I.9 Fundamental Properties of Solutions of the Schrödinger Equ.

I.9.1 Eigenvalues and Eigenfunctions

* Let F be a linear operator (*) on a space $\mathcal{S}$ of functions.

If there exists a $\psi \in \mathcal{S}$ and a $\alpha \in \mathbb{C}$ such that

$$\boxed{F\psi = \alpha\psi}$$

we call α an eigenvalue of F and ψ a eigenfunction or eigenstate.

* This is the natural generalization of the concept of eigenvalue and eigenvector from finite-dimensional vector spaces like $\mathbb{R}^n$.

* If ψ is eigenfunction for F with eigenvalue α then $\lambda\psi$ with any $\lambda \in \mathbb{C}$ is also an eigenfunction. The $\lambda\psi$ represent a 1-dimensional eigenspace.

* If an operator F has more than 1 linearly independent eigenfunction for a given eigenvalue α we call the eigenvalue degenerate with degeneracy k if the eigenspace (the maximum subspace of $\mathcal{S}$ spanned by eigenfunctions) has dimension $k > 1$.

(*) all operators from here on will be linear unless said otherwise

I.9.2 The Time Evolution Operator

* A standard problem of wave mechanics is the following: For a given (time-indep.) Hamilton operator H find the solution $\psi(\vec{r},t)$ of the Schrödinger equation $i\hbar \frac{\partial \psi}{\partial t} = H\psi$ such that the initial condition $\psi(\vec{r},t_0) = \psi_0(\vec{r})$ is satisfied.

* Surprisingly, there is a deceivingly simple formal solution.

Theorem:

$$\boxed{\psi(\vec{r},t) = e^{-\frac{i}{\hbar}H(t-t_0)}\,\psi(\vec{r},t_0)}$$

solves the problem above. Here

$$\boxed{T(t,t_0) = e^{-\frac{i}{\hbar}H(t-t_0)}}$$

is the time evolution operator that advances a wave fct. in time.

Why?

$$i\hbar\frac{\partial \psi}{\partial t} = i\hbar\left[\frac{\partial}{\partial t}e^{-\frac{i}{\hbar}H(t-t_0)}\right]\psi(\vec{r},t_0) =$$

$$= i\hbar\left[\underbrace{\frac{\partial}{\partial t}\mathbb{1}}_{0} - \underbrace{\frac{i}{\hbar}H\frac{\partial}{\partial t}(t-t_0)}_{H\cdot\mathbb{1}} + \frac{1}{2!}\left(-\frac{i}{\hbar}\right)^2 H^2\underbrace{\frac{\partial}{\partial t}(t-t_0)^2}_{H\left[-\frac{i}{\hbar}H(t-t_0)\right]} + \dots\right]\psi(\vec{r},t_0)$$

$$= H\,e^{-\frac{i}{\hbar}H(t-t_0)}\psi(\vec{r},t_0) = H\,\psi(\vec{r},t)$$

and $\psi(\vec{r},t=t_0) = \underbrace{e^{0}}_{\mathbb{1}}\,\psi(\vec{r},t_0)$

* In practice the exponential of $\frac{i}{\hbar} H(t-t_0)$ and its action on the initial cond. are difficult to evaluate.

I.9.3 Stationary Solutions and the Time-Independent Schrödinger Equ.

* The time evolution operator becomes a simple phase factor if the initial condition is an eigenfunction of the Hamilton operator:

Let $\psi_E(\vec{r})$ be an eigenfunction of H with (real) eigenvalue E ($\in \mathbb{R}$), i.e. $H\psi(\vec{r}) = E\psi(\vec{r})$. Then if $\psi_E(\vec{r}) = \psi(\vec{r}, t_0)$ is the solution to the time-dep. S.E. at time t_0 at another time t

(1) $$\boxed{\psi(\vec{r}, t) = e^{-\frac{i}{\hbar}E(t-t_0)}\,\psi(\vec{r}, t_0)}$$

Why? $T(t,t_0)\psi(\vec{r},t_0) = \sum \frac{1}{k!}\left(-\frac{i}{\hbar}\right)^k (t-t_0)^k \underbrace{H^k\psi_E(\vec{r})}_{E^k\psi_E(\vec{r})} = e^{-\frac{i}{\hbar}E(t-t_0)}\psi(\vec{r},t_0)$

