T \\ T & E_0 \end{smallmatrix}\right)$ with T real and negative.

Reading off the matrix

$A_{mn} = \langle m \,|\, \hat{A} \,|\, n\rangle$. Column n is the list of components of $\hat{A}|n\rangle$: act on each basis vector and write the answer as a column.

Example 7.2

In W4.1, $\hat{A}|\phi_L\rangle = -a|\phi_L\rangle$ and $\hat{A}|\phi_R\rangle = +a|\phi_R\rangle$, so

$$A_{11} = -a\langle\phi_L \,|\, \phi_L\rangle = -a, \qquad A_{21} = -a\langle\phi_R \,|\, \phi_L\rangle = 0, \qquad \hat{A} \leftrightarrow \begin{pmatrix} -a & 0 \\ 0 & a \end{pmatrix}.$$

Diagonal, with eigenvalues on the diagonal, because this is its own eigenbasis.

8 Eigenvalues

$\hat{A}|v\rangle = \lambda|v\rangle$ with $|v\rangle \neq 0$: acting with $\hat{A}$ rescales the vector without rotating it.

Recipe

1. $\det(A - \lambda I) = 0$, a polynomial of degree n. (Reason in Part 0.)
2. Solve for the roots.
3. For each root solve $(A - \lambda I)v = 0$
4. Normalise.

Free checks: $\sum_n \lambda_n = \operatorname{Tr} A$ and $\prod_n \lambda_n = \det A$.

For 2×2 the characteristic equation is always

$$\lambda^2 - (\operatorname{Tr} A)\lambda + \det A = 0, \qquad \lambda_\pm = \frac{\operatorname{Tr} A \pm \sqrt{(\operatorname{Tr} A)^2 - 4 \det A}}{2}.$$

Example 8.1

$A = \left(\begin{smallmatrix} 0 & 1 \\ 1 & 0 \end{smallmatrix}\right)$. Then $\det(A - \lambda I) = \lambda^2 - 1$, so $\lambda = \pm 1$, consistent with $\operatorname{Tr} A = 0$ and $\det A = -1$. For $\lambda = +1$: $-v_1 + v_2 = 0$, both rows agreeing, so $v \propto \binom{1}{1}$. For $\lambda = -1$: $v \propto \binom{1}{-1}$. Normalised,

$$v_+ = \tfrac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}, \qquad v_- = \tfrac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}.$$

This is the rotated basis of Example 4.1, and A is σ_x, so these are the spin-x states.

Example 8.2

$\hat{H} = \left(\begin{smallmatrix} E_0 & T \\ T & E_0 \end{smallmatrix}\right)$, W4.1(a). With $\mathrm{Tr} = 2E_0$ and $\det = E_0^2 - T^2$,

$$\lambda^2 - 2E_0\lambda + (E_0^2 - T^2) = 0 \implies \lambda = E_0 \pm T.$$

Eigenvectors as in Example 8.1, because adding $E_0 I$ shifts every eigenvalue and changes no eigenvector. Since $T < 0$,

$$E_g = E_0 + T \text{ with } |\phi_g\rangle = \tfrac{1}{\sqrt{2}}(|\phi_L\rangle + |\phi_R\rangle), \qquad E_e = E_0 - T \text{ with } |\phi_e\rangle = \tfrac{1}{\sqrt{2}}(|\phi_L\rangle - |\phi_R\rangle).$$

The symmetric combination is lower *because* $T < 0$, not by a general rule: this is arbitrary, if we flip the sign of T the labels would swap.

Example 8.3

$\hat{L}_x = \frac{\hbar}{\sqrt{2}} S$ with $S = \left(\begin{smallmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{smallmatrix}\right)$, W5.3. Expanding along the first row,

$$\det(S - \mu I) = -\mu(\mu^2 - 1) + \mu = -\mu(\mu^2 - 2),$$

so $\mu = 0, \pm\sqrt{2}$ and the eigenvalues of $\hat{L}_x$ are $-\hbar, 0, +\hbar$: the same three values as $\hat{L}_z$, since no axis is special.
For $\mu = \sqrt{2}$ the rows read $-\sqrt{2}v_1 + v_2 = 0$, $v_1 - \sqrt{2}v_2 + v_3 = 0$, $v_2 - \sqrt{2}v_3 = 0$. The first gives $v_2 = \sqrt{2}v_1$, the third gives $v_3 = v_1$, and the middle is then automatic. So

$$|{+x}\rangle = \tfrac{1}{2}(1, \sqrt{2}, 1)^{\mathsf{T}}, \quad |0_x\rangle = \tfrac{1}{\sqrt{2}}(1, 0, -1)^{\mathsf{T}}, \quad |{-x}\rangle = \tfrac{1}{2}(1, -\sqrt{2}, 1)^{\mathsf{T}}.$$

$\mathrm{Tr}\, S = 0 = \sqrt{2} + 0 - \sqrt{2}$, and $\langle {+x} \,|\, 0_x\rangle = \frac{1}{2\sqrt{2}} - \frac{1}{2\sqrt{2}} = 0$.

Example 8.4

$\hat{H}_0 = E_0 I$ on $\mathbb{C}^2$: every vector is an eigenvector, the characteristic equation $(E_0 - \lambda)^2 = 0$ has a double root, and the eigenspace is the whole space. This is W4.1 Q3; see Section 18.

Example 8.5, homework A.28

$$T = \begin{pmatrix} 1 & 1-i \\ 1+i & 0 \end{pmatrix}.$$

$T^\dagger$ sends the $(2,1)$ entry to $(1+i)^* = 1 - i$, so $T^\dagger = T$ and the eigenvalues must be real. With $\mathrm{Tr}\, T = 1$ and $\det T = -(1-i)(1+i) = -2$,

$$\lambda^2 - \lambda - 2 = 0 \implies \lambda = 2, -1.$$

For $\lambda = 2$ the first row gives $v_1 = (1-i)v_2$, so $v = (1-i, 1)^{\mathsf{T}}$ with $\|v\|^2 = 2 + 1 = 3$. For $\lambda = -1$, $2v_1 = -(1-i)v_2$, so with $v_2 = 2$, $v = (i-1, 2)^{\mathsf{T}}$ and $\|v\|^2 = 2 + 4 = 6$:

$$\alpha^{(1)} = \tfrac{1}{\sqrt{3}} \begin{pmatrix} 1-i \\ 1 \end{pmatrix}, \qquad \alpha^{(2)} = \tfrac{1}{\sqrt{6}} \begin{pmatrix} i-1 \\ 2 \end{pmatrix}.$$

Orthogonal (as we will see in Theorem B below): $(1+i)(i-1)+2 = (i-1+i^2-i)+2 = -2+2 = 0$.

8.1 Degeneracy

Two eigenvectors sharing an eigenvalue span an eigenspace, and any orthonormal basis of it is an equally good set of eigenvectors.

mathsy stuff

Vectors falling out of a degenerate system need not be mutually orthogonal, so we run 'Gram-Schmidt':

$$|u_1\rangle = |v_1\rangle, \qquad |u_2\rangle = |v_2\rangle - \frac{\langle u_1 \,|\, v_2\rangle}{\langle u_1 \,|\, u_1\rangle}|u_1\rangle,$$

then normalise. Orthogonality across different eigenvalues is automatic; within one eigenvalue it is a choice.

9 Hermitian and unitary

Adjoint

$\hat{A}^\dagger$ is defined by

$$\langle \phi \,|\, \hat{A}\psi\rangle = \langle \hat{A}^\dagger \phi \,|\, \psi\rangle \quad \text{for all } \psi, \phi.$$

Crossing the bar turns an operator into its adjoint. For matrices, $\hat{A}^\dagger = \hat{A}^{*\mathsf{T}}$. Hermitian means $\hat{A}^\dagger = \hat{A}$.

Rules: $(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger$, $(c\hat{A})^\dagger = c^*\hat{A}^\dagger$.

Example 9.1

$\left(\begin{smallmatrix} 2 & 1-i \\ 1+i & 3 \end{smallmatrix}\right)$ is Hermitian: real diagonal, off-diagonal entries conjugate. $\left(\begin{smallmatrix} 0 & 1 \\ -1 & 0 \end{smallmatrix}\right)^\dagger = -\left(\begin{smallmatrix} 0 & 1 \\ -1 & 0 \end{smallmatrix}\right)$ is anti-Hermitian, and i times it is Hermitian.

Example 9.2

On functions vanishing at infinity,

$$\langle \phi \,|\, \tfrac{\mathrm{d}}{\mathrm{d}x}\psi\rangle = \underbrace{[\phi^*\psi]_{-\infty}^{\infty}}_{0} - \int \frac{\mathrm{d}\phi^*}{\mathrm{d}x}\psi \mathrm{d}x = \langle -\tfrac{\mathrm{d}}{\mathrm{d}x}\phi \,|\, \psi\rangle,$$

so $(\mathrm{d}/\mathrm{d}x)^\dagger = -\mathrm{d}/\mathrm{d}x$. Since the adjoint conjugates scalars,

$$\hat{p}^\dagger = (-i\hbar)^* \left(-\frac{\mathrm{d}}{\mathrm{d}x}\right) = -i\hbar\frac{\mathrm{d}}{\mathrm{d}x} = \hat{p}.$$

The $-i$ in the momentum operator is there to make it Hermitian!

Theorem A: real eigenvalues

For $\hat{A}^\dagger = \hat{A}$ and $\hat{A}|\psi\rangle = \lambda|\psi\rangle$, compute $\langle \psi \,|\, \hat{A}\psi\rangle$ twice:

$$\langle \psi \,|\, \hat{A}\psi\rangle = \lambda\langle \psi \,|\, \psi\rangle, \qquad \langle \psi \,|\, \hat{A}\psi\rangle = \langle \hat{A}\psi \,|\, \psi\rangle = \lambda^*\langle \psi \,|\, \psi\rangle,$$

the star appearing because the scalar left from the left slot. Subtracting, $(\lambda - \lambda^*)\langle \psi \,|\, \psi\rangle = 0$ with $\langle \psi \,|\, \psi\rangle > 0$, so λ is real.

Measurement outcomes are readings, so they *have* to be real! That is why observables are required to be Hermitian.

Theorem B: orthogonal eigenvectors

For $\hat{A}|\psi\rangle = \lambda|\psi\rangle$ and $\hat{A}|\chi\rangle = \mu|\chi\rangle$ with $\lambda \neq \mu$,

$$\langle\chi\,|\,\hat{A}\psi\rangle = \lambda\langle\chi\,|\,\psi\rangle \quad \text{and} \quad \langle\chi\,|\,\hat{A}\psi\rangle = \langle\hat{A}\chi\,|\,\psi\rangle = \mu\langle\chi\,|\,\psi\rangle,$$

so $(\lambda-\mu)\langle\chi\,|\,\psi\rangle = 0$ and $\langle\chi\,|\,\psi\rangle = 0$.

The chain (*not* by fleetwood mac)

$$\begin{aligned}\text{Hermitian} \;&\Rightarrow\; \text{orthonormal eigenbasis} \;\Rightarrow\; \text{projection trick works}\\ &\Rightarrow\; c_n = \langle n\,|\,\psi\rangle \;\Rightarrow\; P_n = |c_n|^2.\end{aligned}$$

9.1 Unitary operators

$\hat{U}^\dagger\hat{U} = I$, so $\hat{U}^{-1} = \hat{U}^\dagger$ and inner products are preserved. Recall two appearances of unitary operators: a change of orthonormal basis (Section 5), and time evolution $\hat{U}(t) = e^{-i\hat{H}t/\hbar}$, which is unitary because $\hat{H}$ is Hermitian, which is why total probability stays at one.

