PHYS201 SUMMARY

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Version 4

Definition | **Theory**

Misc.

Date: 2025-05-21

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1/10 Q.M. FORMALISM

Hilbert space $\mathcal{H}$ in Q.M.

All *square-integrable* (L^2) functions on $\mathbb{R}$. In Q.M., all L^2 functions representing bound states approach 0 at $\pm\infty$.

Dirac Bra-ket notation

ket: $|v\rangle$ is a column vector in $\mathcal{H}$

bra: $\langle f|$ is a linear map $f: \mathcal{H} \to \mathbb{C}$

A bra acting on a ket is noted as

$\langle f|\,|v\rangle = \langle f|v\rangle \in \mathbb{C}$

Bras are row vectors in *dual-space* of $\mathcal{H}$

Observable operators *(in position space)*

Name	General def.	Cartesian def.
Position	$\hat{\mathbf{r}} = \mathbf{r}$	$\hat{x} = x, \quad \hat{y} = y, \quad \hat{z} = z$
Momentum	$\hat{\mathbf{p}} = -i\hbar\nabla$	$\hat{p}_k = -i\hbar\frac{\partial}{\partial k}, \quad k = x,y,z$
Kinetic Energy	$\hat{T} = \frac{1}{2m}\hat{\mathbf{p}}\cdot\hat{\mathbf{p}} = -\frac{\hbar^2}{2m}\nabla^2$	$\hat{T}_k = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial k^2}, \quad k = x,y,z$
Potential Energy	$\hat{V} = V(\mathbf{r},t) = V$	*Situation dependent*
Total Energy	Time-dep. pot.: $\hat{E} = i\hbar\frac{\partial}{\partial t}$ Time-indep. pot.: $\hat{E} = E$	*Situation dependent*
Hamiltonian	$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\nabla^2 + V$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V$
Angular Momentum	$\hat{\mathbf{L}} = \hat{\mathbf{r}}\times\hat{\mathbf{p}}$	$\hat{L}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$ $\hat{L}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$ $\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$
Spin-1/2 Angular Momentum	$\hat{\mathbf{S}} = \frac{\hbar}{2}\boldsymbol{\sigma}$ ($\boldsymbol{\sigma}$ = vector whose components are the **Pauli matrices** σ_k)	$\hat{S}_k = \frac{\hbar}{2}\sigma_k, \quad k = x,y,z$ where $\sigma_x = \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} \quad \sigma_y = \begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}$ $\sigma_z = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$
Total Angular Momentum	$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$	$\hat{J}_k = \hat{L}_k + \hat{S}_k, \quad k = x,y,z$

Hermitian operators

An operator $\hat{Q}$ is Hermitian if and only if

$\langle f|\hat{Q}f\rangle = \langle \hat{Q}f|f\rangle \;\forall\, f$

Same as

$\langle f|\hat{Q}|f\rangle = \langle f|\hat{Q}^\dagger|f\rangle \;\forall\, f$

All operators representing observables are Hermitian, because

$\langle Q\rangle \in \mathbb{R}$

$\Rightarrow \langle Q\rangle = \langle Q\rangle^*$

$\Rightarrow \langle f|\hat{Q}f\rangle = \langle \hat{Q}f|f\rangle$

A Hermitian operator is equal to its adjoint (**self-adjoint**)

$\hat{Q} = \hat{Q}^\dagger$

Inner product in $\mathcal{H}$

The inner product of $|f\rangle$ and $|g\rangle$ is

$\langle f|\,|g\rangle = \langle f|g\rangle \equiv \int_{-\infty}^{\infty} f(x)^* g(x)dx \in \mathbb{C}$

where $\langle f| = |f\rangle^\dagger = |f\rangle^{*\intercal}$

Note that $\langle f|g\rangle = \langle g|f\rangle^*$ and that

$\langle f|f\rangle = \int_{-\infty}^{\infty} |f(x)|^2 dx \geq 0 \in \mathbb{R}$

where $\langle f|f\rangle = 0 \iff f(x) = 0$

f **normalized** IFF $\langle f|f\rangle = 1$

f and g **orthogonal** IFF $\langle f|g\rangle = 0$

$\{f_n\}$ **orthonormal** IFF $\langle f_n|f_n\rangle = 1$ and $\langle f_m|f_n\rangle = \delta_{mn}$

$\{f_n\}$ is **complete** if any other function g in $\mathcal{H}$ can be expressed as $g(x) = \sum_{n=1}^{\infty} c_n f_n(x)$ where $c_n = \langle f_n|g\rangle$

*The **adjoint** $\dagger$ is the same as taking the transpose of the complex conjugate.*

If f and g are **discrete**, use sums.

Eigenvalue equation

$\hat{Q}\Psi = q\Psi$

Ψ is an eigenfunction of $\hat{Q}$, and q is the corresponding eigenvalue.

Observable operator

An operator whose eigenvalues represent outcomes of measurements

Completeness "axiom"

The eigenfunctions of an observable operator are complete; meaning any function in $\mathcal{H}$ can be expressed as a lin. comb. of them.

Commutator

The **commutator** of two operators $\hat{A}$ and $\hat{B}$ is the operator

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

$\hat{A}$ and $\hat{B}$ **commute** IFF $\hat{C} = 0$

Notable commutators

$[\hat{x},\hat{p}_x] = i\hbar$	$[\hat{\mathbf{r}},\hat{\mathbf{p}}] = 3i\hbar$	$[\hat{p},\hat{T}] = 0$
$[\hat{L}_x,\hat{L}_y] = i\hbar\hat{L}_z$ $[\hat{L}_y,\hat{L}_z] = i\hbar\hat{L}_x$ $[\hat{L}_z,\hat{L}_x] = i\hbar\hat{L}_y$		$[\hat{S}_x,\hat{S}_y] = i\hbar\hat{S}_z$ $[\hat{S}_y,\hat{S}_z] = i\hbar\hat{S}_x$ $[\hat{S}_z,\hat{S}_x] = i\hbar\hat{S}_y$

Probability

X is a random variable

if X is *discrete*	if X is *continuous*
$\langle X\rangle = \Sigma_{n=1}^{\infty} x_n p_X(x_n)$	$\langle X\rangle = \int_{-\infty}^{\infty} x f_X(x)dx$
$\langle X^2\rangle = \Sigma_{n=1}^{\infty} x_n^2 p_X(x_n)$	$\langle X^2\rangle = \int_{-\infty}^{\infty} x^2 f_X(x)dx$
$\Pr(a \leq x \leq b) = \Sigma_{a\leq x_n\leq b}\, p_X(x_n)$	$\Pr(a \leq x \leq b) = \int_a^b f_X(x)dx$
$\mathrm{V}[X] = \langle X^2\rangle - \langle X\rangle^2$	
$\sigma_X = \sqrt{\mathrm{V}[X]} = \sqrt{\langle X^2\rangle - \langle X\rangle^2}$	

$p_X(x)$ is the **probability mass function** (**PMF**) of X,
$f_X(x)$ is the **probability density function** (**PDF**) of X,
$\langle X\rangle$ is the **expectation value** of X,
$V[X]$ is the **variance**, and σ_X the **standard deviation**.

Operator identities and properties

$\langle a|\hat{A}^\dagger|b\rangle = \langle b|\hat{A}\,|a\rangle^*$		$\hat{A}|a\rangle = \langle a|\hat{A}^\dagger$
$(\hat{A}^\dagger)^\dagger = \hat{A}$	$(\alpha\hat{A})^\dagger = \alpha^*\hat{A}^\dagger$	$(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger$
$\hat{C} = \hat{A} + \hat{B} \quad \Rightarrow \quad \hat{C}\|\Psi\rangle = \hat{A}\|\Psi\rangle + \hat{B}\|\Psi\rangle$		
$\hat{C} = \hat{A}\,\hat{B} \quad \Rightarrow \quad \hat{C}\|\Psi\rangle = \hat{A}\,(\hat{B}\|\Psi\rangle)$		

State of Q.M. system and the wave function

The state of a system $|\Psi(t)\rangle$ is a vector in $\mathcal{H}$, and can be expressed in different bases of eigenfunctions. The basis we almost always use is that of position:

$\Psi(\mathbf{r},t) = \langle \mathbf{r}|\Psi(t)\rangle$

where $|\mathbf{r}\rangle$ is the eigenfunction of $\hat{\mathbf{r}}$, with eigenvalue $\mathbf{r}$, and $\Psi(\mathbf{r},t)$ is the **wave function**.

2/10 WAVE FUNCTIONS

The **wave function** Ψ is the solution to the TDSE. It is the probability amplitude function of the system. We can derive the probability distribution of various observables from Ψ.