* In this case $\psi(\vec{r})$ has to satisfy the time-independent Schrödinger equation

(2) $$\boxed{-\frac{\hbar^2}{2m}\Delta\psi_E(\vec{r}) + V(\vec{r})\psi_E(\vec{r}) = E\psi_E(\vec{r})}$$

(in $\vec{r}$-representation)
or more generally

$$\boxed{H\psi_E(\vec{r}) = E\psi_E(\vec{r})}$$

Why? The time-indep. S.E. is equivalent to looking for an eigenfunction of H with eigenvalue E.

* A solution to the t-dep. S.E. of the form (1) that satisfies (2) is called a stationary solution because the $\vec{r}$-dependence does not change with time except for an overall phase. In particular

$$\rho = |\psi(\vec{r},t)|^2 = |\psi_E(\vec{r})|^2 = \text{const.}$$

Moreover for any physical quantity A not explicitly dependent on time (i.e. $\frac{\partial A}{\partial t} = 0$) the expectation value

$$\langle A \rangle = \text{const.}$$

Why? $\langle A \rangle = \int_{\mathbb{R}^3} A\, |\psi|^2 d^3r$ ($|\psi|^2 = \text{const.}$)

* In particular, measurements of the energy, have expectation value $\langle H \rangle = E = \text{const.}$ where E is the (energy) eigenvalue of the stationary state.

Why? $\langle H \rangle = \int \psi^* H \psi \, d^3r = \int \psi^* E \psi \, d^3r = E$

* However, the solution $\psi(\vec{r},t) = e^{-\frac{i}{\hbar}Et}\psi(\vec{r}) = e^{-i\omega t}\psi_E(\vec{r})$ contains only one possible frequency $\omega = \frac{E}{\hbar}$. Therefore it seems that not only the expectation value of a series of energy measurements has to be E, each individual measurement can only lead to the answer E. This is confirmed by experiment.

I. 9.4 Energy Measurements and Energy Spectrum

* We have restricted our choice of eigenvalues for H to real numbers.

Suppose $E = \varepsilon + i\varepsilon'$ is a complex number with $\varepsilon, \varepsilon' \in \mathbb{R}$ and for a eigenfct. $\psi_E(\vec{r})$: $H\psi_E(\vec{r}) = E\psi_E(\vec{r})$ holds.

Then $\psi(\vec{r},t) = e^{-\frac{i}{\hbar}E(t-t_0)}\psi_E(\vec{r})$ is a solution to the S.E.

However $\rho = |\psi(\vec{r},t)|^2 = |\psi_E(\vec{r})|^2 e^{\frac{2}{\hbar}\varepsilon'(t-t')}$

~~For~~ $\varepsilon' \neq 0$ this solution would violate the continuity equation $\int_{\mathbb{R}^3} \rho\, d^3r = \text{const.}$

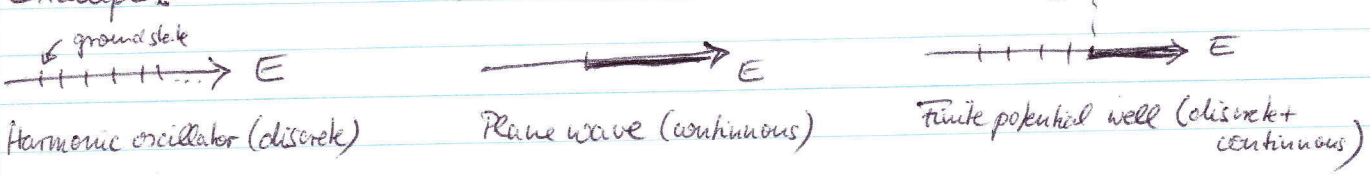
Preliminary conclusion: a proper Hamilton operator should only admit real eigenvalues.

* We'll discuss the existence of real eigenvalues for Hamiltonians further below.

The set of all (real) eigenvalues of H is called the (energy) Spectrum of the system described by H. The spectrum could be discrete or continuous or have both properties.