Aside

$e^{\hat{M}}$ is defined by the same Taylor series as the ordinary exponential. For a diagonal matrix it exponentiates each entry, which is why evolving a state is easy in the energy basis:)

10 Completeness

Substituting $c_n = \langle n\,|\,\psi\rangle$ into $|\psi\rangle = \sum_n c_n|n\rangle$,

$$|\psi\rangle = \sum_n \langle n\,|\,\psi\rangle|n\rangle = \sum_n |n\rangle\langle n\,|\,\psi\rangle = \left(\sum_n |n\rangle\langle n|\right)|\psi\rangle,$$

the middle step only moving the number $\langle n\,|\,\psi\rangle$ past the ket. Since this holds for all $|\psi\rangle$,

$$\boxed{\sum_n |n\rangle\langle n| = I}$$

Each $|n\rangle\langle n|$ is a column times a row, so a matrix: the projector onto that direction.

Example 10.1

$$|1\rangle\langle 1| = \begin{pmatrix}1 & 0\\ 0 & 0\end{pmatrix}, \qquad |2\rangle\langle 2| = \begin{pmatrix}0 & 0\\ 0 & 1\end{pmatrix}, \qquad |1\rangle\langle 1| + |2\rangle\langle 2| = I.$$

$|1\rangle\langle 1|\binom{3}{5} = \binom{3}{0}$: it keeps the part along $|1\rangle$. Projectors satisfy $\hat{P}^2 = \hat{P}$.

A very typical trick is to insert I anywhere and then write as $\sum_n |n\rangle\langle n|$ in whichever basis is convenient.

11 Commutators

$$[\,\hat{A},\hat{B}\,] := \hat{A}\hat{B} - \hat{B}\hat{A},$$

an operator, not a number. Rules:

$$[\,\hat{A},\hat{B}\,] = -[\,\hat{B},\hat{A}\,], \quad [\,\hat{A}\hat{B},\hat{C}\,] = \hat{A}[\,\hat{B},\hat{C}\,] + [\,\hat{A},\hat{C}\,]\hat{B}, \quad [\,\hat{A},\hat{B}\hat{C}\,] = \hat{B}[\,\hat{A},\hat{C}\,] + [\,\hat{A},\hat{B}\,]\hat{C}.$$

Anything proportional to I commutes with everything.

Example 11.1

Acting on a test function:

$$[\,\hat{x},\hat{p}\,]\psi = -i\hbar x\psi' + i\hbar(x\psi)' = -i\hbar x\psi' + i\hbar(\psi + x\psi') = i\hbar\psi,$$

so $[\,\hat{x},\hat{p}\,] = i\hbar$.

Aside

No finite matrices satisfy $[\,A,B\,] = i\hbar I$: the trace of a commutator is zero since $\mathrm{Tr}(AB) = \mathrm{Tr}(BA)$, while $\mathrm{Tr}(i\hbar I) = i\hbar n \neq 0$. Position and momentum need an infinite-dimensional space.

Example 11.2

W4.1(c), with $\hat{A} = \left(\begin{smallmatrix} -a & 0 \\ 0 & a \end{smallmatrix}\right)$. Since $\hat{H}_0 = E_0 I$, $[\,\hat{A},\hat{H}_0\,] = 0$. For $\hat{H}$,

$$\hat{A}\hat{H} = \begin{pmatrix} -aE_0 & -aT \\ aT & aE_0 \end{pmatrix}, \quad \hat{H}\hat{A} = \begin{pmatrix} -aE_0 & aT \\ -aT & aE_0 \end{pmatrix}, \quad [\,\hat{A},\hat{H}\,] = \begin{pmatrix} 0 & -2aT \\ 2aT & 0 \end{pmatrix}.$$

All of it comes from the off-diagonal coupling T. Check: the commutator of two Hermitian operators is anti-Hermitian, so a real symmetric answer here would be wrong.

11.1 What a commutator means

Compatibility

$$[\,\hat{A},\hat{B}\,] = 0 \iff \hat{A} \text{ and } \hat{B} \text{ have a common orthonormal eigenbasis.}$$

There *exists* a basis of joint eigenvectors. It is not true that every eigenvector of one is an eigenvector of the other, and that fails whenever one of them is degenerate (Section 18).

Example 11.3, Griffiths 3.16

If $[\,\hat{P},\hat{Q}\,] \neq 0$ there is no *complete* set of common eigenfunctions. Suppose $\{f_n\}$ were one, with $\hat{P}f_n = a_n f_n$ and $\hat{Q}f_n = b_n f_n$. Then

$$[\,\hat{P},\hat{Q}\,]f_n = (b_n a_n - a_n b_n)f_n = 0,$$

numbers commuting. Completeness gives $[\,\hat{P},\hat{Q}\,]\psi = 0$ for every ψ, so the commutator is the zero operator.
Non-commuting operators can still share one or two eigenvectors: $\hat{L}_z$ and $\hat{L}_x$ both annihilate $|0\,0\rangle$. What they cannot share is a full basis.

Measure $\hat{A}$, then $\hat{B}$, then $\hat{A}$

With no time for evolution in between: if the two commute, the third result repeats the first with certainty. If they do not, the middle measurement collapses the state onto an eigenvector of $\hat{B}$, which is generally not one of $\hat{A}$. again.

Example 11.4

W4.1. Measure $\hat{A}$, get $-a$, so the state is $|\phi_L\rangle = \frac{1}{\sqrt{2}}(|\phi_g\rangle + |\phi_e\rangle)$. Measuring $\hat{H}$ gives E_g or E_e with probability $\frac{1}{2}$ each. From either, measuring $\hat{A}$ again returns $-a$ with probability $|\langle\phi_L\,|\,\phi_g\rangle|^2 = \frac{1}{2}$. So

$$P(\text{third} = \text{first}) = \tfrac{1}{2},$$

which is not zero. Thus, non-commuting does not mean *guaranteed* to differ.
With $\hat{H}_0$ instead, $|\phi_L\rangle$ is already an eigenvector, the middle measurement changes nothing, and the third result is $-a$ with certainty.
As $T \to 0$ the two operators almost commute, yet the eigenvectors of $\hat{H}$ are $(|\phi_L\rangle \pm |\phi_R\rangle)/\sqrt{2}$ for every $T \neq 0$, so the probability stays at $\frac{1}{2}$ all the way down and jumps to 1 only at $T = 0$, where $\hat{H}$ becomes degenerate. The commutator says the eigenbases differ; the overlaps say by how much.

Example 11.5

W5 Q9 and Q10, using Example 8.3.
$\hat{L}_z \to \hat{L}^2 \to \hat{L}_z$. On this space $\hat{L}^2 = 2\hbar^2 I$, so $|+z\rangle$ is already an eigenvector: the middle measurement returns $2\hbar^2$ and changes nothing, and the third gives $+\hbar$ with certainty.
$\hat{L}_z \to \hat{L}_x \to \hat{L}_z$. From $|+z\rangle = (1,0,0)^{\mathsf{T}}$,

$$P(+\hbar) = \left|\tfrac{1}{2}\right|^2 = \tfrac{1}{4}, \quad P(0) = \left|\tfrac{1}{\sqrt{2}}\right|^2 = \tfrac{1}{2}, \quad P(-\hbar) = \tfrac{1}{4}.$$

From $|+x\rangle$ the $\hat{L}_z$ probabilities are $\frac{1}{4}, \frac{1}{2}, \frac{1}{4}$; from $|0_x\rangle$ they are $\frac{1}{2}, 0, \frac{1}{2}$; from $|-x\rangle$ again $\frac{1}{4}, \frac{1}{2}, \frac{1}{4}$. Multiplying along branches and adding,

$$P(+\hbar) = \tfrac{1}{16} + \tfrac{1}{4} + \tfrac{1}{16} = \tfrac{3}{8}, \qquad P(0) = \tfrac{1}{8} + 0 + \tfrac{1}{8} = \tfrac{1}{4}, \qquad P(-\hbar) = \tfrac{3}{8}.$$

Starting from certainty, two measurements leave a $\frac{3}{8}$ chance of the original value and a $\frac{3}{8}$ chance of its opposite.

11.2 Uncertainty

$$\Delta A = \sqrt{\langle \hat{A}^2\rangle - \langle \hat{A}\rangle^2}, \qquad \Delta A\,\Delta B \geq \tfrac{1}{2}\left|\left\langle [\,\hat{A}, \hat{B}\,]\right\rangle\right|.$$

With $[\,\hat{x}, \hat{p}\,] = i\hbar$ this is $\Delta x \Delta p \geq \hbar/2$. Compatible observables have zero on the right and can both be 'sharp'.

Example 11.6

W5 Q4, state $|1,-1\rangle$. Here $\langle \hat{L}_z\rangle = -\hbar$ and $\langle \hat{L}_z^2\rangle = \hbar^2$, so $\Delta L_z = 0$. By symmetry $\langle \hat{L}_x\rangle = \langle \hat{L}_y\rangle = 0$ and $\langle \hat{L}_x^2\rangle = \langle \hat{L}_y^2\rangle$, while

$$\langle \hat{L}_x^2\rangle + \langle \hat{L}_y^2\rangle = \langle \hat{L}^2\rangle - \langle \hat{L}_z^2\rangle = 2\hbar^2 - \hbar^2 = \hbar^2,$$

so $\Delta L_x = \Delta L_y = \hbar/\sqrt{2} \approx 0.71\hbar$.

Spread is not average

$\langle \hat{L}_x \rangle = 0$ does not give $\Delta L_x = 0$. They coincide only in an eigenstate.

11.3 How averages move

With $|\dot{\psi}\rangle = \frac{1}{i\hbar}\hat{H}|\psi\rangle$, whose bra is $\langle\dot{\psi}| = \frac{i}{\hbar}\langle\psi|\hat{H}$ since the scalar conjugates,

$$\frac{\mathrm{d}\langle\hat{Q}\rangle}{\mathrm{d}t} = \langle\dot{\psi}\,|\,\hat{Q}\psi\rangle + \langle\psi\,|\,\hat{Q}\dot{\psi}\rangle = \frac{i}{\hbar}\left\langle [\,\hat{H},\hat{Q}\,]\right\rangle,$$

plus $\langle\partial\hat{Q}/\partial t\rangle$ if $\hat{Q}$ depends on time explicitly.

Conserved means commuting

$\langle\hat{Q}\rangle$ is constant for every state exactly when $[\,\hat{H},\hat{Q}\,] = 0$.

Example 11.7, homework 3.18

$\hat{Q} = I$: normalisation is conserved. $\hat{Q} = \hat{H}$: energy is conserved.
$\hat{Q} = \hat{x}$: the potential commutes with $\hat{x}$, and

$$[\,\hat{p}^2,\hat{x}\,] = \hat{p}[\,\hat{p},\hat{x}\,] + [\,\hat{p},\hat{x}\,]\hat{p} = -2i\hbar\hat{p},$$

so $[\,\hat{H},\hat{x}\,] = -i\hbar\hat{p}/m$ and $\mathrm{d}\langle\hat{x}\rangle/\mathrm{d}t = \langle\hat{p}\rangle/m$.
$\hat{Q} = \hat{p}$: only the potential contributes, and $[\,f(\hat{x}),\hat{p}\,] = i\hbar f'$ gives $\mathrm{d}\langle\hat{p}\rangle/\mathrm{d}t = -\langle V'\rangle$.
Those last two are Ehrenfest's theorem:)

Part III. Measurement

12 The rules

Postulates

With $\hat{A}$ an observable, $\{|n\rangle\}$ its orthonormal eigenbasis, λ_n its real eigenvalues, and $|\psi\rangle = \sum_n c_n|n\rangle$ normalised with $c_n = \langle n\,|\,\psi\rangle$:

1. a state is a normalised vector, defined up to an overall phase;
2. every measurable quantity is a Hermitian operator;
3. the only outcomes are the eigenvalues λ_n;
4. $P(\lambda_n) = |c_n|^2 = |\langle n\,|\,\psi\rangle|^2$;
5. immediately after, the state is $|n\rangle$ (degenerate case in Section 18);
6. between measurements, $i\hbar\,\mathrm{d}|\psi\rangle/\mathrm{d}t = \hat{H}|\psi\rangle$.