TDSE *(Time dep. Schrödinger Equation)*

$$\hat{\mathrm{H}}\Psi = \hat{\mathrm{E}}\Psi$$

which when written out becomes

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + V\,\Psi = i\hbar\frac{\partial}{\partial t}\Psi$$

with $\Psi = \Psi(\mathbf{r}, t)$, and $V = V(\mathbf{r}, t)$

TISE *(Time indep. Schrödinger Equation)*

If the *potential* is not a function of time, one can use **separation of variables** on Ψ:

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r})\phi(t)$$

which, when put in the Schrödinger Equation, leads to the TISE:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi \quad \text{same as:} \quad \hat{\mathrm{H}}\Psi = E\Psi$$

and

$$\phi(t) = \exp(-iEt/\hbar)$$

General solution to TDSE *(discrete sum)*

Given V indep. of time, the general solution Ψ is a linear combination of separable solutions $\{\psi_n\}$

$$\Psi(\mathbf{r}, t) = \sum_{n=1}^{\infty} c_n\psi_n(\mathbf{r})e^{-iE_nt/\hbar}$$

where $|c_n|^2$ is the *probability* that the measured energy is E_n, thus $\Sigma_n|c_n|^2 = 1$

Finding c_n

Given initial wave function

$$\Psi(\mathbf{r}, 0) = \sum_{n=1}^{\infty} c_n\psi_n(\mathbf{r})$$

using Fourier's trick, we get

$$c_n = \int_{\mathbb{R}^3} \psi_n^*(\mathbf{r})\Psi(\mathbf{r}, 0)d\mathbf{r}$$

Bound state

$E < V(\pm\infty)$

Unbound state

$E > V(\pm\infty)$

In real life, most V are 0 at $\pm\infty$

Requirements of Ψ

Ψ must be continuous and have a continuous derivative.

Ψ must be square-integrable.

The cumulative probability of Ψ must be 1 on its domain (normalized):

$$\langle\Psi(t)|\Psi(t)\rangle = \int_{\mathbb{R}^3} |\Psi(\mathbf{r}, t)|^2 d\mathbf{r} = 1$$

If discrete: $\langle\Psi(t)|\Psi(t)\rangle = \Sigma_n|c_n|^2 = 1$

Properties of $\{\psi_n\}$

The infinite set of solutions to TISE $\{\psi_n\}$ has certain properties:

1. If V is symmetric, then the solutions are alternately **even** and **odd** with respect to the center of the well; ψ_1 is even, ψ_2 is odd and so on...

2. As you go up in energy, each successive state has one more **zero crossing**; ψ_1 has none, ψ_2 has one, ...

3. They are mutually **orthogonal**:

$$\int_{\mathbb{R}^3} \psi_m^*\psi_n d\mathbf{r} = \delta_{mn}$$

4. The set is **complete**, meaning any other function f can be expressed as a linear combination of $\{\psi_n\}$:

$$f(\mathbf{r}) = \sum_{n=1}^{\infty} c_n\psi_n(\mathbf{r})$$

Using the completeness and orthogonality of $\{\psi_n\}$ we have

$$c_n = \int_{\mathbb{R}^3} \psi_n^*(\mathbf{r})f(\mathbf{r})d\mathbf{r}$$

Sometimes called "**Fourier's trick**"

Stationary state *(separable solution)*

State where all observables are indep. of time. This occurs when the **probability density** $|\Psi(\mathbf{r}, t)|^2$ is indep. of time.

Eigenstates/Eigenfunctions and Eigenvalues

When a observable Q is measured, then the system "collapses" from being in a discrete or continuous superposition of eigenstates/eigenfunctions to ONE eigenstate/eigenfunction. The result of the measurement is the eigenvalue related to that eigenstate/eigenfunction. Eigenstates/eigenfunctions and eigenvalues for a observable Q are found using the eigenvalue equation $\hat{\mathrm{Q}}\Psi = q\Psi$

Spectrum

Collection of all eigenvalues q of an operator $\hat{\mathrm{Q}}$. If two or more linearly independent eigenfunctions Ψ share the same eigenvalue, the spectrum is **degenerate**.

If the spectrum of $\hat{\mathrm{Q}}$ is **discrete**, then its eigenfunctions Ψ lie in $\mathcal{H}$ and physically constitute realizable states. Its eigenvalues are real, and eigenfunctions belonging to *distinct* eigenvalues are orthonormal.

If the spectrum of $\hat{\mathrm{Q}}$ is **continuous**, then its eigenfunctions Ψ are not normalizable, and thus not realizable states. Though a lin.comb. of them may be normalizable and thus physically realizable.

Expectation value

For an operator $\hat{\mathrm{Q}}$ representing an observable Q we have

$$\langle Q\rangle = \langle\Psi(t)|\hat{\mathrm{Q}}|\Psi(t)\rangle = \int_{\mathbb{R}^3} \Psi(\mathbf{r}, t)^*\,\hat{\mathrm{Q}}\,\Psi(\mathbf{r}, t)d\mathbf{r}$$

Q.M. expectation values follow classical dynamics

Note that

$$\langle Q^2\rangle = \int_{\mathbb{R}^3} \Psi(\mathbf{r}, t)^*\,\hat{\mathrm{Q}}^2\,\Psi(\mathbf{r}, t)d\mathbf{r}$$

Probability density *(in pos. space)*

$$\Pr(a \le x \le b) = \int_a^b \Psi(x, t)^*\,\Psi(x, t)dx = \int_a^b |\Psi(x, t)|^2 dx$$

where $\Psi(x, t)^*\,\Psi(x, t) = |\Psi(x, t)|^2$ is the PDF of Ψ

Expectation value trick

$$\langle\mathbf{p}\rangle = m\frac{d}{dt}\langle\mathbf{r}\rangle$$

Momentum-space

Operators become:

$$\hat{\mathbf{p}} = \mathbf{p} \quad \text{and} \quad \hat{\mathbf{r}} = i\hbar\nabla_p$$

$$\nabla_p = \frac{\partial}{\partial p_x} + \frac{\partial}{\partial p_y} + \frac{\partial}{\partial p_z}$$

Eulers formula

$$e^{i\varphi} = \cos(\varphi) + i\sin(\varphi)$$

$$\cos(\varphi) = \frac{1}{2}(e^{i\varphi} + e^{-i\varphi})$$

$$\sin(\varphi) = \frac{1}{2i}(e^{i\varphi} - e^{-i\varphi})$$

$$\left|e^{i\varphi}\right| = 1$$

Momentum-space ↔ Position-space

$$\Psi(\mathbf{r}, t) = \langle\mathbf{r}|\Psi(t)\rangle = \int \langle\mathbf{r}|\mathbf{p}\rangle\langle\mathbf{p}|\Psi(t)\rangle d\mathbf{p}$$

$$\Psi(\mathbf{p}, t) = \langle\mathbf{p}|\Psi(t)\rangle = \int \langle\mathbf{p}|\mathbf{r}\rangle\langle\mathbf{r}|\Psi(t)\rangle d\mathbf{r}$$

Complex conjugate

$$(a + ib)^* = (a - ib)$$

$$(e^{i\varphi})^* = e^{-i\varphi}$$

Modulus of complex number

$$|a + bi| = \sqrt{a^2 + b^2}$$

$$\Psi = a + ib \Rightarrow |\Psi|^2 = a^2 + b^2$$

$$\Psi = re^{i\varphi} \Rightarrow |\Psi|^2 = r^2$$

3/10 SOLUTIONS

Infinite square well (1D)

$$V(x) = \begin{cases} 0, & x \in [0, L] \\ \infty, & \text{otherwise} \end{cases}$$

TISE becomes:

$$\frac{d^2\psi}{dx^2} = -k^2\psi, \qquad k \equiv \frac{\sqrt{2mE}}{\hbar}$$

General solution to this is:

$$\psi(x) = A\sin kx + B\cos kx$$

Since ψ must be 0 outside the well, continuity of ψ means:

$$\psi(0) = \psi(a) = 0$$

$$\Rightarrow B = 0 \text{ and } k = \frac{n\pi}{L}, \quad n \in \mathbb{Z}_+$$

Solving $\frac{n\pi}{L} = \frac{\sqrt{2mE}}{\hbar}$ gives

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\pi^2\hbar^2}{2mL^2}n^2$$

A can be found by normalizing ψ

$$|A|^2 = 2/L \;\Rightarrow A = \sqrt{2/L}$$

$$\therefore \psi_n(x) = \sqrt{2/L}\sin\left(\frac{n\pi}{L}x\right)$$

Ladder operators

$$\hat{a}_\pm \equiv \frac{1}{\sqrt{2\hbar m\omega}}(\mp i\hat{p} + m\omega\hat{x})$$