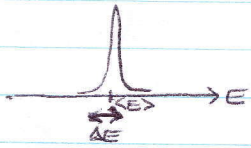
Eigenstates to the smallest energy eigenvalue, if it exists, are called the ground state, all others are excited states.

Examples: (details later)



Harmonic oscillator (discrete) Plane wave (continuous) Finite potential well (discrete + continuous)

* Stationary states that live for an infinite time allow for a sharp, infinitely precise measurement of their energy. This suggests that states with finite lifetime Δt do not allow for infinitely precise energy measurements. Rather they have a width ΔE around $\langle E \rangle$.



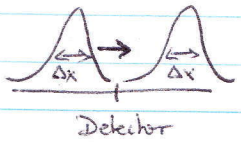
Example: if the excited state of an atom can transition to the ground state we expect it to have finite width ΔE.

* This suggests a kind of uncertainty relation between ΔE and Δt:

$\Delta E \cdot \Delta t \sim$ finite

Back to wave packets of free particles: ~~for~~ a packet of not too large width Δp_x in momentum space (propagating in x-direction) the associated energy uncertainty is $\Delta E = \Delta\left(\frac{p_x^2}{2m}\right) = \frac{p_x}{m}\Delta p_x = v_x \Delta p_x$

The uncertainty of when a packet passes a detector is



$$\Delta t = \frac{\Delta x}{v_x} \geq \frac{\hbar}{2}\frac{1}{v_x \Delta p_x} \geq \frac{\hbar}{2}\frac{1}{\Delta E} \Rightarrow \boxed{\Delta E\, \Delta t \geq \frac{\hbar}{2}}$$

$$\Delta x \Delta p_x \geq \frac{\hbar}{2}$$

I 9.5 Solutions in Momentum Space

* If $\psi_E(\vec{r})$ is a solution to the time-independent S.E. $\left[-\frac{\hbar^2}{2m}\Delta + V(\vec{r})\right]\psi_E(\vec{r}) = E\psi_E(\vec{r})$ then its Fourier transform $\phi_E(\vec{p})$ (if it exists) satisfies the time-independent S.E. in momentum space

$$\boxed{\left[\frac{p^2}{2m} + V\left(i\hbar\nabla_p\right)\right]\phi_E(\vec{p}) = E_E\phi(\vec{p})}$$

i.e. E and $\phi(\vec{p})$ are eigenvalues and eigenfct. of the Hamiltonoperator in $\vec{p}$-space.

Why? Clear.

* Such a $\phi_E(\vec{p})$ represents a stationary state and its time evolution

$$\phi(\vec{p},t) = e^{-\frac{i}{\hbar}E(t)}\,\phi_E(\vec{p})$$

satisfies the t-dependent S.E. in momentum space.

* Obviously plane waves $e^{\frac{i}{\hbar}(\vec{p}\cdot\vec{r}-Et)}$ are stationary states. They satisfy at any time the relevant t-independent S.E.:

$\psi_{\vec{p}_0} = e^{\frac{i}{\hbar}\vec{p}_0\cdot\vec{r}}$ satisfies $-\frac{\hbar^2}{2m}\Delta\psi_{\vec{p}_0}(\vec{r}) = E\psi_{\vec{p}_0}(\vec{r})$ with $E = \frac{p_0^2}{2m}$

The FT $\phi_{\vec{p}_0} = (2\pi\hbar)^{3/2}\delta^{(3)}(\vec{p}-\vec{p}_0)$ satisfies $\frac{p^2}{2m}\phi_{\vec{p}_0}(\vec{p}) = E\phi_{\vec{p}_0}(\vec{p})$!!

There is a continuous degeneracy to each allowed eigenvalue $E>0$. All $\vec{p}$ on a sphere with $|\vec{p}| = \sqrt{2mE}$ are eigenstates to E. The energy spectrum is the positive real line and the point $E=0$.

I.9.6 General Solutions

* We can build more general solutions of the t-dependent S.E. as linear combinations of stationary solutions.