Two consequences follow from orthonormality alone.

Probabilities sum to one.

$$1 = \langle\psi\,|\,\psi\rangle = \sum_{m,n} c_m^* c_n \langle m\,|\,n\rangle = \sum_{m,n} c_m^* c_n \delta_{mn} = \sum_n |c_n|^2,$$

the star on c_m coming from the left slot. This is Parseval's theorem.

Expectation values.

$$\langle\psi\,|\,\hat{A}\,|\,\psi\rangle = \sum_{m,n} c_m^* c_n \lambda_n \langle m\,|\,n\rangle = \sum_n \lambda_n |c_n|^2,$$

so the compact formula and "outcomes weighted by probabilities" are the same statement. For a wave function,

$$\langle\hat{A}\rangle = \int \psi^*\,(\hat{A}\psi)\,\mathrm{d}x,$$

with the operator between ψ^* and ψ. For $\hat{p}$ this matters: $\int \psi^*(-i\hbar\psi')\mathrm{d}x$ is not $-i\hbar\int(\psi^*\psi)'\mathrm{d}x$, which is zero.

Example 12.1

W5.3(c). $|\Psi_1\rangle = \sqrt{\tfrac{1}{8}}|{+z}\rangle + \sqrt{\tfrac{3}{8}}|0_z\rangle + \sqrt{\tfrac{4}{8}}|{-z}\rangle$, so the probabilities are read straight off and

$$\langle\hat{L}_z\rangle = \hbar\left(\tfrac{1}{8} - \tfrac{4}{8}\right) = -\tfrac{3}{8}\hbar.$$

For $\hat{L}_x$ that shortcut fails, since $\hat{L}_x$ is not diagonal here. Sandwich the matrix:

$$\langle\hat{L}_x\rangle = \frac{\hbar}{\sqrt{2}} \cdot 2\sqrt{\tfrac{3}{8}}\left(\sqrt{\tfrac{1}{8}} + \sqrt{\tfrac{4}{8}}\right) = \frac{3\sqrt{6}}{8}\hbar \approx 0.92\hbar.$$

Writing it as $\sum_m |c_m|^2(\cdots)$ would throw away the off-diagonal structure.

Example 12.2

W5.3(e). $|\Psi_3\rangle = 3i|{+z}\rangle + 2|0_z\rangle - i|{-z}\rangle$ is not normalised:

$$\langle\Psi_3\,|\,\Psi_3\rangle = 9 + 4 + 1 = 14,$$

noting $|3i|^2 = 9$, not -9. So

$$\langle \hat{L}_z \rangle = \frac{\hbar(9-1)}{14} = \frac{4}{7}\hbar.$$

Skipping the division gives $8\hbar$, larger than the biggest eigenvalue and so visibly impossible.

Two shortcuts

$\langle \hat{A} \rangle = \sum_n \lambda_n |c_n|^2$ needs $\{|n\rangle\}$ to be the eigenbasis *of* $\hat{A}$; otherwise sandwich the matrix. Remember (perhaps from the double slit experiment intuition) that amplitudes superpose, probabilities do not: $|c_1 + c_2|^2 \neq |c_1|^2 + |c_2|^2$ unless the cross term vanishes. That cross term is the interference (Section 16).

13 Time evolution

With $\hat{H}|n\rangle = E_n|n\rangle$,

$$|\psi(t)\rangle = \sum_n c_n e^{-iE_n t/\hbar}|n\rangle.$$

Energy probabilities are constant, since $|c_n e^{-iE_n t/\hbar}|^2 = |c_n|^2$. Everything that moves comes from relative phases between terms of different energy.

Example 13.1

W4.1(h) and (i). Start in the left well, $|\psi(0)\rangle = \frac{1}{\sqrt{2}}(|\phi_g\rangle + |\phi_e\rangle)$. The matrix elements of $\hat{A}$ in the energy basis are

$$\langle \phi_g \,|\, \hat{A} \,|\, \phi_g \rangle = \langle \phi_e \,|\, \hat{A} \,|\, \phi_e \rangle = 0, \qquad \langle \phi_g \,|\, \hat{A} \,|\, \phi_e \rangle = -a,$$

the diagonal ones vanishing because a stationary state of a symmetric double well sits equally in both wells. Then

$$\begin{aligned} \langle \hat{A} \rangle(t) &= \tfrac{1}{2}\left[(-a)e^{-i(E_e-E_g)t/\hbar} + (-a)e^{+i(E_e-E_g)t/\hbar}\right] \\ &= -a\cos\left(\frac{(E_e-E_g)t}{\hbar}\right) = -a\cos\left(\frac{2|T|t}{\hbar}\right), \end{aligned}$$

using $E_e - E_g = -2T = 2|T|$. The particle starts fully left, tunnels fully right, and returns, at angular frequency $2|T|/\hbar$.
The diagonal elements set the constant part and the off-diagonal ones drive the motion. Only the energy difference appears, which is why shifting $\hat{H}$ by a constant changes nothing observable.

Example 13.2

W5.3(g), $\hat{H} = \gamma B \hat{L}_z$. For $|\Psi_5\rangle = \frac{1}{\sqrt{2}}(|{+z}\rangle + |0_z\rangle)$ the $|0_z\rangle$ phase is $e^0 = 1$, so

$$|\Psi(t)\rangle = \tfrac{1}{\sqrt{2}}\left(e^{-i\gamma Bt}|{+z}\rangle + |0_z\rangle\right),$$

$$\langle \hat{L}_x \rangle(t) = \frac{\hbar}{2\sqrt{2}}\left(e^{i\gamma Bt} + e^{-i\gamma Bt}\right) = \frac{\hbar}{\sqrt{2}}\cos(\gamma Bt).$$

Larmor precession at $\omega_L = \gamma B$, with $\langle \hat{L}_z \rangle$ constant because $[\,\hat{H}, \hat{L}_z\,] = 0$.

Evolve the state

Put the phases on the coefficients first, then sandwich the operator. Keep the $\hbar$: $E_n t/\hbar$ is what is dimensionless.

Part IV. The standard objects

14 Pauli matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \qquad \hat{S}_j = \tfrac{\hbar}{2}\sigma_j.$$

1. $\sigma_j^\dagger = \sigma_j$, so real eigenvalues.
2. $\operatorname{Tr}\sigma_j = 0$ and $\det\sigma_j = -1$, so by the trace and determinant checks the eigenvalues are $+1$ and -1 for all three: $\hat{S}_j$ gives $\pm\hbar/2$ along every axis.
3. $\sigma_j^2 = I$, so $\hat{S}_j^2 = \frac{\hbar^2}{4}I$ and a measurement of $\hat{S}_j^2$ always returns $\hbar^2/4$.
4. $\sigma_x\sigma_y = i\sigma_z$ and cyclic, from Example T.2.
5. $\sigma_j\sigma_k + \sigma_k\sigma_j = 2\delta_{jk}I$: they anticommute.
6. $[\,\sigma_x, \sigma_y\,] = 2i\sigma_z$, hence $[\,\hat{S}_x, \hat{S}_y\,] = i\hbar\hat{S}_z$.
7. Every Hermitian 2×2 matrix is $aI + b_x\sigma_x + b_y\sigma_y + b_z\sigma_z$ with a, b_j real.

Eigenvectors:

$$\sigma_z:\ \begin{pmatrix}1\\0\end{pmatrix},\ \begin{pmatrix}0\\1\end{pmatrix}; \qquad \sigma_x:\ \tfrac{1}{\sqrt{2}}\begin{pmatrix}1\\\pm 1\end{pmatrix}; \qquad \sigma_y:\ \tfrac{1}{\sqrt{2}}\begin{pmatrix}1\\\pm i\end{pmatrix}.$$

The σ_x pair was derived in Example 8.1. For σ_y and $\lambda = +1$ the first row gives $-v_1 - iv_2 = 0$, so $v_2 = iv_1$.

Example 14.1

From Examples 8.2 and 7.2,

$$\hat{H} = E_0 I + T\sigma_x, \qquad \hat{A} = -a\,\sigma_z,$$

so the commutator follows from rule 6 without multiplying anything:

$$[\,\hat{A}, \hat{H}\,] = -aT[\,\sigma_z, \sigma_x\,] = -2iaT\sigma_y = \begin{pmatrix} 0 & -2aT \\ 2aT & 0 \end{pmatrix},$$

matching Example 11.2. The eigenvalues follow too: σ_x has ± 1, so $\hat{H}$ has $E_0 \pm T$ with the σ_x eigenvectors.
Every two-level system is this one 2×2 problem with the axes relabelled: a spin in a field, the double well, ammonia, a two-state atom in a laser.

about spin

Guys don't take "spinning ball" literally physicists just be making up stuff: equating $\frac{2}{5}m_e r v$ to $\hbar/2$ at the classical electron radius gives a surface speed around $170c$.

Example 14.2

W5.2(e). $|\Psi_0\rangle = \sqrt{\frac{2}{3}}|\uparrow\rangle + i\sqrt{\frac{1}{3}}|\downarrow\rangle$ with $\hat{H} = -\gamma B_z\hat{S}_z$, so $\omega_L = \gamma B_z$. Since $\hat{S}_z$ is diagonal,

$$\langle\hat{S}_z\rangle = \tfrac{2}{3}\cdot\tfrac{\hbar}{2} - \tfrac{1}{3}\cdot\tfrac{\hbar}{2} = \tfrac{\hbar}{6}, \quad \text{constant.}$$

The transverse components come from the off-diagonal sandwich, $\langle\hat{S}_x\rangle = \hbar\,\mathrm{Re}(c_\uparrow^* c_\downarrow)$ and

$\langle \hat{S}_y \rangle = \hbar \,\mathrm{Im}(c_\uparrow^* c_\downarrow)$:

$$\langle \hat{S}_x \rangle = \frac{\sqrt{2}}{3}\hbar \sin(\omega_L t), \qquad \langle \hat{S}_y \rangle = \frac{\sqrt{2}}{3}\hbar \cos(\omega_L t).$$

Check: $\left(\frac{\hbar}{6}\right)^2 + \frac{2}{9}\hbar^2 = \frac{\hbar^2}{4}$, so the mean spin vector has full length $\hbar/2$ at all times, tilted at $\cos\theta = \frac{1/6}{1/2} = \frac{1}{3}$, about 70.5°. Dropping the i shifts the phase of the precession; using the same phase on both components makes it global and nothing precesses.

If you've ever seen an MRI machine

$hf = \gamma \hbar B_z$ for a proton gives 42.58 MHz per tesla. That number is the basis of magnetic resonance imaging and is printed on the side of clinical scanners.

15 The $l = 1$ matrices

In the $\hat{L}_z$ basis with eigenvalues $+\hbar, 0, -\hbar$:

$$\hat{L}_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad \hat{L}_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad \hat{L}_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix},$$

and $\hat{L}^2 = 2\hbar^2 I$.