The Hamiltonian can be written as

$$\hat{H} = \hbar\omega\left(\hat{a}_+\hat{a}_- + \frac{1}{2}\right) = \hbar\omega\left(\hat{a}_-\hat{a}_+ - \frac{1}{2}\right)$$

$$[\hat{a}_+\hat{a}_-] = -1 \qquad [\hat{a}_-\hat{a}_+] = 1$$

Exact actions of ladder operators:

$$\hat{a}_+\psi_n = \sqrt{n+1}\,\psi_{n+1}$$

$$\hat{a}_-\psi_n = \sqrt{n}\,\psi_{n-1}$$

Eigenvalue equations:

$$\hat{H}(\hat{a}_-\psi_n) = (E_n - \hbar\omega)(\hat{a}_-\psi_n)$$

$$\hat{H}(\hat{a}_+\psi_n) = (E_n + \hbar\omega)(\hat{a}_+\psi_n)$$

Harmonic Oscillator (1D)

$$V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2x^2 \quad \text{where} \quad \omega^2 = k/m$$

Write TISE using the Hamiltonian expressed with the ladder operators:

$$\hbar\omega\left(\hat{a}_+\hat{a}_- + \frac{1}{2}\right)\psi = E\psi$$

One cannot apply $\hat{a}_-$ forever. At the **ground state**, ψ_0, we have $\hat{a}_-\psi_0 = 0$ which can be used to determine ψ_0:

$$\psi_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\exp\left(-\frac{m\omega}{2\hbar}x^2\right)$$

Which when plugged into TISE gives:

$$E_0 = \frac{1}{2}\hbar\omega$$

By continuous application of $\hat{a}_+$ one finds that

$$\psi_n(x) = A_n(\hat{a}_+)^n\psi_0(x)$$

with energy

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right)$$

One can use the exact action of the ladder operators to show that $A_n = 1/\sqrt{n!}$

Putting it all together:

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\frac{1}{\sqrt{2^n n!}}H_n\left(x\sqrt{m\omega/\hbar}\right)e^{-\frac{m\omega}{2\hbar}x^2}$$

Physicist's Hermite polynomials

$$H_n(x) = (-1)^n\, e^{x^2}\frac{d^n}{dx^n}e^{-x^2}$$

Dirac delta function

$$\delta(x) = \begin{cases} 0, x \neq 0 \\ 1, x = 0 \end{cases} \quad \text{and} \quad \int_{-\infty}^{\infty}\delta(x)dx = 1$$

Kronecker-delta

$$\delta_{mn} = \begin{cases} 0, m \neq n \\ 1, m = n \end{cases}$$

Dirac-orthonormality

$$\langle x''|\hat{\mathbf{p}}|x'\rangle = \hat{\mathbf{p}}\delta(x'' - x')$$

x'' and x' are position eigenstates

Free particle (1D)

$$V(x) = 0$$

TISE becomes:

$$\frac{d^2\psi}{dx^2} = -k^2\psi, \qquad k \equiv \frac{\sqrt{2mE}}{\hbar}$$

General solution to this is

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$

$$\Rightarrow \Psi(x,t) = Ae^{ik\left(x - \frac{\hbar k}{2m}t\right)} + Be^{-ik\left(x + \frac{\hbar k}{2m}t\right)}$$

Redefine $k \equiv \pm\frac{\sqrt{2mE}}{\hbar}$

$$\Rightarrow \Psi(x,t) = Ae^{i\left(kx - \frac{\hbar k^2}{2m}t\right)}$$

However, this is not correct. Because

$$\int \Psi_k^*\Psi_k dx = |A|^2 \cdot \infty$$

i.e. Ψ not normalizable.

This means separable solutions (stationary states) do not represent physical states of free particles. Meaning: *free particles do not have definite energy*.

General solution to TDSE is still a lin. comb. of separable solutions though, but it's an integral now, not a sum:

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} f(k)e^{i\left(kx - \frac{\hbar k^2}{2m}t\right)}dk$$

Here the product $1/\sqrt{2\pi}\,f(k)dk$ take the role of c_n. One can find $f(k)$ by

$$f(k) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\Psi(x,0)e^{-ikx}dx$$

We say that Ψ carries a range of k and energy values. Calling it a **wave packet**.

Infinite cube (3D)

$$V(\mathbf{r}) = \begin{cases} 0, & x,y,z \in [0, L] \\ \infty, & \text{otherwise} \end{cases}$$

$$\psi_{a,b,c}(\mathbf{r}) = \left(\frac{2}{L}\right)^{3/2}\sin\left(\frac{a\pi}{L}x\right)\sin\left(\frac{b\pi}{L}y\right)\sin\left(\frac{c\pi}{L}z\right)$$

$$E_{a,b,c} = \frac{\pi^2\hbar^2}{2mL^2}(a^2 + b^2 + c^2)$$

where $a, b, c \in 1,2,3, \ldots$

Harmonic Oscillator (3D)

$$V(\mathbf{r}) = \frac{1}{2}k\mathbf{r}^2 = \frac{1}{2}m\omega^2\mathbf{r}^2$$

$$\psi_{a,b,c}(\mathbf{r}) = \psi_a(x)\psi_b(y)\psi_c(z)$$

$$E_{a,b,c} = \hbar\omega(a + b + c + 3/2)$$

where $a, b, c = 0,1,2,3, \ldots$ and ψ_n is solutions to 1D H.O.

Degeneracy

How many states with the same energy. For Infinite Square well, and 1D-Harmonic Oscillator, a specific state is indicated by a specific value of n.

For example: $n = 1, 2, 3, 4$, etc.

For the 3D counterparts, a specific state is indicated by a specific (a, b, c) combination.

For example: $(a, b, c) = (1,1,2), (2,1,1), (1,2,3)$, etc.

4/10 SPHERICAL, HYDROGEN and HELIUM

Spherical ↔ Cartesian

$$x = r\sin\theta\cos\phi \quad y = r\sin\theta\sin\phi \quad z = r\cos\theta$$

$$dV = dx\,dy\,dz = r^2\sin\theta\,dr\,d\theta\,d\phi$$

$$r^2 = x^2 + y^2 + z^2 \qquad \cos\theta = z/r \qquad \tan\phi = y/x$$

r is distance to origin, $\theta \in [0,\pi]$ is **polar angle**, and $\phi \in [0,2\pi]$ is **azimuth angle**.

Spherical Laplacian

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)$$

Spherical TISE

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2\psi}{\partial\phi^2}\right)\right] + V\psi = E\psi$$

Radial and Angular equations

Assuming $\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$, and $V = V(r)$, then from TISE we get

The **radial equation**:

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = Eu$$

where $u(r) = rR(r)$, and $\ell(\ell+1)$ is a separation constant

And the **angular equation**:

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{\partial^2 Y}{\partial\theta^2} = -\ell(\ell+1)\sin^2\theta\ Y$$

Radial equation determines the dependence of ψ on r, and the angular equation determines the dependence of ψ on θ and ϕ.

Solving radial equation

The radial equation is identical to TISE in 1D, with **effective potential**

$$V_{\text{eff}} = V + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}$$

To solve the radial equation for R, we need an expression for V

Solution to angular equation

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

where $Y_\ell^m = Y_\ell^m(\theta,\phi)$. This is called the **spherical harmonics.**

This is assuming we can write $Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$

Legendre Polynomial

$$P_\ell(x) = \frac{1}{2^\ell\ell!}\left(\frac{d}{dx}\right)^\ell(x^2-1)^\ell$$

Associated Legendre Function ($m \geq 0$)

$$P_\ell^m(x) = (-1)^m(1-x^2)^{m/2}\left(\frac{d}{dx}\right)^m P_\ell(x)$$

Reduced mass

$$\mu = \frac{m_e Z m_p}{m_e + Z m_p}$$

Bohr radius

$$a_\mu = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}$$

Associated Laguerre Polynomials

$$L_q^p(x) = \frac{x^{-p}e^x}{q!}\left(\frac{d}{dx}\right)^q(e^{-x}x^{p+q})$$

Associated Legendre Function ($m < 0$)

$$P_\ell^{-m}(x) = (-1)^m\frac{(\ell-m)!}{(\ell+m)!}P_\ell^m(x)$$

Coulomb's Law

$$V(r) = -\frac{1}{4\pi\varepsilon_0}\frac{Z\,e^2}{r}$$

The Bohr Formula (allowed energies of Hydrogen-like atom)

$$E_n = -\left[\frac{Z^2\mu e^4}{32\pi^2\varepsilon_0^2\hbar^2}\right]\frac{1}{n^2} \approx -13.6\text{eV}\cdot\frac{Z^2}{n^2}$$

Hydrogen-like atoms

Systems consisting of ONE electron and Z protons centered at the origin. Allowed energies follow the Bohr formula, and the potential of the electron is given by Coulomb's law.