In particular: Suppose[1] the initial condition $\psi(\vec{r},t_0)$ can be decomposed as

$$\psi(\vec{r},t_0) = \sum_E \sum_{j=1}^{k_E} c_E \psi_{E,j}(\vec{r})$$

[1] More on the existence later

for a discrete energy spectrum where k_E is the degeneracy of E and $\psi_{E,j}$, $j=1,\dots,k_E$ span the eigenspace of E; the $c_E \in \mathbb{C}$ are coefficients.

Then

$$\boxed{\psi(\vec{r},t) = \sum_E \sum_{j=1}^{k_E} c_E e^{-\frac{i}{\hbar}E(t-t_0)} \psi_{E,j}(\vec{r})}$$

is solution to the S.E.

* We will sometimes just write "$\sum_E$" and agree that the sum over degeneracies is included.

For continuous energy spectrum the decomposition would be of the form

$$\psi(\vec{r},t_0) = \int_{\text{spectrum}} c(E)\, \psi_E(\vec{r})\, dE$$

again degeneracies have to be summed/integrated implicitly

For mixed discrete/continuous spectra sometimes

$$\psi(\vec{r},t_0) = \int\!\!\!\!\!\!\sum_E c(E)\, \psi_E(\vec{r})\, dE$$

is used as a notation.

* The continuity equation puts an important constraint on solutions of the time-indep. S.E.:

For finite potential energy $V(\vec{r})$ the solution $\psi(\vec{r})$ to the S.E. has to be continuous and differentiable and its partial derivatives are also continuous.

Why? HW II, [4]

I.10 The Virial Theorem

* For a system with t-indep. Hamilton op. H and position and mom. operators $\vec{r}, \vec{p}$ resp. we have

$$[\vec{r}\cdot\vec{p}, H] \overset{\hbar}{=} (2T - \vec{r}\cdot\nabla V(\vec{r})) = [\vec{p}\cdot\vec{r}, H]$$

where T and V are kin. and pot. energy resp. (cf. HW IV, [2])

Hence $$\frac{d}{dt}\langle \vec{r}\cdot\vec{p}\rangle = 2\langle T\rangle - \langle \vec{r}\cdot\nabla V\rangle = 2\langle T\rangle + \langle \vec{r}\cdot\vec{F}\rangle$$

* Defining a time average of a quantity A as usual as $\overline{A} = \lim_{T\to\infty} \frac{1}{T}\int_0^T A(t)\,dt$ we find that for a bound system (i.e. $\langle r\rangle < c_1$, $\langle p\rangle < c_2$ always):

$$\boxed{2\overline{\langle T\rangle} = \overline{\langle \vec{r}\cdot\nabla V\rangle}}$$

Why? $\overline{\frac{d}{dt}\langle \vec{r}\cdot\vec{p}\rangle} = 0$ for bound system (check!)

This is the virial theorem in quantum mechanics. Recall in classical mechanics for bound systems $2\overline{T} = \overline{\vec{r}\cdot\nabla V}$ for cl. positions $\vec{r}$, pot. en. V and kin. en. T.

* For stationary states expectation values are constant thus we obtain the stronger statement

$$2\langle T\rangle = \langle \vec{r}\cdot\nabla V\rangle$$

I.11 Hilbert Spaces and Hermitian Operators

I.11.1 Hilbert Spaces

* Let $\mathcal{S}$ be a (complex) vector space of functions on $\mathbb{R}^n$ ($n \in \mathbb{N}$). If the integral

$$\int_{\mathbb{R}^n} g^*(\vec{r})\, f(\vec{r})\, d^n r \quad \text{exists for all } f, g \in \mathcal{S}$$

then this it defines a scalar product (or inner product) on $\mathcal{S}$. We write

$$\boxed{\langle g | f \rangle := \int_{\mathbb{R}^n} g^*(\vec{r})\, f(\vec{r})\, d^n r} \quad \in \mathbb{C}$$

One can check that it satisfies all properties of a scalar product over $\mathbb{C}$:

(1)
- $\langle g|f\rangle = \langle f|g\rangle^*$, $\langle \alpha g + h | f\rangle = \alpha^* \langle g|f\rangle + \langle h|f\rangle$, $\langle f | \alpha g + h\rangle = \alpha \langle f|g\rangle + \langle f|h\rangle$ (skewed bilinearity)
- $\langle f|f\rangle \geq 0$ (positive definiteness)

for all $f, g, h \in \mathcal{S}$, $\alpha \in \mathbb{C}$

* The scalar product defines a norm and a metric on $\mathcal{S}$:

$$\text{Norm} \quad \|f\| = \sqrt{\langle f|f\rangle} = \left(\int_{\mathbb{R}^n} |f|^2 d^n r \right)^{1/2}$$

$$\text{Metric} \quad d(f,g) = \|f - g\| = \int_{\mathbb{R}^n} |f(\vec{r}) - g(\vec{r})|^2 d r$$

($d(f,g)$: "distance" of f and g)

This makes $\mathcal{S}$ also a metric space and thus a topological space

To be a metric space we need $d(f,g) \leq d(f,h) + d(h,g)$ (2) (triangle inequality)

which follows from the Schwarz inequality (cf. I.4.2) [w/o proof here]

* A topology allows us a notion of convergence in $\mathcal{S}$. A series of functions f_n, $n \in \mathbb{N}$ in $\mathcal{S}$ is said to converge to a limit $g \in \mathcal{S}$ ($f_n \to g$) if $\lim_{n\to\infty} d(f_n, g) = 0$ or $\lim_{n\to\infty} \| f_n - g \| = 0$ or

$$\lim_{n\to\infty} \int_{\mathbb{R}^3} |f_n(\vec{r}) - g(\vec{r})|^2 d^3r \to 0$$

Note that this is a much "weaker" convergence criterion than a pointwise convergence $f_n(\vec{r}) \to g(\vec{r})$ for <u>all</u> $\vec{r} \in \mathbb{R}^3$.

* <u>Any</u> vector space with a scalar product with the properties (1) and (2) is called a pre-Hilbert space. It is called a Hilbert space $\mathcal{H}$ if the following additional property is fulfilled (separability):

(3) For any series $f_n \in \mathcal{H}$ ($n \in \mathbb{N}$) with $\sum_{n\in\mathbb{N}} \|f_n\| < \infty$ converging (this is a $\mathbb{R}$-valued series) it also converges in $\mathcal{H}$, i.e. there is a $g \in \mathcal{H}$ such that $\sum_{n\in\mathbb{N}} f_n \to g$, i.e. $\lim_{n\to\infty} \| \sum_{i=1}^{n} f_i - g \| = 0$

* Example: the space $L^2(\mathbb{R}^n)$ of square-integrable fcts. is a Hilbert space with the scalar product defined above.

Generally, the eligible spaces for wave fcts. in quantum mechanics will be Hilbert spaces with this scalar product.

I.11.2 Hermitian Operators

* Let F be a (linear) operator on a Hilbert space $\mathcal{H}$. The operator $F^\dagger$ on $\mathcal{H}$ is called the adjoint operator to F if for all $f, g \in \mathcal{H}$

$$\boxed{\langle Ff | g \rangle = \langle f | F^\dagger g \rangle}$$

or, for $\mathcal{H}$ a space of fcts.

$$\boxed{\int_{\mathbb{R}^n} (Ff(\vec{r}))^* \, g(\vec{r}) \, d^n r = \int_{\mathbb{R}^n} f^*(\vec{r}) \, F^\dagger g(\vec{r}) \, d^n r}$$

* An operator F is called self-adjoint or Hermitian if $F = F^\dagger$, i.e.

$$\boxed{\langle Ff | g \rangle = \langle f | Fg \rangle} \text{ or (for fct. spaces)}$$

$$\boxed{\int_{\mathbb{R}^n} (Ff(\vec{r}))^* \, g(\vec{r}) \, d^n r = \int_{\mathbb{R}^n} f^*(\vec{r}) \, Fg(\vec{r}) \, d^n r}$$

* The adjoining operation has some basic properties:

- $(\lambda F + G)^\dagger = \lambda^* F^\dagger + G^\dagger$ (anti-linearity)
- $\mathbb{1}^\dagger = \mathbb{1}$ (Hermiticity of the identity)
- $(FG)^\dagger = G^\dagger F^\dagger$
- $(F^\dagger)^\dagger = \mathbb{1}$

for F, G operators on $\mathcal{H}$ and $\lambda \in \mathbb{C}$

Why? Check!