- $\hat{L}^2 |l\, m\rangle = \hbar^2 l(l+1)|l\, m\rangle$, $\hat{L}_z |l\, m\rangle = \hbar m |l\, m\rangle$.
- $|\vec{L}| = \sqrt{2}\hbar$ exceeds the largest L_z of $\hbar$. If they were equal the vector would point exactly along z, giving $L_x = L_y = 0$ sharp, contradicting $[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z \neq 0$.
- $[\hat{L}^2, \hat{L}_j] = 0$, so $\hat{L}^2$ and one component can be sharp together; two components cannot.
- $\vec{n} \cdot \hat{\vec{L}}$ has spectrum $-\hbar, 0, +\hbar$ for every unit $\vec{n}$.
- $\hat{L}_x$ is real symmetric and $\hat{L}_y$ imaginary antisymmetric because $\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y$ are real in the standard phase convention.

Eigenvalues of a sum

For $\hat{L}_n = (\hat{L}_z + \hat{L}_x)/\sqrt{2}$ the outcomes are again $-\hbar, 0, +\hbar$, not $\pm\hbar/\sqrt{2}$. Adding eigenvalues is valid only for commuting operators. The classical projection $\hbar\cos\theta$ survives as the *expectation value*: from $|1, +1\rangle$ at 45° the probabilities are $\cos^4(\theta/2)$, $\frac{1}{2}\sin^2\theta$, $\sin^4(\theta/2)$, numerically 0.73, 0.25, 0.02, with mean $0.71\hbar$.

16 Symmetric and antisymmetric combinations

Two localised states $|\phi_L\rangle$, $|\phi_R\rangle$ and two combinations:

$$|\phi_g\rangle = \frac{|\phi_L\rangle + |\phi_R\rangle}{\sqrt{2}}, \qquad |\phi_e\rangle = \frac{|\phi_L\rangle - |\phi_R\rangle}{\sqrt{2}},$$

inverted by adding and subtracting:

$$|\phi_L\rangle = \frac{|\phi_g\rangle + |\phi_e\rangle}{\sqrt{2}}, \qquad |\phi_R\rangle = \frac{|\phi_g\rangle - |\phi_e\rangle}{\sqrt{2}}.$$

In the L, R basis position is sharp and energy is not; in the g, e basis the reverse.

Example 16.1

W4.1(f). With $|\Psi\rangle = \sqrt{\frac{1}{3}}|\phi_g\rangle + \sqrt{\frac{2}{3}}|\phi_e\rangle$,

$$|\Psi\rangle = \frac{\sqrt{\frac{1}{3}} + \sqrt{\frac{2}{3}}}{\sqrt{2}}|\phi_L\rangle + \frac{\sqrt{\frac{1}{3}} - \sqrt{\frac{2}{3}}}{\sqrt{2}}|\phi_R\rangle = \frac{1+\sqrt{2}}{\sqrt{6}}|\phi_L\rangle + \frac{1-\sqrt{2}}{\sqrt{6}}|\phi_R\rangle,$$

$$P(L) = \frac{(1+\sqrt{2})^2}{6} = \frac{3+2\sqrt{2}}{6} \approx 0.971, \qquad P(R) = \frac{3-2\sqrt{2}}{6} \approx 0.029,$$

summing to 1.

So how did we go from $\frac{1}{3}$ and $\frac{2}{3}$, to 0.97 and 0.03?

Signs. $|\phi_g\rangle$ contributes + to both wells; $|\phi_e\rangle$ contributes + on the left and − on the right. The left amplitudes reinforce, the right ones partly cancel.

Squaring. $\sqrt{1/3} = 0.577$ and $\sqrt{2/3} = 0.816$, so the left amplitude goes like 1.393 and the right like −0.239. A factor of about 5.8 in amplitude is a factor of about 34 in probability.

Probabilities do not add

Adding probabilities instead would give $\frac{1}{2}$ for each well, the classical answer. The gap between 0.971 and 0.5 is the cross term $2\,\mathrm{Re}(c_g^* c_e)$.

Example 16.2

W5.3(d). $|\Psi_2\rangle = \frac{1}{\sqrt{3}}(|+z\rangle + |0_z\rangle + |-z\rangle)$, measuring $\hat{L}_x$ with the eigenvectors of Example 8.3:

$$P(+\hbar) = \left|\tfrac{1}{\sqrt{3}}\left(\tfrac{1}{2} + \tfrac{1}{\sqrt{2}} + \tfrac{1}{2}\right)\right|^2 = \frac{(2+\sqrt{2})^2}{12} \approx 0.971, \quad P(0) = 0, \quad P(-\hbar) \approx 0.029.$$

The same numbers as Example 16.1, by the same mechanism: all three components add against $|+x\rangle$, whose entries are all positive, and partly cancel against $|-x\rangle$. The zero is structural: $|\Psi_2\rangle$ is symmetric under $z \to -z$ and $|0_x\rangle$ is antisymmetric.

17 Parity

Even and odd

f is even if $f(-x) = f(x)$, odd if $f(-x) = -f(x)$. Then

$$\int_{-a}^{a} f\,\mathrm{d}x = 0 \ (f \text{ odd}), \qquad \int_{-a}^{a} f\,\mathrm{d}x = 2\int_{0}^{a} f\,\mathrm{d}x \ (f \text{ even}),$$

and parities multiply like signs: even×even and odd×odd are even, even×odd is odd.

The odd case holds because substituting $x \to -x$ turns one half of the interval into minus the other. The interval must be symmetric about the centre of symmetry, and most functions are neither even nor odd.

Odd: x, x^3, $\sin x$, $\tan x$. Even: 1, x^2, $\cos x$, $|x|$, e^{-x^2}.

The parity operator is $\hat{\Pi}\psi(x) := \psi(-x)$, with $\hat{\Pi}^2 = I$, so its eigenvalues are ± 1: $+1$ for even functions, -1 for odd. If $V(-x) = V(x)$ then $[\hat{H}, \hat{\Pi}] = 0$ and the stationary states can be chosen with definite parity; when the spectrum is nondegenerate, they must be.

Example 17.1

W4.3(a). On $[-a/2, a/2]$ the states alternate: $\cos(n\pi x/a)$ for odd n (even parity), $\sin(n\pi x/a)$ for even n (odd parity). The ground state is even.

Example 17.2

The dipole operator $\hat{D} = e\hat{x}$ is odd.
Diagonal. For any state of definite parity, $\phi_n^* \phi_n$ is even, so $\phi_n^* x \phi_n$ is odd and $\langle \phi_n \,|\, \hat{x} \,|\, \phi_n \rangle = 0$. No stationary state of a symmetric well has a displaced average position.
Off-diagonal. If ϕ_n and ϕ_m have the same parity their product is even, the integrand is odd, and $\langle \phi_n \,|\, \hat{x} \,|\, \phi_m \rangle = 0$. Opposite parity gives something non-zero.
W4.3(d) follows: the oscillating part of $\langle \hat{D} \rangle(t)$ is carried by the off-diagonal elements (Example 13.1), and no oscillating dipole means no photon. From ϕ_4 (odd parity), ϕ_3 and ϕ_1 are allowed and ϕ_2 is forbidden, so the routes are $4 \to 1$ emitting $15E_1$, or $4 \to 3 \to 2 \to 1$ emitting $7E_1$, $5E_1$, $3E_1$. The step $3 \to 1$ is forbidden. In atoms the same argument with spherical harmonics gives $\Delta l = \pm 1$.

Example 17.3

$\psi = Ax(L - x)$ is symmetric about $L/2$, and ϕ_n is symmetric about $L/2$ for odd n and antisymmetric for even n. So $c_n = 0$ for even n, as computed in Example 4.5.

18 Degeneracy

For a degenerate eigenvalue the collapse uses the projector onto the eigenspace:

$$|\psi\rangle \longmapsto \frac{\hat{P}_n|\psi\rangle}{\|\hat{P}_n|\psi\rangle\|}, \qquad \hat{P}_n = \sum_k |n,k\rangle\langle n,k|, \qquad P(\lambda_n) = \|\hat{P}_n|\psi\rangle\|^2.$$

Example 18.1

W4.1 Q3. With $T = 0$, $\hat{H}_0 = E_0 I$ and the eigenspace is the whole space, so $\hat{P}_{E_0} = I$ and the state is untouched. There is no collapse onto $|\phi_L\rangle$ or $|\phi_R\rangle$, even though $[\,\hat{H}_0, \hat{A}\,] = 0$.
No contradiction: the theorem says a common eigenbasis exists, not that every eigenvector of one is an eigenvector of the other.

every eigenvector of $\hat{A}$ (nondegenerate) is one of $\hat{H}_0$	true
every eigenvector of $\hat{H}_0$ (degenerate) is one of $\hat{A}$	false

The eigenvectors of $\hat{A}$ are one convenient basis of the E_0 eigenspace among infinitely many.

A set of commuting observables whose joint eigenvalues label every state uniquely is a complete set of commuting observables. In W4.1, $\hat{A}$ resolves the degeneracy of $\hat{H}_0$; in hydrogen, $\hat{H}$, $\hat{L}^2$, $\hat{L}_z$ label $|n\,l\,m\rangle$.

Conceptually

Degeneracy signals a symmetry, and breaking the symmetry splits the levels. Hydrogen's E_n is n^2-fold degenerate: at $n = 3$, $l = 0, 1, 2$ give $1 + 3 + 5 = 9$ states. The m degeneracy comes from rotational symmetry; the l degeneracy is special to $1/r$ and is lifted in alkali atoms, where inner electrons screen the nucleus.

19 Continuous bases

$$\langle x \,|\, x' \rangle = \delta(x - x'), \qquad \int |x\rangle\langle x| \mathrm{d}x = I, \qquad |\psi\rangle = \int \psi(x)|x\rangle \mathrm{d}x,$$

and applying $\langle x|$ to the last,

$$\boxed{\psi(x) = \langle x \,|\, \psi \rangle}$$

What that says

The wave function is the list of components in the position basis, exactly as c_n was the list in the energy basis. One state, several lists: $\psi(x)$, $\tilde{\psi}(p)$, c_n. The Fourier transform is the change of basis between the first two.

$|x\rangle$ is not normalisable, since $\langle x \,|\, x \rangle = \delta(0)$, so it is not in $\mathcal{H}$.

20 Spherical coordinates

$$\langle \phi \,|\, \psi \rangle = \int \phi^* \psi \, \mathrm{d}V, \qquad \mathrm{d}V = r^2 \sin\theta \, \mathrm{d}r \, \mathrm{d}\theta \, \mathrm{d}\varphi.$$

The $r^2 \sin\theta$ is the Jacobian:)

Density against distribution

$|\psi|^2$ is a probability per unit *volume*. The probability of lying between r and $r + \mathrm{d}r$ in any direction is

$$P(r)\mathrm{d}r = \left(\int |\psi|^2 r^2 \mathrm{d}\Omega \right) \mathrm{d}r \overset{\text{spherical } \psi}{=} 4\pi r^2 |\psi(r)|^2 \mathrm{d}r.$$

These two functions generally peak in different places.

Example 20.1

W4.6, with $\psi = (\pi r_0^3)^{-1/2} e^{-r/r_0}$.
$|\psi|^2$ decreases monotonically, so the density is largest at $r = 0$.
$P(r) = (4r^2/r_0^3) e^{-2r/r_0}$, and

$$\frac{\mathrm{d}P}{\mathrm{d}r} \propto \left(2r - \frac{2r^2}{r_0} \right) e^{-2r/r_0} = 0 \implies r = r_0,$$

so the radial distribution peaks at the Bohr radius: r^2 is greater than the exponential near the origin and lesser further out. Both statements hold at once: the point $r = 0$ is the most likely single location; the shell at r_0 is the most likely radius, because there is far more of it.

$$\langle r \rangle = \frac{4}{r_0^3} \int_0^\infty r^3 e^{-2r/r_0} \mathrm{d}r = \frac{4}{r_0^3} \cdot \frac{r_0^4}{16} \cdot 3! = \frac{3r_0}{2},$$

substituting $x = 2r/r_0$. Larger than r_0 because of the tail.
$\langle x \rangle = \langle y \rangle = \langle z \rangle = 0$ by symmetry, while $\langle r \rangle \neq 0$ because $r \geq 0$ and cannot cancel. $\langle r \rangle$ and $|\langle \vec{r} \rangle|$ are different objects.