The **wave function**

$$\psi_{n,\ell,m}(r,\theta,\phi) = R_{n,\ell}(r)Y_\ell^m(\theta,\phi)$$

where $R_{n,\ell}(r)$ is the **radial wave function** (solution to radial equation with Coloumb's potential)

$$R_{n,\ell}(r) = \sqrt{\left(\frac{2Z}{na_\mu}\right)^3\frac{(n-\ell-1)!}{2n(n+\ell)!}}\left(\frac{2Zr}{na_\mu}\right)^\ell e^{-\frac{Zr}{na_\mu}}L_{n-\ell-1}^{2\ell+1}\left(\frac{2Z}{na_\mu}r\right)$$

Physical interpretations of ℓ, n, and m *(not the mass)*

$\ell \in [0, n-1]$ is the angular momentum, and $m \in [-\ell,\ell]$ is the magnetic quantum number. The principal quantum number $n = 1,2,3,\ldots$ represents the energy level. Note $\Delta\ell = \pm1$ and $\Delta m = -1,0,1$. $\ell(\ell+1)$ and m^2 appear as separation constants when solving radial and angular eqs.

Hamiltonian for Helium-like atoms

Two-electron Hamiltonian for helium-like atoms is

$$\hat{\mathrm{H}} = \hat{\mathrm{H}}_1 + \hat{\mathrm{H}}_2 + V_{ee}$$

where:

$$\hat{\mathrm{H}}_1 = -\frac{\hbar^2}{2m}\nabla_{\mathbf{r}1}^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} \qquad \hat{\mathrm{H}}_2 = -\frac{\hbar^2}{2m}\nabla_{\mathbf{r}2}^2 - \frac{Ze^2}{4\pi\epsilon_0 r_2}$$

$$V_{ee} = \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

Where $\mathbf{r}_1$ and $\mathbf{r}_2$ is the distance vectors of electron 1 and 2 with respect to the nucleus (static at origin), and V_{ee} is the electron-electron repulsion.

5/10 OPERATOR MATRICIES and VECTOR REPRESENTATION

Wavefunction as a column vector

The wavefunction $\Psi(\mathbf{r},t)$ is the same as a column-vector $|\Psi(t)\rangle$ in $\mathcal{H}$ in the position basis

$$|\Psi(t)\rangle = \int_{\mathbb{R}^3} \Psi(\mathbf{r},t)\,|\mathbf{r}\rangle d\mathbf{r}$$

Where $\{|\mathbf{r}\rangle\}$ is the position basis spanning $\mathcal{H}$.

Another basis is that of energy, which unlike position is discrete

$$|\Psi(t)\rangle = \sum_{n=1}^{\infty} c_n(t)\,|E_n\rangle$$

Where $\{|E_n\rangle\}$ is the energy basis spanning $\mathcal{H}$.

Visualizing function as a column vector

This is not completely mathematically rigorous, but gives an idea of how a function can be represented as a vector

$\Psi(x,t)$ represented as $\begin{pmatrix} \vdots \\ \Psi(-2\epsilon,t) \\ \Psi(-\epsilon,t) \\ \Psi(0,t) \\ \Psi(\epsilon,t) \\ \Psi(2\epsilon,t) \\ \vdots \end{pmatrix}$ where $\epsilon \to 0$

In other words, you can think of the ket $|\Psi(t)\rangle$ as holding all possible values of Ψ through time, and which can be represented in a certain basis.

Operator as matrix

An operator $\widehat{\mathrm{Q}}$ acting on a wave function $\Psi(x,t)$, is the same as that operator's matrix representation $\mathbf{Q}$ *(in the position basis in this case)*, acting on the vector $|\Psi(t)\rangle$

Common eigenfunctions

$[\widehat{\mathrm{A}},\widehat{\mathrm{B}}] = 0 \Leftrightarrow$ they have common eigenfunctions:

$$\widehat{\mathrm{A}} f_n = a_n f_n$$
$$\widehat{\mathrm{B}} f_n = b_n f_n$$

Ladder operator matrices (H.O.)

$$\hat{\mathrm{a}}_+|n\rangle = \sqrt{n+1}\,|n+1\rangle \Rightarrow \langle m|\hat{\mathrm{a}}_+|n\rangle = \sqrt{n+1}\,\delta_{m,n+1}$$

$$\Rightarrow \hat{\mathrm{a}}_+ \to \mathbf{a}_+ = \begin{pmatrix} 0 & 0 & 0 & \cdots \\ \sqrt{1} & 0 & 0 & \cdots \\ 0 & \sqrt{2} & 0 & \cdots \\ 0 & 0 & \sqrt{3} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

$$\hat{\mathrm{a}}_-|n\rangle = \sqrt{n}\,|n-1\rangle \Rightarrow \langle m|\hat{\mathrm{a}}_-|n\rangle = \sqrt{n}\,\delta_{m,n-1}$$

$$\Rightarrow \hat{\mathrm{a}}_- \to \mathbf{a}_- = \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & \cdots \\ 0 & 0 & \sqrt{2} & 0 & \cdots \\ 0 & 0 & 0 & \sqrt{3} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

Where the basis $\{|n\rangle\}$ is such that

$$|1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix},\quad |2\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix},\quad |3\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \\ \vdots \end{pmatrix}, \text{ etc.}$$

and $\langle m| = |n\rangle^\dagger \Rightarrow \langle m|n\rangle = \delta_{mn}$

Hamiltonian operator matrix (H.O.)

$$\widehat{\mathrm{H}} = \hbar\omega\left(\hat{\mathrm{a}}_+\hat{\mathrm{a}}_- + \frac{1}{2}\right) \Rightarrow \mathbf{H} = \langle m|\hbar\omega\left(\hat{\mathrm{a}}_+\hat{\mathrm{a}}_- + \frac{1}{2}\right)|n\rangle$$

$$\Rightarrow \widehat{\mathrm{H}} \to \mathbf{H} = \hbar\omega\begin{pmatrix} 1/2 & 0 & 0 & \cdots \\ 0 & 3/2 & 0 & \cdots \\ 0 & 0 & 5/2 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

The eigenvalues of a diagonal matrix are the values along the diagonal, which in this case we see matches the eigen energies for the 1D H.O.

Of course, using the same basis $\{|n\rangle\}$ as above

Four ways to attack a Q.M problem

1. Choose a space, like the position space ($\Psi(\mathbf{r},t) = \langle\mathbf{r}|\Psi(t)\rangle$), and solve TDSE
2. Define operators which allow to take or add energy (such as the ladder operators in H.O.)
3. Chose basis vectors, and compute the eigenvalues of the $\mathbf{H}$ matrix (Hamiltonian matrix)
4. Use an approximation method.

UNCERTAINTY

Variance

$$\sigma_Q^2 = \langle Q^2\rangle - \langle Q\rangle^2 = \left\langle \left(\widehat{\mathrm{Q}} - \langle Q\rangle\right)^2 \right\rangle$$

Standard deviation

$$\sigma_Q = \sqrt{\langle Q^2\rangle - \langle Q\rangle^2}$$

Generalized uncertainty principle

$$\sigma_A\sigma_B \geq 1/2 \cdot \left|\,\langle\Psi|[\widehat{\mathrm{A}},\widehat{\mathrm{B}}]|\Psi\rangle\,\right|$$

The uncertainty principle

$$\sigma_x\sigma_p \geq \hbar/2$$

Energy-time uncertainty principle

$$\Delta E\Delta t \geq \hbar/2$$

Where $\Delta E \equiv \sigma_H$ and $\Delta t \equiv \sigma_Q / \left|\frac{d}{dt}\langle Q\rangle\right|$.

Δt represents the amount of time it takes the expectation value of Q to change by one standard deviation. *There is no time operator.*

Generalized Ehrenfest theorem

$$\frac{d}{dt}\langle Q\rangle = \frac{i}{\hbar}\langle\Psi|[\widehat{\mathrm{H}},\widehat{\mathrm{Q}}]|\Psi\rangle + \left\langle\frac{\partial\widehat{\mathrm{Q}}}{\partial t}\right\rangle$$

If $[\widehat{\mathrm{H}},\widehat{\mathrm{Q}}] = 0$ and $\langle\partial\widehat{\mathrm{Q}}/\partial t\rangle = 0$, then $\langle Q\rangle$ is constant, i.e. **conserved.**

Results from Ehrenfest theorem

$$\langle p\rangle = m\frac{d}{dt}\langle x\rangle \qquad \frac{d}{dt}\langle p\rangle = -\left\langle\frac{dV}{dx}\right\rangle$$

Note that $\left\langle\frac{dV}{dx}\right\rangle \neq \frac{d}{dt}\langle V\rangle$

Minimum uncertainty

$$\sigma_x\sigma_p = \hbar/2$$

For the one-dimensional Harmonic Oscillator, this happens at the ground state.