* Multiplication operators with real numbers (e.g. operator $\vec{r}$ or any $f(\vec{r}) \in \mathbb{R}$ in coordinate space or $\vec{p}$ or real fcts. thereof in mom. space) are Hermitian.

$-i\hbar\nabla_r \; (= \vec{p}_{\vec{r}})$ and $i\hbar\nabla_p \; (= \vec{r}_{\vec{p}})$ are Hermitian

(check: $\int_{\mathbb{R}^3} f^*(\vec{r})\, -i\hbar\nabla_r\, g(\vec{r})\, d^3r \underset{\text{part. Int.}}{=} \int_{\mathbb{R}^3} (-i\hbar\nabla_r f(\vec{r}))^*\, g(\vec{r})\, d^3r$ for suff. fast falling fcts. f, g.)

Generally: $F_{\vec{r}}$ Hermitian in $\vec{r}$-space $\Leftrightarrow$ $F_{\vec{p}}$ Hermitian in $\vec{p}$-space.

All important operators from I.7.1 are Hermitian.

* Let F be an operator representing a physical quantity. Obviously we demand that the expectation value $\langle F \rangle$ of measurements be <u>real</u> for any wave function ψ in which the expect. value is taken.

Thus: $\langle F \rangle^* = \left(\int_{\mathbb{R}^3} \psi^* F \psi \, d^3r \right)^* = \int_{\mathbb{R}^3} (F\psi)^* \psi \, d^3r \overset{!}{=} \langle F \rangle = \int_{\mathbb{R}^3} \psi^* F \psi \, d^3r$

for all ψ

$\Rightarrow$ F is Hermitian. (check!)

I.e. operators representing physical observables must be Hermitian.

* Recall: measurements of the Hamilton op. H in an eigenstate ψ_E of H only yield the value E.

Generalization: If a system is in an eigenstate ψ_α (with real eigenvalue α) of an Hermitian operator A representing a phys. quantity A, then measurements of A yield only the value α.

Why? On average $\langle A \rangle = \langle \psi_\alpha | A \psi_\alpha \rangle = \langle \psi_\alpha | \alpha \psi_\alpha \rangle = \alpha$

$$(\Delta A)^2 = \langle (A - \langle A \rangle)^2 \rangle = \langle \psi_\alpha | (A-\alpha)^2 \psi_\alpha \rangle = 0 \qquad \square$$

* Recall: in a finite-dimensional Hilbert space of dim. n (e.g. $\mathbb{R}^n$) any Hermitian operator (matrix) A has n real eigenvalues and their eigenvectors can be chosen to form an orthonormal basis of the space.

Generalization:

For a Hermitian operator A on a Hilbert space $\mathcal{H}$ of functions

- eigenvalues are real (check!)
- eigenfcts. for different eigenvalues are orthogonal

Why? For α_1, ψ_1 and α_2, ψ_2 eigenvalues/-fcts.

$$\left.\begin{aligned} A\psi_1 &= \alpha_1 \psi_1 \\ A\psi_2 &= \alpha_2 \psi_2 \end{aligned}\right\} \quad \int \psi_2^* \alpha_1 \psi_1 \, d^3r - \int \psi_1 (\alpha_2 \psi_2)^* d^3r = \underbrace{\int (\psi_2^* A \psi_1 - \psi_2^* A \psi_1) d^3r}_{A \text{ hermitian}} = 0$$

$$= (\alpha_1 - \alpha_2^*) \int \psi_2^* \psi_1 \, d^3r$$

For $\psi_1 = \psi_2$ (and $\alpha_1 = \alpha_2$) $\quad \text{Im}\,\alpha = 0$

For $\alpha_1 \neq \alpha_2 \quad \int \psi_2^* \psi_1 \, d^3r = 0 \quad$ or $\quad \langle \psi_2 | \psi_1 \rangle = 0$

- For a large class of operators the eigenfcts. span the entire space $\mathcal{H}$ (completeness); we will always assume this to hold for QM operators.