Carry the measure

Normalisation is $\int |\psi|^2 r^2 \sin\theta \, \mathrm{d}r \, \mathrm{d}\theta \, \mathrm{d}\varphi = 1$. The spherical harmonics are normalised so $\int |Y_l^m|^2 \mathrm{d}\Omega = 1$, which is why a separated $\psi = R_{nl} Y_l^m$ needs only $\int_0^\infty |R_{nl}|^2 r^2 \mathrm{d}r = 1$.

21 Tensor products

Ok this one is a bit scary (at least for me) but just build some intuition instead. Particle 1 with d_1 basis states and particle 2 with d_2: the joint space is $\mathcal{H}_1 \otimes \mathcal{H}_2$ of dimension $d_1 d_2$, with basis all products $|i\rangle_1 |j\rangle_2$.

Multiply, not add

Two spin halves give $2 \times 2 = 4$ states. Ten qubits give 2^{10}.

For two spin halves the product basis is $|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle$, the first arrow being particle 1. Inner products go factor by factor,

$$(\langle a|_1 \langle b|_2)\,(|c\rangle_1 |d\rangle_2) = \langle a\,|\,c\rangle \langle b\,|\,d\rangle,$$

so $\langle\uparrow\downarrow \mid \downarrow\uparrow\rangle = 0$ and the four are orthonormal.

An operator belonging to particle 1 ignores particle 2:

$$\hat{S}_z^{(1)} |\uparrow\downarrow\rangle = \tfrac{\hbar}{2} |\uparrow\downarrow\rangle, \qquad \hat{S}_z |\uparrow\downarrow\rangle = \left(\tfrac{\hbar}{2} - \tfrac{\hbar}{2}\right) |\uparrow\downarrow\rangle = 0.$$

Every product state is an eigenstate of $\hat{S}_z$ with eigenvalue $\hbar(m_1 + m_2)$.

Lengths do not add

$$\hat{S}^2 = (\hat{S}^{(1)})^2 + (\hat{S}^{(2)})^2 + 2\,\hat{\vec{S}}^{(1)} \cdot \hat{\vec{S}}^{(2)},$$

and the cross term mixes the particles, so most product states are not eigenstates of $\hat{S}^2$.

22 Clebsch-Gordan coefficients

Ok now this one is surely scary for everyone. Two orthonormal bases of the same space:

	product	coupled
labels	$\lvert j_1 m_1\rangle \lvert j_2 m_2\rangle$	$\lvert j\, m\rangle$
diagonalises	$\hat{J}_1^2, \hat{J}_{1z}, \hat{J}_2^2, \hat{J}_{2z}$	$\hat{J}_1^2, \hat{J}_2^2, \hat{J}^2, \hat{J}_z$
known	each particle's z component	total length and total z component

$$|j\, m\rangle = \sum_{m_1, m_2} \underbrace{\langle j_1 m_1\, j_2 m_2 \,|\, j\, m\rangle}_{\text{Clebsch-Gordan}} |j_1 m_1\rangle |j_2 m_2\rangle.$$

What a coefficient is

An entry of the unitary matrix between two orthonormal bases of one space: the projection trick of Section 4 applied to two particles.
$\langle j_1 m_1\, j_2 m_2 \,|\, j\, m\rangle$ is the amplitude that a state of definite total angular momentum has those individual z components. Its square is the probability.

Both label sets cannot be used at once, since $[\,\hat{J}^2, \hat{J}_{1z}\,] \neq 0$.

22.1 Which j occur

Since $m = m_1 + m_2$, count product states by total m and peel multiplets off the top.

Example 22.1

Two spin halves:

m	product states	count
$+1$	$\lvert\uparrow\uparrow\rangle$	1
0	$\lvert\uparrow\downarrow\rangle,\ \lvert\downarrow\uparrow\rangle$	2
-1	$\lvert\downarrow\downarrow\rangle$	1

The largest m is $+1$, so there is a $j = 1$ multiplet, taking one state from each row. One state at $m = 0$ is left, which must be $j = 0$:

$$\tfrac{1}{2} \otimes \tfrac{1}{2} = 1 \oplus 0, \qquad 3 + 1 = 4.$$

Example 22.2

W5.4, $l = 2$ with $s = \frac{1}{2}$. The totals $\pm\frac{5}{2}$ occur once, $\pm\frac{3}{2}$ and $\pm\frac{1}{2}$ twice. Thus we get $j = \frac{5}{2}$ (six states), leaving $j = \frac{3}{2}$ (four):

$$2 \otimes \tfrac{1}{2} = \tfrac{5}{2} \oplus \tfrac{3}{2}, \qquad 6 + 4 = 10 = 5 \times 2.$$

Rule

$$j \in \{|j_1 - j_2|, \ldots, j_1 + j_2\}, \qquad m = m_1 + m_2, \qquad \sum_j (2j+1) = (2j_1+1)(2j_2+1).$$

Half-integer plus integer is half-integer, so an electron in a d orbital has $j = \frac{5}{2}$ or $\frac{3}{2}$, never 2.

22.2 Building them with ladder operators

$$\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y, \qquad \hat{J}_\pm |j\, m\rangle = \hbar\sqrt{j(j+1) - m(m\pm 1)}\, |j, m\pm 1\rangle,$$

and for a pair $\hat{J}_\pm = \hat{J}_\pm^{(1)} + \hat{J}_\pm^{(2)}$, each term acting on its own particle. For spin half,

$$\hat{S}_-|\uparrow\rangle = \hbar|\downarrow\rangle, \quad \hat{S}_+|\downarrow\rangle = \hbar|\uparrow\rangle, \quad \hat{S}_+|\uparrow\rangle = \hat{S}_-|\downarrow\rangle = 0.$$

Example 22.3, Griffiths 4.37

Only one product state has $m = +1$, so

$$|1\,1\rangle = |\uparrow\uparrow\rangle.$$

Apply $\hat{S}_-$. On the left, $\sqrt{1(2) - 1(0)} = \sqrt{2}$:

$$\hat{S}_-|1\,1\rangle = \sqrt{2}\,\hbar|1\,0\rangle, \qquad \left(\hat{S}_-^{(1)} + \hat{S}_-^{(2)}\right)|\uparrow\uparrow\rangle = \hbar|\downarrow\uparrow\rangle + \hbar|\uparrow\downarrow\rangle,$$

$$\boxed{|1\,0\rangle = \tfrac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right)}$$

The $1/\sqrt{2}$ came out of the ladder formula rather than being inserted to normalise, and the two Clebsch-Gordan coefficients are both $1/\sqrt{2}$.
Again: $\hat{S}_-|1\,0\rangle = \sqrt{2}\,\hbar|1\,{-1}\rangle$, while on the right $\hat{S}_-$ annihilates a down arrow, leaving $\frac{\hbar}{\sqrt{2}} \cdot 2|\downarrow\downarrow\rangle = \sqrt{2}\hbar|\downarrow\downarrow\rangle$. So $|1\,{-1}\rangle = |\downarrow\downarrow\rangle$ and one more application gives zero, terminating the ladder.
The $m = 0$ subspace is two-dimensional and the triplet used one direction, so

$$\boxed{|0\,0\rangle = \tfrac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)}$$

and

$$\hat{S}_-|0\,0\rangle = \tfrac{\hbar}{\sqrt{2}}\left(|{\downarrow\uparrow}\rangle - |{\downarrow\uparrow}\rangle\right) = 0, \qquad \hat{S}_+|0\,0\rangle = 0.$$

A state killed from both ends has $j = 0$, but note that with a plus sign instead it would be $|1\,0\rangle$.

Example 22.4, Griffiths 4.37(c)

Write the cross term with ladder operators,

$$2\,\hat{\vec{S}}^{(1)}\cdot\hat{\vec{S}}^{(2)} = \hat{S}_+^{(1)}\hat{S}_-^{(2)} + \hat{S}_-^{(1)}\hat{S}_+^{(2)} + 2\hat{S}_z^{(1)}\hat{S}_z^{(2)}.$$

On $|{\uparrow\downarrow}\rangle$: the single-particle squares give $\frac{3}{4}\hbar^2 + \frac{3}{4}\hbar^2$; the z term gives $-\frac{\hbar^2}{2}$; $\hat{S}_+^{(1)}$ annihilates the up arrow, and $\hat{S}_-^{(1)}\hat{S}_+^{(2)}|{\uparrow\downarrow}\rangle = \hbar^2|{\downarrow\uparrow}\rangle$. So

$$\hat{S}^2|{\uparrow\downarrow}\rangle = \hbar^2\left(|{\uparrow\downarrow}\rangle + |{\downarrow\uparrow}\rangle\right),$$

and by mirror image the same for $|{\downarrow\uparrow}\rangle$. Hence

$$\hat{S}^2|1\,0\rangle = 2\hbar^2|1\,0\rangle, \qquad \hat{S}^2|0\,0\rangle = 0.$$

Neither $|{\uparrow\downarrow}\rangle$ nor $|{\downarrow\uparrow}\rangle$ is an eigenstate of $\hat{S}^2$: each is an equal mixture, $|{\uparrow\downarrow}\rangle = \frac{1}{\sqrt{2}}(|1\,0\rangle + |0\,0\rangle)$.

22.3 The table

	$\lvert1\,1\rangle$	$\lvert1\,0\rangle$	$\lvert0\,0\rangle$	$\lvert1\,{-1}\rangle$
$\lvert{\uparrow\uparrow}\rangle$	1	0	0	0
$\lvert{\uparrow\downarrow}\rangle$	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	0
$\lvert{\downarrow\uparrow}\rangle$	0	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	0
$\lvert{\downarrow\downarrow}\rangle$	0	0	0	1

Unitary: the columns are the components of orthonormal coupled states, and the rows are orthonormal too, so the inverse is the transpose and the relation reads both ways.

Block diagonal in m: a coupled state of given m can contain only product states of the same total, so the zeros are forced before any calculation. Printed tables are organised into these blocks.

The non-trivial 2×2 block is $\frac{1}{\sqrt{2}}\left(\begin{smallmatrix}1 & 1\\ 1 & -1\end{smallmatrix}\right)$, the change of basis of Section 16 and the σ_x eigenvectors of Section 14.

Table convention

A square root is understood over every entry and the sign sits outside it. An entry printed $-2/5$ means $-\sqrt{2/5}$.

Example 22.5, W5.5

$l = 2$, $s = \frac{1}{2}$, state $|\frac{3}{2},\frac{1}{2}\rangle$. Only two product states have $m_l + m_s = \frac{1}{2}$, so

$$|\tfrac{3}{2},\tfrac{1}{2}\rangle = \alpha|2,+1\rangle|\tfrac{1}{2},-\tfrac{1}{2}\rangle + \beta|2,0\rangle|\tfrac{1}{2},+\tfrac{1}{2}\rangle, \qquad \alpha = \sqrt{\tfrac{3}{5}},\ \beta = -\sqrt{\tfrac{2}{5}},$$

with $\alpha^2 + \beta^2 = 1$. The closed formula for $j = l - \frac{1}{2}$,

$$|l-\tfrac{1}{2},m\rangle = -\sqrt{\frac{l-m+\frac{1}{2}}{2l+1}}|m-\tfrac{1}{2}\rangle|{\uparrow}\rangle + \sqrt{\frac{l+m+\frac{1}{2}}{2l+1}}|m+\tfrac{1}{2}\rangle|{\downarrow}\rangle,$$

gives the same pair at $l = 2$, $m = \frac{1}{2}$.