Consequence of the uncertainty principle in 1D

For all 1D systems, we have $E_g > -V_0$. Meaning the ground state energy is always greater than the minimum potential. This is a consequence of the uncertainty principle.

Ground state energy

For an arbitrary *normalized* state Ψ, we have

$$E_g \leq \langle\Psi|\widehat{\mathrm{H}}|\Psi\rangle = \langle H\rangle$$

where E_g is the ground state energy.

If Ψ is not normalized, then $E_g \leq \frac{\langle\Psi|\widehat{\mathrm{H}}|\Psi\rangle}{\langle\Psi|\Psi\rangle}$

6/10 ANGULAR MOMENTUM

Angular momentum operators

$$\hat{\mathrm{L}}_x = y\hat{\mathrm{p}}_z - z\hat{\mathrm{p}}_y \qquad \hat{\mathrm{L}}_y = z\hat{\mathrm{p}}_x - x\hat{\mathrm{p}}_z \qquad \hat{\mathrm{L}}_z = x\hat{\mathrm{p}}_y - y\hat{\mathrm{p}}_x$$

$$\hat{\mathrm{L}}^2 = \hat{\mathrm{L}}_x^2 + \hat{\mathrm{L}}_y^2 + \hat{\mathrm{L}}_z^2$$

Angular momentum operators *(spherical)*

$$\hat{\mathrm{L}}_x = -i\hbar\left[-\sin(\phi)\frac{\partial}{\partial\theta} - \cos(\phi)\cos(\theta)\frac{\partial}{\partial\phi}\right]$$

$$\hat{\mathrm{L}}_y = -i\hbar\left[\cos(\phi)\frac{\partial}{\partial\theta} - \sin(\phi)\cos(\theta)\frac{\partial}{\partial\phi}\right]$$

$$\hat{\mathrm{L}}_z = -i\hbar\frac{\partial}{\partial\phi}$$

Hamiltonian using angular momentum

$$\hat{\mathrm{H}} = \frac{1}{2mr^2}\left[-\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + L^2\right] + V$$

Angular momentum commutators

$$\left[\hat{\mathrm{L}}_x, \hat{\mathrm{L}}_y\right] = i\hbar\hat{\mathrm{L}}_z \qquad \left[\hat{\mathrm{L}}_y, \hat{\mathrm{L}}_z\right] = i\hbar\hat{\mathrm{L}}_x \qquad \left[\hat{\mathrm{L}}_z, \hat{\mathrm{L}}_x\right] = i\hbar\hat{\mathrm{L}}_y$$

$$\left[\hat{\mathrm{L}}^2, \hat{\mathrm{L}}_k\right] = 0 \text{ for } k = x, y, z$$

Generally:

$$\left[\hat{\mathrm{L}}_i, \hat{\mathrm{L}}_j\right] = i\hbar\,\varepsilon_{ijk}\,\hat{\mathrm{L}}_k$$

Angular momentum uncertainty

$$\sigma_{L_i}\sigma_{L_j} \geq \frac{\hbar}{2}\,|\langle L_k\rangle|\,|\,\varepsilon_{ijk}|$$

i.e., if for example L_z is well known, then L_x and L_y are not.

Angular momentum ladder operator

$$\hat{\mathrm{L}}_\pm = \hat{\mathrm{L}}_x \pm i\hat{\mathrm{L}}_y$$

A useful relation: $\hat{\mathrm{L}}_\pm\hat{\mathrm{L}}_\mp = \hat{\mathrm{L}}^2 - \hat{\mathrm{L}}_z^2 \pm \hbar\hat{\mathrm{L}}_z$

Angular momentum eigen equations

Using angular momentum ladder operator, one can show

$$\hat{\mathrm{L}}^2 f_\ell^m = \hbar^2\ell(\ell+1)f_\ell^m \quad \text{and} \quad \hat{\mathrm{L}}_z f_\ell^m = \hbar m f_\ell^m$$

Where the eigen function f_ℓ^m happens to be the spherical harmonics Y_ℓ^m. *Some also represent* f_ℓ^m *as* $|\ell\ m\rangle$.

Three-dimension Levi-Civita symbol

$$\varepsilon_{ijk} = \begin{cases} -1 & \text{if } (i,j,k) \text{ is } (z,y,x), (x,z,y), \text{or } (y,x,z) \\ 0 & \text{if } i = j \text{ or } j = k \text{ or } k = i \\ 1 & \text{if } (i,j,k) \text{ is } (x,y,z), (y,z,x), \text{or } (z,x,y) \end{cases}$$

Pauli matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Hamiltonian in mag. field. using spin

For particle in uniform field magnetic field $\mathbf{B} = B_0\mathbf{e}_z$

$$\hat{\mathrm{H}} = -\gamma B_0\hat{\mathrm{S}}_z = -\alpha_0\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

where $\alpha_0 = \gamma B_0\hbar/2$

Spin expectation value

State of a particle expressed with spin

$$|\Psi(t)\rangle = a\begin{pmatrix} 1 \\ 0 \end{pmatrix}e^{-iE_\uparrow t/\hbar} + b\begin{pmatrix} 0 \\ 1 \end{pmatrix}e^{-iE_\downarrow t/\hbar}$$

where $E_\uparrow = -\alpha_0 = -\gamma B_0\hbar/2$

and $E_\downarrow = \alpha_0 = \gamma B_0\hbar/2$

This state can be written as a spinor

$$|\Psi(t)\rangle = \begin{pmatrix} ae^{i\gamma B_0 t/2} \\ be^{-i\gamma B_0 t/2} \end{pmatrix}$$

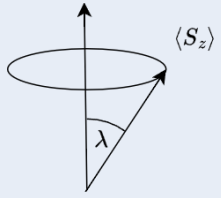
$$\Rightarrow \langle\Psi(t)| = \begin{pmatrix} a^*e^{-i\gamma B_0 t/2} & b^*e^{i\gamma B_0 t/2} \end{pmatrix}$$

Which can be used to find the expectation value:

$$\langle S_k\rangle = \langle\Psi(t)|\hat{\mathrm{S}}_k|\Psi(t)\rangle = \frac{\hbar}{2}\langle\Psi(t)|\sigma_k|\Psi(t)\rangle$$

For S_z it becomes:

$$\langle S_z\rangle = \frac{\hbar}{2}(a^*a - b^*b) = \frac{\hbar}{2}\cos(\lambda)$$



For S_x it becomes:

$$\langle S_x\rangle = \frac{\hbar}{2}(a^*be^{-i\gamma B_0 t} + b^*ae^{i\gamma B_0 t})$$

SPIN

Spin

An *intrinsic* angular momentum carried by elementary particles; somewhat analogous to classical spin.

Spin 1/2

Particles with $s = 1/2$. There are only two spin eigenstates:

Spin up: $|\uparrow\rangle = |s\ m_s\rangle = \left|\frac{1}{2}\ \frac{1}{2}\right\rangle$

Spin down: $|\downarrow\rangle = |s\ m_s\rangle = \left|\frac{1}{2}\ \left(-\frac{1}{2}\right)\right\rangle$

Spin-1/2 operators

$$\hat{\mathbf{S}} = \frac{\hbar}{2}\boldsymbol{\sigma}$$

($\boldsymbol{\sigma}$ = vector whose components are the **Pauli matrices**)

Spin commutators

$$\left[\hat{\mathrm{S}}_x, \hat{\mathrm{S}}_y\right] = i\hbar\hat{\mathrm{S}}_z \qquad \left[\hat{\mathrm{S}}_y, \hat{\mathrm{S}}_z\right] = i\hbar\hat{\mathrm{S}}_x \qquad \left[\mathrm{S}_z, \hat{\mathrm{S}}_x\right] = i\hbar\hat{\mathrm{S}}_y$$

NB: Same relations as with angular momentum operators!

Spinors for spin-1/2 particles

A particles general state can be represented by a 2×1 matrix called a spinor:

$$|\psi\rangle = \begin{pmatrix} a \\ b \end{pmatrix} = a\begin{pmatrix} 1 \\ 0 \end{pmatrix} + b\begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

where $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ representing spin up (↑)

and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ representing spin down (↓)

Spin ladder operator

$$\hat{\mathrm{S}}_\pm = \hat{\mathrm{S}}_x \pm i\hat{\mathrm{S}}_y$$

$$\hat{\mathrm{S}}_- = \hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \qquad \hat{\mathrm{S}}_+ = \hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad \leftarrow \text{acts on spinors}$$

Spin eigen equations

Using the spin ladder operator, one can show

$$\hat{\mathrm{S}}^2|s\ m_s\rangle = \hbar^2 s(s+1)|s\ m_s\rangle \quad \& \quad \hat{\mathrm{S}}_z|s\ m_s\rangle = \hbar m_s|s\ m_s\rangle$$

Unlike ang. mom., $|s\ m_s\rangle$ is not the spherical harmonics, thus no need to omit half-integers s and m_s values:

$$s = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots \qquad m_s = -s, -s+1, \ldots, s-1, s$$

7/10 TOTAL ANGULAR MOMENTUM

Total angular momentum operators

$$\hat{\mathbf{J}}_k = \hat{\mathbf{L}}_k + \hat{\mathbf{S}}_k, \quad k = x, y, z$$

Total angular momentum commutators

$$[\hat{\mathbf{J}}_x, \hat{\mathbf{J}}_y] = i\hbar\hat{\mathbf{J}}_z \qquad [\hat{\mathbf{J}}_y, \hat{\mathbf{J}}_z] = i\hbar\hat{\mathbf{J}}_x \qquad [\hat{\mathbf{J}}_z, \hat{\mathbf{J}}_x] = i\hbar\hat{\mathbf{J}}_y$$

NB: Same relations as with angular momentum operators!

Total angular momentum ladder operator

$$\hat{\mathbf{J}}_\pm = \hat{\mathbf{J}}_x \pm i\hat{\mathbf{J}}_y$$

$$\hat{\mathbf{J}}_\pm |j\ m_j\rangle = \hbar\sqrt{j(j+1) - m_j(m_j \pm 1)}\ |j\ (m_j \pm 1)\rangle$$

Total angular momentum eigen equations

$$\hat{\mathbf{J}}^2 |j\ m_j\rangle = \hbar^2 j(j+1)|j\ m_j\rangle \quad \text{and} \quad \hat{\mathbf{J}}_z |j\ m_j\rangle = \hbar m_j |j\ m_j\rangle$$

$$|\ell - s| \leq j \leq \ell + s$$

Total angular momentum operator matrices

$$\hat{\mathbf{J}}_x = \frac{1}{2}(\hat{\mathbf{J}}_+ + \hat{\mathbf{J}}_-)$$

$$\hat{\mathbf{J}}_y = \frac{1}{2i}(\hat{\mathbf{J}}_+ - \hat{\mathbf{J}}_-)$$

$$\hat{\mathbf{J}}_z = \hbar \begin{pmatrix} j & \cdots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \cdots & -j \end{pmatrix}$$

A matrix with zero everywhere except along the diagonal, where it starts at j and moves down with integer steps to $-j$

QUANTUM NUMBERS

	Name	Range	Usage
n	Principle	$[1, \infty)$	E_n
ℓ	Azimuthal	$[0, n-1]$	$L = \sqrt{\ell(\ell+1)}\hbar$
m	Magnetic	$[-\ell, \ell]$	$L_z = m\hbar$
s	Spin	Int. and Half-int.	$S = \sqrt{s(s+1)}\hbar$
m_s	Spin magnetic	$[-s, s]$	$S_z = m_s\hbar$
j	Tot. ang. moment.	$[\lvert\ell - s\rvert, \ell + s]$	$J = \sqrt{j(j+1)}\hbar$
m_j	Tot. ang. moment. proj.	$[-j, j]$	$J_z = m_j\hbar$

All having integer steps within their range

TWO PARTICLES and TOTAL SPIN

Addition of spin angular momentum

Particle 1 has spin s_1 and m_1, represented by the eigenstate $|s_1\ m_1\rangle$, likewise for a second particle in eigenstate $|s_2\ m_2\rangle$. The composite state is denoted by $|s_1\ s_2\ m_1\ m_2\rangle$. The eigenequations become:

$$\hat{\mathbf{S}}_1^2 |s_1\ s_2\ m_1\ m_2\rangle = s_1(s_1+1)\hbar^2 |s_1\ s_2\ m_1\ m_2\rangle$$
$$\hat{\mathbf{S}}_2^2 |s_1\ s_2\ m_1\ m_2\rangle = s_2(s_2+1)\hbar^2 |s_1\ s_2\ m_1\ m_2\rangle$$
$$\hat{\mathbf{S}}_{1_z} |s_1\ s_2\ m_1\ m_2\rangle = m_1\hbar |s_1\ s_2\ m_1\ m_2\rangle$$
$$\hat{\mathbf{S}}_{2_z} |s_1\ s_2\ m_1\ m_2\rangle = m_2\hbar |s_1\ s_2\ m_1\ m_2\rangle$$

What is the total spin angular momentum?

$$\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$$

Same as asking: what is the net spin s, and what is the z component m_s?

The value of m_s is trivial

$$\hat{\mathbf{S}}_z |s_1\ s_2\ m_1\ m_2\rangle = (\hat{\mathbf{S}}_{1_z} + \hat{\mathbf{S}}_{2_z}) |s_1\ s_2\ m_1\ m_2\rangle$$
$$\Rightarrow \hbar m = \hbar(m_1 + m_2)$$
$$m_s = m_1 + m_2$$

Regarding the net spin s, the answer is that you get every spin from $s_1 + s_2$, down to $s_1 - s_2$ in integer steps (assuming $s_1 > s_2$):

$$s = (s_1 + s_2), (s_1 + s_2 - 1), (s_1 + s_2 - 2) \ldots, (s_1 - s_2)$$

Highest spin when they are parallel, lowest and antiparallel.

Two spin-1/2 particles

Consider a system with two spin-1/2 particles *(e.g. proton and electron in Hydrogen ground state).* Measured on a given axis (usually the z-axzs), each particle can be either spin up ↑, or spin down ↓, giving us four basis states:

$$|\uparrow\uparrow\rangle, \quad |\uparrow\downarrow\rangle, \quad |\downarrow\uparrow\rangle, \quad |\downarrow\downarrow\rangle,$$

$|\uparrow\uparrow\rangle$ and $|\downarrow\downarrow\rangle$ are aligned in z-direction

$\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$ is aligned in x or y direction

Total spin here is $s = 1$ when aligned, thus:

$$(\textbf{triplet state})\ s = 1 \begin{cases} |\uparrow\uparrow\rangle \\ \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ |\downarrow\downarrow\rangle \end{cases}$$

$\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$ is not aligned in any direction, this $s = 0$

$$(\textbf{singlet state})\ s = 0 \begin{cases} \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \end{cases}$$

Bosons (e.g. gluon and photon) have integer spins

Fermions (e.g. quarks, muons, electron, neutrino) have half-integer spin

Two particle system *(no interaction)*

$$\psi(1,2) = \psi_a(1)\psi_b(2)$$

Where $1, 2$ represent all coordinates, spin, etc. of particle 1 and 2 respectively. The indexes a and b represent states.

If $a = b$ then $\psi(1,2) = \psi(2,1)$ else $\psi(1,2) \neq \psi(2,1)$

Bosons:

$$\psi_B(1,2) = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)]$$

Fermions:

$$\psi_F(1,2) = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)]$$

If $a = b$ then $\psi_F(1,2) = 0 \Rightarrow$ Two fermions cannot be in the same state (**Pauli exclusion principle**)

PERTURBATION THEORY

Nondegenerate Perturbation *(time indep.)*

Suppose the TISE cannot be solved exactly

$$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$$

To approximate a solution rewrite $\hat{H}$ so the TISE becomes

$$(\hat{H}_0 + \hat{H}_1)|\psi_n\rangle = E_n|\psi_n\rangle$$

where $\hat{H}_1$ is a small disturbance/perturbation, and

$$\hat{H}_0|\phi_n^0\rangle = \varepsilon_n^0|\phi_n^0\rangle$$

has known analytical solutions ε_n^0 and ϕ_n^0. Where there is no degeneracy.