Measuring the spin and finding it up selects the β term, so $P(\uparrow) = |\beta|^2 = \frac{2}{5}$. The minus sign belongs to the amplitude, where it matters for interference. Afterwards the state is $|2,0\rangle|\uparrow\rangle$, no longer an eigenstate of $\hat{J}^2$, as the non-commuting pair $\hat{J}^2, \hat{S}_z$ requires.
The other column of the same block, $j = \frac{5}{2}$, has $\sqrt{3/5}$ and $\sqrt{2/5}$ in the opposite order, giving $P(\uparrow) = \frac{3}{5}$. The two add to 1 because the columns are orthonormal and span the same $m = \frac{1}{2}$ subspace.

Two sum rules

$$\sum_{m_1 m_2} |\langle j_1 m_1\, j_2 m_2 \,|\, j\, m\rangle|^2 = 1, \qquad \sum_{j,m} |\langle j_1 m_1\, j_2 m_2 \,|\, j\, m\rangle|^2 = 1.$$

The first fixes a coupled state and asks for the individual components; the second fixes a product state and asks for the total j.

23 Identical particles

If no measurement distinguishes two particles, swapping labels cannot change a prediction: $|\Psi(r_2, r_1)|^2 = |\Psi(r_1, r_2)|^2$, leaving $\Psi(r_2, r_1) = \pm\Psi(r_1, r_2)$.

Symmetrization

$$\Psi_\pm(r_1, r_2) = \tfrac{1}{\sqrt{2}} \left[\psi_a(r_1)\psi_b(r_2) \pm \psi_b(r_1)\psi_a(r_2)\right],$$

with $+$ for integer spin (bosons) and $-$ for half-integer spin (fermions).

Setting $b = a$ in the lower sign gives $\Psi_- = 0$: two identical fermions cannot occupy the same one-particle state. Pauli exclusion is thus a consequence here!

The exchange operator $\hat{P}|\alpha\rangle_1|\beta\rangle_2 = |\beta\rangle_1|\alpha\rangle_2$ satisfies $\hat{P}^2 = I$, so its eigenvalues are ± 1, and $\hat{P}$ commutes with any Hamiltonian built from identical particles, so symmetry type is conserved.

For composites, count the fermions: an even number gives integer total angular momentum, hence a boson. Hydrogen is a boson; deuterium is a fermion.

Spin carries half the antisymmetry

$\Psi_\pm$ written as a function of positions alone is only the whole story when the spin state is fixed and symmetric. For two electrons in a spin singlet the spin part is antisymmetric, so the *spatial* part must be symmetric, and conclusions reverse. Pauli forbids the same one-particle *state*, not the same point.

23.1 Where the particles are

Example 23.2

Two particles in the double well with $E_T = E_g + E_e$. The antisymmetric state is

$$|\Psi_T\rangle_{AS} = \tfrac{1}{\sqrt{2}} \left(|\phi_{g1}\rangle|\phi_{e2}\rangle - |\phi_{e1}\rangle|\phi_{g2}\rangle\right).$$

Expanding both products in the L, R basis,

$$|\phi_{g1}\rangle|\phi_{e2}\rangle = \tfrac{1}{2} \left(|L_1 L_2\rangle - |L_1 R_2\rangle + |R_1 L_2\rangle - |R_1 R_2\rangle\right),$$

$$|\phi_{e1}\rangle|\phi_{g2}\rangle = \tfrac{1}{2} \left(|L_1 L_2\rangle + |L_1 R_2\rangle - |R_1 L_2\rangle - |R_1 R_2\rangle\right).$$

Subtracting, the same-well terms cancel:

$$|\Psi_T\rangle_{AS} = \tfrac{1}{\sqrt{2}}\left(|R_1L_2\rangle - |L_1R_2\rangle\right), \qquad P_{LL} = P_{RR} = 0.$$

Adding instead, with the symmetric combination, the cross terms cancel:

$$|\Psi_T\rangle_{S} = \tfrac{1}{\sqrt{2}}\left(|L_1L_2\rangle - |R_1R_2\rangle\right), \qquad P_{LR} = P_{RL} = 0.$$

Pauli: the same-well amplitudes are exactly what antisymmetrisation kills.

	P_{LL}	P_{LR}	P_{RL}	P_{RR}
fermions	0	$\frac{1}{2}$	$\frac{1}{2}$	0
distinguishable	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
bosons	$\frac{1}{2}$	0	0	$\frac{1}{2}$

A minus sign between terms is not antisymmetry

$|\Psi_T\rangle_S$ above has a minus sign in it and is still symmetric:

$$\hat{P}\left(|L_1L_2\rangle - |R_1R_2\rangle\right) = |L_1L_2\rangle - |R_1R_2\rangle,$$

since each term is separately invariant. The sign *under exchange* and a relative sign *between terms* are different things.

23.2 Atoms

Closed (filled) subshells contribute nothing: every m is occupied twice with opposite spin, so $L = 0$ and $S = 0$. Only the open subshell matters, and the term symbol is ${}^{2S+1}L_J$.

Hund's rules, in order: highest S consistent with Pauli; then highest L at that S; then $J = |L-S|$ if the subshell is at most half filled, $J = L + S$ if more.

Example 23.5, Griffiths 5.18

(a) Highest S is the triplet, orthohelium, which lies below parahelium. The triplet spin state is symmetric, so the spatial state is antisymmetric, so the electrons avoid each other and the Coulomb energy is lower. The rule is electrostatics routed through symmetry, not a spin-spin force.
(b) Carbon's two $2p$ electrons have $S = 1$ by rule one, so the spatial state must be antisymmetric. Test $L = 2$ at the top of its ladder, where there is only one term:

$$|2\,2\rangle = |1\,1\rangle_1|1\,1\rangle_2,$$

manifestly symmetric. Since $\hat{L}_-$ is symmetric under exchange it commutes with $\hat{P}$, so every state of the multiplet inherits that symmetry, and $L = 2$ is incompatible with $S = 1$. Rule two then gives $L = 1$.
(c) Boron has one electron in a six-slot subshell, so $J = |L - S| = \frac{1}{2}$ and the ground state is ${}^2P_{1/2}$.
(d) Carbon: $S = 1$, $L = 1$, less than half filled, so $J = 0$ and the term is ${}^3P_0$. Nitrogen: $S = \frac{3}{2}$, whose top rung is all three spins up and symmetric, so the orbital state is totally antisymmetric. With all spins up the three orbital states must be distinct, hence $|1\,1\rangle, |1\,0\rangle, |1\,{-1}\rangle$, one each, forcing $M_L = 0$ always, so $L = 0$. Exactly half filled gives $J = \frac{3}{2}$ and ${}^4S_{3/2}$.

A subshell with one hole has the same L and S as one with one electron, so fluorine $(2p)^5$ is ${}^2P$ like boron. Oxygen $(2p)^4$ has $S = 1$, $L = 1$ by the same counting, but is more than half filled, so $J = L + S = 2$ and the term is ${}^3P_2$ against carbon's ${}^3P_0$.

Counting check

Six p spin-orbitals choose two gives $\binom{6}{2} = 15$ states. The surviving carbon terms ${}^1D$, ${}^3P$, ${}^1S$ give $5 + 9 + 1 = 15$. Angular momentum addition alone would allow six (L, S) pairs, but antisymmetry cuts it down to three.

24 Matching conditions and the finite well

In each region of constant V,

$$\psi'' = \frac{2m}{\hbar^2}(V - E)\psi,$$

giving oscillations $e^{\pm ikx}$ when $E > V$ and real exponentials $e^{\pm \kappa x}$ when $E < V$. The problem reduces to writing the general solution in each region and gluing.

Conditions

ψ is always continuous. ψ' is continuous wherever V is finite.

Could yap a lot about the proof but just remember this.

24.1 Bound states

$V = -V_0$ on $|x| \le a$ and 0 outside, with $-V_0 < E < 0$. Define

$$\kappa = \frac{\sqrt{-2mE}}{\hbar} \ (|x| > a), \qquad l = \frac{\sqrt{2m(E + V_0)}}{\hbar} \ (|x| < a), \qquad \kappa^2 + l^2 = \frac{2mV_0}{\hbar^2}.$$

Here l measures height above the bottom of the well and κ depth below the top.

V is even, so $[\hat{H}, \hat{\Pi}] = 0$, and since 1D bound states are nondegenerate every eigenstate is itself even or odd. That allows matching at $x = +a$ only.

Example 24.1, Griffiths 2.29

Even: $\psi = D\cos(lx)$ inside, $Fe^{-\kappa x}$ outside, so

$$D\cos(la) = Fe^{-\kappa a}, \quad -lD\sin(la) = -\kappa Fe^{-\kappa a} \implies l\tan(la) = \kappa.$$

Odd: $\psi = D\sin(lx)$ inside, giving $l\cot(la) = -\kappa$.
With $z = la$ and $z_0 = \frac{a}{\hbar}\sqrt{2mV_0}$, so that $\kappa a = \sqrt{z_0^2 - z^2}$,

$$\tan z = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1} \quad \text{(even)}, \qquad -\cot z = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1} \quad \text{(odd)},$$

both on $0 < z < z_0$. The right-hand side falls from $+\infty$ at $z \to 0^+$ to 0 at $z = z_0$. Intersections with $\tan z$ and $-\cot z$ interleave: even, odd, even, odd.
Always one even state. As $z \to 0^+$ the even left side goes to 0 while the right side goes to $+\infty$; at $z = z_0$ the right side is 0 while $\tan z_0 > 0$ for $z_0 < \pi/2$. They cross whatever the depth or width.
Odd states need $z_0 > \pi/2$. As $z \to 0^+$ the odd left side goes to $-\infty$ while the right side goes to $+\infty$, so there is no crossing near the origin, and the first branch only turns positive past

$\pi/2$. So an odd state exists iff

$$V_0 > \frac{\pi^2\hbar^2}{8ma^2}, \qquad N = \left\lceil \frac{2z_0}{\pi} \right\rceil .$$

Deep well, $z_0 \to \infty$. Roots approach $z \to n\pi/2$, so $l = n\pi/(2a)$ and

$$E_n + V_0 = \frac{n^2\pi^2\hbar^2}{2m(2a)^2},$$

the infinite well of width $2a$ measured from the bottom, with even n giving the odd wave functions.
Shallow well, $z_0 \to 0$. Only the even state survives, and expanding gives $\kappa \approx 2mV_0a/\hbar^2$, so with $\alpha = 2aV_0$,

$$E \approx -\frac{2mV_0^2a^2}{\hbar^2} = -\frac{m\alpha^2}{2\hbar^2},$$

the delta-well bound state.

Example 24.2, Griffiths 2.48

$V = \infty$ for $x < 0$, $-32\hbar^2/ma^2$ on $[0, a]$, 0 beyond. The wall forces $\psi(0) = 0$, which is the odd half of Example 24.1 with half-width a:

$$z_0 = \frac{a}{\hbar}\sqrt{2m \cdot \frac{32\hbar^2}{ma^2}} = 8.$$

Odd states sit at half-integer multiples of π below z_0: 1.571, 4.712, 7.854 qualify and 10.996 does not, so there are three. Solving $-\cot z = \sqrt{(8/z)^2 - 1}$,

$$z_1 = 2.7859, \quad z_2 = 5.5215, \quad z_3 = 7.9573, \qquad E = \frac{\hbar^2}{2ma^2}(z^2 - 64),$$

$$E_1 = -28.12\frac{\hbar^2}{ma^2}, \quad E_2 = -16.76\frac{\hbar^2}{ma^2}, \quad E_3 = -0.3405\frac{\hbar^2}{ma^2}.$$

The top state is bound by about 1% of the well depth. Its

$$\kappa a = \sqrt{64 - 63.319} = 0.8253, \qquad 1/\kappa = 1.212\,a,$$

a penetration depth longer than the well. With $\psi = D\sin(lx)$ inside and $Fe^{-\kappa x}$ outside,

$$\frac{P_{\text{in}}}{D^2a} = \frac{1}{2} - \frac{\sin 2la}{4la} = 0.5065, \qquad \frac{P_{\text{out}}}{D^2a} = \frac{\sin^2(la)}{2\kappa a} = 0.5993,$$

$$\frac{P_{\text{out}}}{P_{\text{in}} + P_{\text{out}}} = 0.542.$$

A barely bound state has $\kappa \to 0$ and a tail that extends almost forever. Bound means normalisable, not localised in the well.