A 1st order approximation of the wave function and the energy can be expressed as:

$$|\psi_n\rangle \simeq |\phi_n^0\rangle + \sum_{m\neq n} \frac{\langle\phi_m^0|\hat{H}_1|\phi_n^0\rangle}{\varepsilon_n^0 - \varepsilon_m^0}|\phi_m^0\rangle$$
$$E_n \simeq \varepsilon_n^0 + \langle\phi_n^0|\hat{H}_1|\phi_n^0\rangle$$

Note! $\hat{H}_1$ should be relatively small, i.e.,

$$\left|\langle\phi_m^0|\hat{H}_1|\phi_n^0\rangle\right| \ll |\varepsilon_n^0 - \varepsilon_m^0|$$

Degenerate Perturbation *(time indep.)*

If ε_n^0 of $\hat{H}_0$ has degeneracy g; then there exists g orthonormal solutions $X_i^0, i = 1,2,3,\dots,g$ of the equation

$$\hat{H}_0 X_i^0 = \varepsilon_n^0 X_i^0$$

Thus, by linear algebra, we can write

$$\phi_n^0 = \sum_{i=1}^{g} c_i X_i^0$$

Where $\{c_i\}$ are found by the g-number of equations

$$\sum_{i=1}^{g} (H_{ji} - \varepsilon_n^1\delta_{ji})c_i = 0\,, \quad j = 1,2,3,\dots g$$

where $H_{ji} = \langle X_j^0|\hat{H}_1|X_i^0\rangle$ and $\varepsilon_n^1 = \langle\phi_n^0|\hat{H}_1|\phi_n^0\rangle$

The approximations become

$$|\psi_n\rangle \simeq \phi_n^0 = \sum_{i=1}^{g} c_i X_i^0$$
$$E_n \simeq \varepsilon_n^0 + \varepsilon_n^1$$

Note! If $H_{ji} = H_{ji}\delta_{ij}$ then $\varepsilon_n^1 = \varepsilon_i^1 = \langle X_i^0|\hat{H}_1|X_i^0\rangle$
$i = 1,2,3,\dots,g$

Time-Dependent Perturbation Theory

Consider a Hamiltonian consisting of a time-independent part $\hat{H}_0$ and time dependent part $V(t)$:

$$\hat{H} = \hat{H}(t) = \hat{H}_0 + V(t)$$

where $V(t)$ is a disturbance/perturbation. A solution to TDSE can be written as

$$|\Psi(t)\rangle = \Sigma_n\, c_n(t)|\psi_n\rangle e^{-iE_n t/\hbar}$$

where $|\psi_n\rangle$ and E_n are known solutions to the TISE with $\hat{H}_0$. We need to find $\{c_n(t)\}$, which follow the equations

$$i\hbar\dot{c}_m = \sum_n c_n V_{nm} e^{i\omega_{mn}t}\,, \quad m = 1,2,3,\dots$$

where $\dot{c}_m = \frac{d}{dt}c_m$, $V_{nm} = \langle\psi_m|V|\psi_n\rangle$, and $\omega_{mn} = \frac{E_m - E_n}{\hbar}$

Suppose the disturbance $V(t)$ is weak, such that the coefficients $c_n(t)$ vary vert slowly with time, meaning

$$c_m(t) \simeq c_m(t_0) + \frac{1}{i\hbar}\sum_n c_n(t_0)\int_{t_0}^{t} V_{mn}(t')e^{i\omega_{mn}t'}dt'$$

^ **First order general time-dependent perturbation**

If the system is in one of its eigenstates $|\psi_n\rangle$ of $\hat{H}_0$ at time $t = t_0$, we have a **special first order result**:

$$c_m(t) \simeq \delta_{nm} + \frac{1}{i\hbar}\int_{t_0}^{t} V_{mn}(t')e^{i\omega_{mn}t'}dt'$$

The **transition amplitude** $c_f(t)$ from initial state $|\psi_i\rangle$ with energy E_i to a final state $|\psi_f\rangle$ with energy E_f we have

$$c_f(t) \simeq \frac{1}{i\hbar}\int_{t_0}^{t} V_{fi}(t')e^{i\omega_{fi}t'}dt' \quad \text{assuming} \quad f \neq i$$

Transition probability from state i to f is given by

$$P_{i\to f}(t) = |c_f(t)|^2$$

Harmonic Perturbations

Let $V(t) = V_0(\mathbf{r})\cos(\omega t)$ Note $\omega \neq \omega_{fi}$

$$c_{\text{emission}}(t) \simeq \frac{1}{2}\langle\psi_f|V_0|\psi_i\rangle\frac{1 - e^{i(\omega_{fi}+\omega)t}}{E_f - E_i + \hbar\omega} \quad \text{if } E_f < E_i$$

$$c_{\text{absorption}}(t) \simeq \frac{1}{2}\langle\psi_f|V_0|\psi_i\rangle\frac{1 - e^{i(\omega_{fi}-\omega)t}}{E_f - E_i - \hbar\omega} \quad \text{if } E_f > E_i$$

Density of states (DOS)

Number of allowed states per energy

$$\rho(E) = \frac{d}{dE}N(E)$$

Density of states for Fermions

For Fermions with mass m:

$$\rho(E) = V_0 2\pi\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}$$

where V_0 is a general "normalization volume", i.e., the box volume where all wavefunctions are normalized within.

Fermis Golden Rule

Transition probability per unit time (**Transition Rate**) for a transition from an initial state into a continuum of final states becomes constant

$$R_{i\to f} = \frac{d}{dt}P_{i\to f} = \frac{2\pi}{\hbar}|V_{fi}|^2\rho(E_f)$$

Variational Principle (Helium Ground State)

The Hamiltonian for Helium ($Z = 2$), is not possible to solve exactly because of the V_{ee} term. We ignore the term, and the exact solution to TISE with Hamiltonian $\hat{H} = \hat{H}_1 + \hat{H}_2$ becomes

$$\Psi_0(\mathbf{r}_1,\mathbf{r}_2) = \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) = \frac{Z^3}{\pi a_0^3}\exp\left(-\frac{Z}{a_0}[r_1 + r_2]\right)$$

with $Z = 2$

We create a trial wavefunction

$$\phi(\mathbf{r}_1,\mathbf{r}_2)\frac{\alpha^3}{\pi a_0^3}\exp\left(-\frac{\alpha}{a_0}[r_1 + r_2]\right)$$

where α is a variational parameter.

We have

$$E_g \leq E(\alpha) = \langle\phi|\hat{H}|\phi\rangle = \langle H\rangle$$

One would now find $E(\alpha)$ and minimize it as to estimate the ground state of the Helium atom.

One would first rewrite the Hamiltonian to

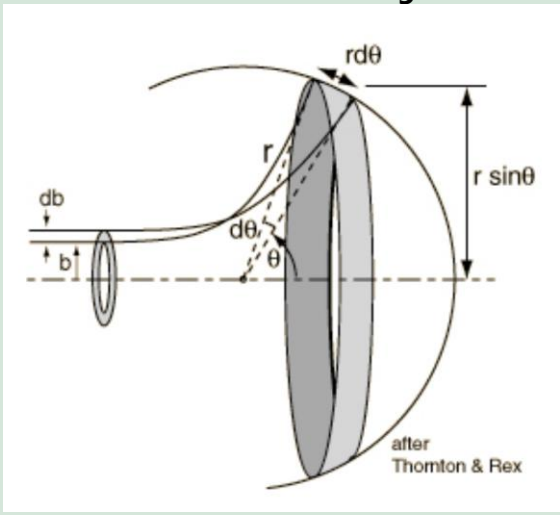
$$\hat{H} = \hat{H}_1 + G\frac{1}{r_1} + \hat{H}_2 + G\frac{1}{r_2} + V_{ee} \text{ where } G = \frac{(\alpha - Z)e^2}{4\pi\epsilon_0}$$

Then find $E(\alpha)$ by

$$E(\alpha) = \langle\phi|\hat{H}_1|\phi\rangle + \langle\phi|\hat{H}_2|\phi\rangle + \langle\phi|V_{ee}|\phi\rangle$$
$$+ G\langle\phi|1/r_1|\phi\rangle + G\langle\phi|1/r_2|\phi\rangle$$

9/10 SCATTERING

Classical Scattering



Source: https://www.tcm.phy.cam.ac.uk/~bds10/aqp/lec20-21.pdf

Scattering angle θ is determined by impact parameter b. We have

$$\frac{d\sigma}{d\Omega} \equiv D(\theta) d\Omega$$

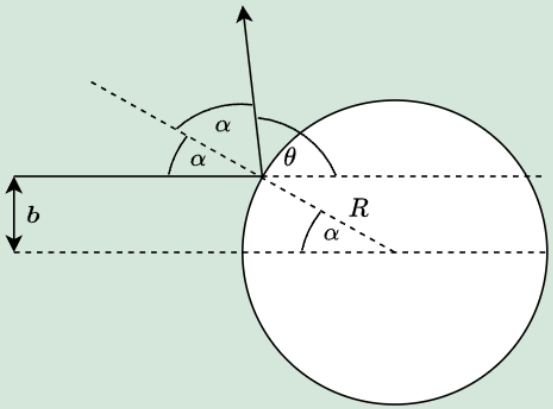
$$D(\theta) = \frac{b\, db\, d\phi}{\sin\theta\, d\theta\, d\phi} = \frac{b}{\sin\theta}\left|\frac{db}{d\theta}\right|$$

where σ is the **cross section** and $d\Omega = \sin\theta\, d\theta\, d\phi$ is the **solid angle.**

$$\sigma = \int d\sigma = \int D(\theta) d\Omega$$

$$= \frac{\#\text{ scattered particles (any angle) per time}}{\#\text{ incident particles per time}}$$

Hard Sphere Scattering



$$\theta = \pi - 2\alpha \qquad \alpha = \frac{\pi}{2} - \frac{\theta}{2}$$

Impact parameter can be expressed as:

$$b = R\sin(\alpha) = R\sin\left(\frac{\pi}{2} - \frac{\theta}{2}\right) = R\cos\left(\frac{\theta}{2}\right)$$

Which implies

$$\theta = \begin{cases} 2\arccos(b/R) & \text{if } b \le R \\ 0 & \text{if } b \ge R \end{cases}$$

$$\left|\frac{db}{d\theta}\right| = \frac{1}{2}R\sin\left(\frac{\theta}{2}\right)$$

$$\Rightarrow D(\theta) = \frac{R\cos(\theta/2)}{\sin(\theta)} \cdot \frac{1}{2}R\sin\left(\frac{\theta}{2}\right)$$

Cross section becomes

$$\sigma = \int d\sigma = \int D(\theta) d\Omega = \pi R^2$$

i.e., size of scattering object

Hard Sphere Scattering Mean Free Path

If there is a quantum probability P_s for scattering in/at the hard sphere, then the total cross section for the transition question becomes

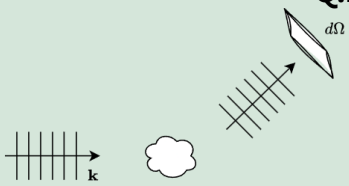
$$\sigma = P_s \pi R^2$$

The smaller P_S, the smaller the geometrical cross section, and the longer becomes an impinging particle mean free path in a medium of spheres:

$$L = 1/\sigma\rho,$$

where ρ is the number of spheres per volume unit. The mean free path is the average distance a particle travels before changing direction or energy due to collisions.

Q.M Scattering



Asymptotic incomming:

$$\psi_{\text{in}} = \frac{1}{\sqrt{v}} e^{i\mathbf{k}\cdot\mathbf{r}} = c e^{i\mathbf{k}\cdot\mathbf{r}}$$

Scattered form of wavefunction

$$\psi_{\text{sc}} = c\, f(\theta,\phi)\, e^{i\mathbf{k}\cdot\mathbf{r}}/r$$

where c some complex constant, and f the **scattering amplitude**.

ψ_{in} and ψ_{sc} are boundry conditions for the TISE

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

which can be reqritten to

$$(\nabla^2 + k^2)\,\psi(\mathbf{r}) = u(r)\,\psi(\mathbf{r})$$

Where $k^2 = 2mE/\hbar^2$ and $u(r) = 2m/\hbar^2 V(r)$

Current density $\rho(\mathbf{r},t) = |\psi(\mathbf{r},t)|^2 \Rightarrow \int_V \rho(\mathbf{r},t)dV = 1$

From the realm of electromagnitism, we have

$$\frac{\partial}{\partial t}\int_V \rho(\mathbf{r},t)dV = -\int_S \mathbf{j}\cdot d\mathbf{S} = \int_V \nabla\cdot\mathbf{j}\, dV$$

Which gives us what is called "**conservation of probability**"

$$\frac{\partial\rho}{\partial t} + \nabla\cdot\mathbf{j} = 0$$

Knowing that $\frac{\partial\rho}{\partial t} = \frac{\partial}{\partial t}\psi^*\psi$, we can use TDSE to find the **current**

$$\mathbf{j} = \text{Re}\left(\psi^*\frac{\hbar}{im}\nabla\psi\right)$$

$$\mathbf{j}_{\text{in}} = \text{Re}\left(\psi^*_{\text{in}}\frac{\hbar}{im}\frac{\partial}{\partial r}\psi_{\text{in}}\cdot\mathbf{e}_{\mathbf{r}}\right) = |c|^2\frac{\hbar\mathbf{k}}{m}$$

$$\mathbf{j}_{\text{sc}} = |c|^2\,|f(\theta,\phi)|^2\,\frac{\hbar\mathbf{k}}{mr^2}$$

The number of particles into $d\Omega$ per time is thus $j_{sc}\cdot r^2 d\Omega$

$$\Rightarrow d\sigma = \frac{j_{\text{sc}}\cdot r^2 d\Omega}{j_{\text{in}}} \Rightarrow \frac{d\sigma}{d\Omega} = |f(\theta,\phi)|^2$$

where $f(\theta,\phi)$ can be approximated as the **Born Approximation** to

$$f(\theta,\phi) \simeq f^B(\theta,\phi) = -\frac{1}{4\pi}\int e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}u(\mathbf{r})\, d\mathbf{r}$$

$\mathbf{k}'$ is for the final plane wave

MISCELLANEOUS

Electron volt unit conversions

Quantity	Unit	Value (3 sig. dig.)
Energy	eV	1.60×10^{-19} J
Momentum	eV/c	5.34×10^{-28} kg · m/s
Mass	$\mathrm{eV/c^2}$	1.78×10^{-36}kg

Fundamental constants

Name	Symbol	Value (3 sig. dig.)	In natural units
Planck's reduced constant	$\hbar$	1.05×10^{-34} Js	1
Speed of light	c	3.00×10^{8} m/s	1
Electron mass	m_e	9.11×10^{-31} kg	0.511 MeV
Proton mass	m_p	1.67×10^{-27} kg	938 MeV
Proton charge	e	1.60×10^{-19} C	$\sqrt{4\pi\alpha}$
Electron charge	$-e$	-1.60×10^{-19} C	$-\sqrt{4\pi\alpha}$
Permittivity of space	ϵ_0	8.85×10^{-12} $\mathrm{C^2/Jm}$	1
Fine structure constant	α	$e^2/(4\pi\epsilon_0\hbar c) \simeq 1/137 \simeq 7.30 \times 10^{-3}$	$e^2/(4\pi)$
Bohr radius (Hydrogen atom)	a_0	$4\pi\epsilon_0\hbar^2/(m_e e^2) \simeq 5.29 \times 10^{-11}$ m	$4\pi/(m_e e^2)$

Common integrals

$$\int x\sin(ax)dx = \frac{1}{a^2}\sin(ax) - \frac{x}{a}\cos(ax)$$

$$\int x\cos(ax)dx = \frac{1}{a^2}\cos(ax) + \frac{x}{a}\sin(ax)$$

Integration by parts

$$\int_a^b f\frac{dg}{dx}\,dx = -\int_a^b \frac{df}{dg}g dx + fg\,\Big|_a^b$$

Exponential integrals

$$\int_0^\infty x^n e^{-x/a}dx = n!\,a^{n+1}$$

$$\int_{-\infty}^{\infty} e^{-ax^2}dx = \sqrt{\frac{\pi}{a}}$$

$$\int_{-\infty}^{\infty} xe^{-ax^2}dx = 0$$

$$\int_{-\infty}^{\infty} x^2 e^{-ax^2}dx = \frac{\sqrt{\pi}}{2\sqrt{a^3}}$$

Gaussian integrals

$$\int_0^\infty x^{2n} e^{-x^2/a^2}dx = \sqrt{\pi}\frac{(2n)!}{n!}\left(\frac{a}{2}\right)^{2n+1}$$

$$\int_0^\infty x^{2n+1} e^{-x^2/a^2}dx = \frac{n!}{2}a^{2n+2}$$

Law of cosines

$$c^2 = a^2 + b^2 - 2ab\cos(\theta)$$

Trigonometric identities

$$\sin(a \pm b) = \sin(a)\cos(b) \pm \cos(a)\sin(b)$$

$$\cos(a \pm b) = \cos(a)\cos(b) \mp \sin(a)\sin(b)$$

$$\sin(a)\sin(b) = \frac{\cos(a-b) - \cos(a+b)}{2}$$

$$\sin(2\theta) = 2\sin\theta\cos\theta$$

$$\cos(2\theta) = \cos^2\theta - \sin^2\theta$$

$$\sin^2\theta = \frac{1-\cos(2\theta)}{2}$$

$$\cos^2\theta = \frac{1+\cos(2\theta)}{2}$$