Example 24.3, Griffiths 2.30

Normalising the even state, with $F = D\cos(la)e^{\kappa a}$,

$$1 = 2D^2\left[\frac{a}{2} + \frac{\sin(2la)}{4l} + \frac{\cos^2(la)}{2\kappa}\right].$$

Using the matching condition $\kappa = l\tan(la)$,

$$\frac{\sin(2la)}{2l} + \frac{\cos^2(la)}{\kappa} = \frac{\sin(la)\cos(la)}{l} + \frac{\cos^3(la)}{l\sin(la)} = \frac{\cos(la)}{l\sin(la)} = \frac{1}{\kappa},$$

so

$$\boxed{D = \left(a + \frac{1}{\kappa}\right)^{-1/2}}$$

the normalisation of a particle spread uniformly over a box of half-width $a_{\text{eff}} = a + 1/\kappa$. The well behaves as though wider by one penetration depth on each side, which is why finite-well energies lie below the infinite-well values: a longer effective box means a longer wavelength.

25 Barriers

For $E > 0$ nothing is normalisable, every energy is allowed, and the question is what fraction of an incoming wave returns and what fraction gets through. With A incident, B reflected, F transmitted, four unknowns and four matching conditions close the system.

Coefficients are current ratios

$$J = \frac{\hbar}{m}\operatorname{Im}(\psi^*\psi'), \qquad R = \frac{|B|^2}{|A|^2}, \qquad T = \frac{J_{\text{trans}}}{J_{\text{inc}}} = \frac{k'}{k}\frac{|F|^2}{|A|^2}.$$

$T = |F|^2/|A|^2$ only when the potential returns to its starting value, so that $k' = k$.

Example 25.1, Griffiths 2.34

Step up to V_0 at $x = 0$, with $k = \sqrt{2mE}/\hbar$.
$E < V_0$. With $\psi = Ce^{-\kappa x}$ beyond, matching gives $A + B = C$ and $ik(A - B) = -\kappa C$, so

$$\frac{B}{A} = \frac{ik + \kappa}{ik - \kappa}, \qquad R = \frac{k^2 + \kappa^2}{k^2 + \kappa^2} = 1.$$

Total reflection, yet $C \neq 0$: there is a nonzero probability of being found in the forbidden region, decaying over $1/\kappa$. Nothing flows there, since ψ is real up to a phase and $J = 0$. The reflected wave is phase shifted by $\arg(B/A)$.
$E > V_0$. With $k' = \sqrt{2m(E - V_0)}/\hbar$,

$$\frac{B}{A} = \frac{k - k'}{k + k'}, \qquad \frac{C}{A} = \frac{2k}{k + k'}, \qquad R = \left(\frac{k - k'}{k + k'}\right)^2,$$

the Fresnel formula at normal incidence. Then

$$T = \frac{k'}{k}\cdot\frac{4k^2}{(k + k')^2} = \frac{4kk'}{(k + k')^2}, \qquad R + T = \frac{(k - k')^2 + 4kk'}{(k + k')^2} = 1.$$

At $E = 2V_0$: $k'/k = 0.7071$, $R = 0.0294$, $T = 0.9706$.
Dropping the k'/k counts particles per unit length instead of per unit time; on the right they move faster, so the same flux is a smaller density.

Thick barrier

For $\kappa L \gg 1$ with $L = 2a$, using $\sinh^2(\kappa L) \approx \frac{1}{4}e^{2\kappa L}$,

$$T \approx \frac{16E(V_0 - E)}{V_0^2}\, e^{-2\kappa L}, \qquad \kappa = \frac{\sqrt{2m(V_0 - E)}}{\hbar}.$$

Part V. Reference

26 Just some basic mathematical errors to look out for

I assure you every physicist has been tortured by *at least* one of these:

1. $\psi(x)$ and c_n are both component lists of the same object in different bases.
2. Probability density is $\psi^*\psi$, not ψ^2.
3. $\langle c\psi \,|\, \phi\rangle = c^*\langle\psi \,|\, \phi\rangle$.
4. $|3i|^2 = 9$,not -9.
5. Normalise before averaging.
6. The operator goes inside: $\int \psi^*(\hat{A}\psi)\mathrm{d}x$.
7. $\langle\hat{A}\rangle = \sum \lambda_n |c_n|^2$ only in the eigenbasis of $\hat{A}$.
8. Amplitudes add, probabilities do not.
9. Non-commuting does not mean always different (Example 11.4 gives $\frac{1}{2}$).
10. Collapse between successive measurements (Example 11.5).
11. Orthogonality is an integral, not an angle (well, for all quantum intents and purposes).
12. Degenerate eigenvalues do not collapse onto one vector (Section 18).
13. Eigenvalues of $\hat{A}+\hat{B}$ are not $\lambda_A + \lambda_B$ unless they commute.
14. $\Delta A = 0$ needs an eigenstate, not a zero mean.
15. Keep $\hbar$ in $e^{-iE_nt/\hbar}$.
16. Which combination is the ground state depends on the sign of the coupling.
17. Two-particle dimensions multiply.
18. $\hat{S}^2 \neq (\hat{S}^{(1)})^2 + (\hat{S}^{(2)})^2$.
19. Sharp m does not give sharp j: $|{\uparrow\downarrow}\rangle$ is half triplet, half singlet.
20. Clebsch-Gordan entries hide a square root.
21. $j = j_1 + j_2$ is only the largest value.
22. Carry the $r^2 \sin\theta$ Jacobian.
23. A minus sign between terms is not antisymmetry under exchange.
24. Antisymmetrising the spatial part alone assumes the spin state is symmetric.
25. $\langle x\rangle_{nm}$ is off-diagonal and is not $\langle x\rangle_n\langle x\rangle_m$.
26. T is a ratio of currents; $|F/A|^2$ needs $k' = k$.
27. ψ' is continuous only where V is finite.
28. Use $\int |\psi'|^2$ for kinetic energy when continuity is in doubt.
29. Barrier width is $2a$, and the exponent carries 2κ.
30. $\kappa = \sqrt{2m|E|}/\hbar$ for a bound state; l measures from the bottom of the well, κ from the top.

27 ‘Cheat sheet’ of sorts

Linear algebra	**Wave mechanics**	**Dirac**
$v \in \mathbb{C}^n$	$\psi(x)$	$\lvert\psi\rangle$
row $v^{*\mathsf{T}}$	$\int \psi^*(\cdot)\mathrm{d}x$	$\langle\psi\rvert$
$\sum_i u_i^* v_i$	$\int \phi^*\psi \mathrm{d}x$	$\langle\phi \,\vert\, \psi\rangle$
component v_i	value $\psi(x)$	$\langle i \,\vert\, \psi\rangle$, $\langle x \,\vert\, \psi\rangle$
δ_{ij}	$\delta(x - x')$	$\langle m \,\vert\, n\rangle$, $\langle x \,\vert\, x'\rangle$
matrix A	$\hat{x}$, $\hat{p} = -i\hbar\,\mathrm{d}/\mathrm{d}x$	$\hat{A}$
$A^{*\mathsf{T}}$	integrate by parts	$\hat{A}^\dagger$
eigenvector	stationary state	$\lvert n\rangle$
$\det(A - \lambda I) = 0$	$\hat{H}\psi = E\psi$	characteristic equation
$\sum_i e_i e_i^{\mathsf{T}} = I$	$\sum_n \phi_n(x)\phi_n(x')^* = \delta(x - x')$	$\sum_n \lvert n\rangle\langle n\rvert = I$
$R^{\mathsf{T}} R = I$	norm preserving	$\hat{U}^\dagger \hat{U} = I$

Formulas

inner product	$\langle\phi\,\vert\,\psi\rangle = \int \phi^*\psi \mathrm{d}x, \quad \langle\phi\,\vert\,\psi\rangle = \langle\psi\,\vert\,\phi\rangle^*$
conjugate linearity	$\langle c\psi\,\vert\,\phi\rangle = c^*\langle\psi\,\vert\,\phi\rangle, \quad \langle\psi\,\vert\,c\phi\rangle = c\langle\psi\,\vert\,\phi\rangle$
orthonormality	$\langle m\,\vert\,n\rangle = \delta_{mn}$
projection	$\vert\psi\rangle = \sum_n c_n \vert n\rangle, \quad c_n = \langle n\,\vert\,\psi\rangle$
completeness	$\sum_n \vert n\rangle\langle n\vert = I$
Parseval	$\sum_n \vert c_n\vert^2 = 1$
Born rule	$P(\lambda_n) = \vert c_n\vert^2$
expectation	$\langle\hat{A}\rangle = \langle\psi\,\vert\,\hat{A}\,\vert\,\psi\rangle = \sum_n \lambda_n \vert c_n\vert^2$
spread	$\Delta A = \sqrt{\langle\hat{A}^2\rangle - \langle\hat{A}\rangle^2}, \quad \Delta A \Delta B \geq \frac{1}{2}\left\vert\langle[\,\hat{A},\hat{B}\,]\rangle\right\vert$
matrix elements	$A_{mn} = \langle m\,\vert\,\hat{A}\,\vert\,n\rangle, \quad A' = \hat{U}^\dagger A \hat{U}$
eigenvalues	$\det(A-\lambda I) = 0, \quad \sum \lambda_n = \operatorname{Tr} A, \quad \prod \lambda_n = \det A$
evolution	$\vert\psi(t)\rangle = \sum_n c_n e^{-iE_n t/\hbar}\vert n\rangle, \quad \frac{\mathrm{d}\langle\hat{Q}\rangle}{\mathrm{d}t} = \frac{i}{\hbar}\left\langle[\,\hat{H},\hat{Q}\,]\right\rangle$
algebra	$[\,\hat{x},\hat{p}\,] = i\hbar, \quad [\,\hat{L}_x,\hat{L}_y\,] = i\hbar\hat{L}_z$
spin half	$\hat{S}_j = \frac{\hbar}{2}\sigma_j, \quad \sigma_j^2 = I, \quad \text{eigenvalues } \pm\frac{\hbar}{2}$
ladder	$\hat{J}_\pm\vert j\,m\rangle = \hbar\sqrt{j(j+1)-m(m\pm1)}\vert j, m\pm1\rangle$
addition	$j \in \{\vert j_1-j_2\vert, \ldots, j_1+j_2\}, \quad m = m_1+m_2$
triplet, singlet	$\vert 1\,0\rangle = \frac{1}{\sqrt{2}}(\vert\uparrow\downarrow\rangle + \vert\downarrow\uparrow\rangle), \quad \vert 0\,0\rangle = \frac{1}{\sqrt{2}}(\vert\uparrow\downarrow\rangle - \vert\downarrow\uparrow\rangle)$
exchange	$\langle(x_1-x_2)^2\rangle_\pm = \langle(x_1-x_2)^2\rangle_{\text{dist}} \mp 2\vert\langle x\rangle_{nm}\vert^2$
radial	$P(r)\mathrm{d}r = 4\pi r^2\vert\psi\vert^2\mathrm{d}r, \quad \mathrm{d}V = r^2\sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\varphi$
matching	ψ continuous always, $\quad \psi'$ continuous where V finite
kinetic energy	$\langle T\rangle = \dfrac{\hbar^2}{2m}\displaystyle\int \left\vert\psi'\right\vert^2 \mathrm{d}x$
finite well	$l\tan(la) = \kappa$ (even), $\quad l\cot(la) = -\kappa$ (odd), $\quad a_{\text{eff}} = a + \frac{1}{\kappa}$
scattering	$R = \vert B/A\vert^2, \quad T = \frac{k'}{k}\vert F/A\vert^2, \quad T \approx \frac{16E(V_0-E)}{V_0^2}e^{-2\kappa L}$

28 Exercises

Part 0

W1. Compute AB and BA for $A = \left(\begin{smallmatrix}1 & 2\\ 0 & 1\end{smallmatrix}\right)$, $B = \left(\begin{smallmatrix}1 & 0\\ 3 & 1\end{smallmatrix}\right)$.

W2. Compute $\det\left(\begin{smallmatrix}2 & 1 & 0\\ 1 & 2 & 1\\ 0 & 1 & 2\end{smallmatrix}\right)$.

W3. Solve $\left(\begin{smallmatrix}1 & -2\\ -2 & 4\end{smallmatrix}\right) v = 0$.

W4. Write $A^\dagger$ for $A = \left(\begin{smallmatrix}2i & 1\\ 0 & 3-i\end{smallmatrix}\right)$.

W5. Eigenvalues of $\left(\begin{smallmatrix} 5 & 0 \\ 0 & -2 \end{smallmatrix}\right)$, checked against trace and determinant.

Real Quantum core

1. $|u\rangle = \binom{2}{-i}$, $|v\rangle = \binom{1+i}{3}$. Find $\langle u|$, $\langle u \,|\, v\rangle$, $\langle v \,|\, u\rangle$, $\langle u \,|\, u\rangle$, $\|u\|$.
2. $f(v) = v_1 - 2iv_2$ on $\mathbb{C}^2$. Write it as a row and find $|w\rangle$ with $f(\cdot) = \langle w \,|\, \cdot\rangle$.
3. Eigenvalues and normalised eigenvectors of $\left(\begin{smallmatrix} 3 & 1 \\ 1 & 3 \end{smallmatrix}\right)$.
4. Eigenvalues of σ_y from the characteristic equation; eigenvector for $\lambda = -1$.
5. Show $\vec{n} \cdot \vec{\sigma}$ has eigenvalues ± 1 using only the trace and $(\vec{n} \cdot \vec{\sigma})^2 = I$.
6. Show $\{\frac{1}{\sqrt{2}}\binom{1}{i}, \frac{1}{\sqrt{2}}\binom{1}{-i}\}$ is orthonormal and expand $\binom{2}{0}$ in it.
7. Compute $[\,\hat{x}^2, \hat{p}\,]$ two ways.
8. A spin starts in $|+x\rangle$. Measure S_z, then S_x. Probability of $+\hbar/2$?
9. For $\chi = \frac{1}{5}\binom{3i}{4}$ find $\langle \hat{S}_x \rangle$, $\langle \hat{S}_y \rangle$, $\langle \hat{S}_z \rangle$ (4.30).
10. $\psi = A \sin^3(\pi x/L)$ with $\sin^3\theta = \frac{3}{4}\sin\theta - \frac{1}{4}\sin 3\theta$. Read off the expansion and get A from $\sum |c_n|^2 = 1$.
11. Which of $\langle \phi_2 \,|\, \hat{x} \,|\, \phi_5 \rangle$, $\langle \phi_2 \,|\, \hat{x} \,|\, \phi_4 \rangle$, $\langle \phi_3 \,|\, \hat{x}^2 \,|\, \phi_1 \rangle$ vanish by parity?
12. Prove $\hat{A}\hat{B}$ is Hermitian iff $[\,\hat{A}, \hat{B}\,] = 0$.
13. Show $|\psi\rangle\langle\phi|$ is an operator and find its adjoint.
14. Repeat Example 16.1 with the coefficients swapped. Do the probabilities swap?
15. For Example 4.5, give $P(E_2)$ without calculating.
16. Show $\langle 1/r \rangle = 1/r_0$ for the hydrogen ground state, and compare with $1/\langle r \rangle$.
17. Use $\mathrm{d}\langle \hat{Q} \rangle / \mathrm{d}t$ to show $\langle \hat{p} \rangle$ is constant and $\langle \hat{x} \rangle$ moves uniformly for a free particle.
18. Write $|{\downarrow}{\uparrow}\rangle$ in the coupled basis.
19. Two spin halves in the singlet. Measure S_z of particle 1: probabilities, and what follows for particle 2?
20. Decompose $1 \otimes 1$ by counting.
21. For $|\frac{5}{2}, \frac{1}{2}\rangle$ with $l = 2$, give $P(\uparrow)$.
22. Two particles in states ψ_1, ψ_3 of the infinite well. Why is $\langle (x_1 - x_2)^2 \rangle$ the same for bosons, fermions and distinguishable particles?
23. Carbon is $(1s)^2(2s)^2(2p)^2$. Give the ground-state term symbol, and oxygen's.
24. A finite well has $z_0 = 5$. How many bound states, and how many are odd?
25. Show that R for a step is unchanged under $k_1 \leftrightarrow k_2$, and say what that means physically.
26. A barrier has $\kappa L = 6$. Estimate T at $E = V_0/2$, then say what happens if L doubles.

Harder

H1. From $[\,\hat{L}_i, \hat{L}_j\,] = i\hbar\epsilon_{ijk}\hat{L}_k$ prove $[\,\hat{L}^2, \hat{L}_z\,] = 0$.

H2. Prove $\mathrm{Tr}[\,A, B\,] = 0$ and deduce that no finite matrices satisfy $[\,A, B\,] = i\hbar I$.

H3. Show $e^{i\hat{A}}$ is unitary for Hermitian $\hat{A}$.

H4. Orthonormalise $\binom{1}{1}$ and $\binom{1}{0}$ inside a degenerate eigenspace.

H5. Rewrite the singlet in terms of the σ_x eigenstates of each particle.

H6. Show $\hat{p}$ has no eigenfunctions with $\psi(0) = \psi(L) = 0$, and reconcile this with $\hat{p}$ being Hermitian on the line.

H7. Show the $a + 1/\kappa$ result of Example 24.3 also holds for the odd states.

H8. A state ψ_2 equals ψ_1 on one side of a point and $-\psi_1$ on the other. Show $\langle V \rangle$ and all position statistics agree, and that $\langle T \rangle$ diverges.

Answers

Part 0

W1. $AB = \left(\begin{smallmatrix} 7 & 2 \\ 3 & 1 \end{smallmatrix}\right)$, $BA = \left(\begin{smallmatrix} 1 & 2 \\ 3 & 7 \end{smallmatrix}\right)$.

W2. 4.

W3. $\det = 0$ and $v_1 = 2v_2$, so $\frac{1}{\sqrt{5}}\binom{2}{1}$.

W4. $\left(\begin{smallmatrix} -2i & 0 \\ 1 & 3+i \end{smallmatrix}\right)$, not Hermitian.

W5. 5 and -2; trace 3, determinant -10.

Real Quantum core

1. $\langle u| = (2 \;\; i)$; $2 + 5i$; $2 - 5i$; 5; $\sqrt{5}$.
2. $(1 \;\; -2i)$, so $|w\rangle = \binom{1}{2i}$.
3. 4 and 2, with $\frac{1}{\sqrt{2}}\binom{1}{1}$ and $\frac{1}{\sqrt{2}}\binom{1}{-1}$.
4. $\lambda^2 = 1$; for $\lambda = -1$, $v_2 = -iv_1$.
5. $(\vec{n} \cdot \vec{\sigma})^2 = I$ forces $\lambda^2 = 1$; zero trace forces one of each.
6. $c_1 = c_2 = \sqrt{2}$.
7. $2i\hbar\hat{x}$.
8. $\frac{1}{2}$.
9. 0, $-\frac{12}{25}\hbar$, $-\frac{7}{50}\hbar$.
10. $c_1 = \frac{3}{4}A\sqrt{L/2}$, $c_3 = -\frac{1}{4}A\sqrt{L/2}$; $A = \sqrt{32/5L}$.
11. The first two vanish; the third does not, since x^2 is even.
12. $(\hat{A}\hat{B})^\dagger = \hat{B}\hat{A}$.
13. $|\psi\rangle\langle\phi||\chi\rangle = \langle\phi\,|\,\chi\rangle|\psi\rangle$; adjoint $|\phi\rangle\langle\psi|$.
14. No. Both amplitudes are now positive, so the left still gets 0.971. Flipping the *sign* of the $|\phi_e\rangle$ coefficient is what exchanges them.
15. Zero, by parity (Example 17.3).
16. $\frac{4}{r_0^3}\int r e^{-2r/r_0}\mathrm{d}r = \frac{1}{r_0}$, while $1/\langle r\rangle = 2/3r_0$. The average of a function is not the function of the average.
17. $[\,\hat{H}, \hat{p}\,] = 0$ for $V = 0$, then $\mathrm{d}\langle\hat{x}\rangle/\mathrm{d}t = \langle\hat{p}\rangle/m$ is constant.

18. $\frac{1}{\sqrt{2}}(|1\,0\rangle - |0\,0\rangle)$.

19. $\frac{1}{2}$ each; particle 2 is certainly the opposite.

20. m has multiplicities $1, 2, 3, 2, 1$, giving $j = 2, 1, 0$ and $5 + 3 + 1 = 9$.

21. $\frac{3}{5}$.

22. Same parity, so $\langle x \rangle_{13} = 0$ and the exchange term vanishes.

23. ${}^3P_0$ and ${}^3P_2$.

24. $N = \lceil 10/\pi \rceil = 4$, of which two are odd ($z_0$ exceeds $\pi/2$ and $3\pi/2$ but not $5\pi/2$).

25. $R = \left(\frac{k_1 - k_2}{k_1 + k_2}\right)^2$ is symmetric, so a drop reflects like a rise: reflection comes from sharpness, not sign.

26. $T \approx 4e^{-6} \approx 10^{-2}$; doubling L gives e^{-12}, down by e^6.

Harder

H1. $[\,\hat{L}_x^2, \hat{L}_z\,] = -i\hbar(\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x)$ and the $\hat{L}_y^2$ term gives the opposite; they cancel.

H2. $\mathrm{Tr}(AB) = \mathrm{Tr}(BA)$, while $\mathrm{Tr}(i\hbar I) = i\hbar n$.

H3. $(e^{i\hat{A}})^\dagger = e^{-i\hat{A}}$ and the exponents commute.

H4. Keep $\frac{1}{\sqrt{2}}\binom{1}{1}$, then $\binom{1}{0} - \frac{1}{2}\binom{1}{1} = \frac{1}{2}\binom{1}{-1}$.

H5. It keeps its form, $\frac{1}{\sqrt{2}}(|+x\rangle|-x\rangle - |-x\rangle|+x\rangle)$ up to a phase: $j = 0$ is rotationally invariant.

H6. e^{ikx} cannot vanish at two points. On $[0, L]$ the operator is symmetric but not self-adjoint; on the line the boundary term vanishes for a different reason.

H7. Same cancellation with $\kappa = -l\cot(la)$.

H8. $\langle f(\hat{x}) \rangle = \int f|\psi|^2$ for every f, and $|\psi_2|^2 = |\psi_1|^2$ pointwise. But ψ_2 jumps, so $\int |\psi_2'|^2 = \infty$.