I.11.3 Completeness

* Recall: General solutions of the t-dep. Schrödinger eqn. can be built from eigenfcts. of the Hamiltonop. H. On the other hand those eigenfcts. form a complete basis of the Hilbert space $\mathcal{H}$.

(A) Spectrum of H discrete $\Rightarrow$ Dimension of $\mathcal{H}$ is infinite and countable (or finite)

(B) Spectrum of H continuous $\Rightarrow$ Dimension of $\mathcal{H}$ is infinite and uncountable

CASE (A)

* For any Hermitian op. A on $\mathcal{H}$ (and in particular the Hamilton op. H) with orthogonal eigenstates ψ_α, $\alpha \in I$ ($I = \mathbb{N}$ or a subset thereof) completeness means that for any other fct. $\phi \in \mathcal{H}$

$$\boxed{\phi(\vec{r}) = \sum_{\alpha \in I} c_\alpha \psi_\alpha(\vec{r})}$$

← degeneracies are summed over implicitly as usual

with complex coefficients c_α, $\alpha \in I$.

* It follows that all ϕ are square-integrable, i.e. $\mathcal{H} \subset L^2(\mathbb{R}^3)$

Then we can choose the eigenfct. basis to be orthonormal, i.e. $\boxed{\langle \psi_\alpha | \psi_{\alpha'} \rangle = \int \psi_\alpha^* \psi_{\alpha'} d^3r = \delta_{\alpha\alpha'}}$

and $$\boxed{c_\alpha = \langle \psi_\alpha | \phi \rangle = \int_{\mathbb{R}^3} \psi_\alpha^*(\vec{r})\, \phi(\vec{r})\, d^3r}$$

Why? $\int_{\mathbb{R}^3} \psi_\alpha^* \phi \, d^3r = \sum_{\alpha' \in I} c_{\alpha'} \underbrace{\int_{\mathbb{R}^3} \psi_\alpha^* \psi_{\alpha'} \, d^3r}_{\delta_{\alpha\alpha'}} = c_\alpha$ finite

* Moreover $\langle \phi | \phi \rangle = \int_{\mathbb{R}^3} \phi^*(\vec{r}) \, \phi(\vec{r}) \, d^3r = \sum_{\alpha \in I} |c_\alpha|^2$ Why? clear!

In particular for a wave fct. normalized to 1: $\|\phi\| = \sum_{\alpha \in I} |c_\alpha|^2 = 1$

* For the Hermitian operator A the expectation value with respect to a normalized wave fct. ϕ is

$$\boxed{\langle A \rangle = \sum_\alpha \alpha |c_\alpha|^2} \qquad (\Pi)$$

where α are the eigenvalues of A and the c_α the expansion coefficients of ϕ w.r.t the orthonormal eigenfct. basis ψ_α.

Generally for any fct. $f(A)$

$$\boxed{\langle f(A) \rangle = \sum_\alpha f(\alpha) |c_\alpha|^2}$$

Why? Check!

* Sometimes it is useful to have the completeness or closure relation:

$$\boxed{\sum_{\alpha \in I} \psi_\alpha^*(\vec{r}') \, \psi_\alpha(\vec{r}) = \delta^{(3)}(\vec{r} - \vec{r}')}$$

for an orthonormal basis ψ_α, $\alpha \in I$

Why? $\int_{\mathbb{R}^3} \phi(\vec{r}') \Big(\sum_\alpha \psi_\alpha^*(\vec{r}') \, \psi_\alpha(\vec{r}) \Big) d^3r' = \sum_\alpha \psi_\alpha(\vec{r}) \overbrace{\int_{\mathbb{R}^3} \psi_\alpha^*(\vec{r}') \, \phi(\vec{r}') \, d^3r'}^{\text{expansion coeff. } c_\alpha \text{ for } \phi}$

$= \sum_\alpha c_\alpha \psi_\alpha(\vec{r}) = \phi_\alpha(\vec{r})$ for any $\phi \in \mathcal{H}$, same as $\int \phi(\vec{r}) \, \delta^{(3)}(\vec{r} - \vec{r}') \, d^3r'$

* Equation (□) suggests the following interpretation:

(i) $|c_\alpha|^2$ is the probability to measure the value α if a measurement of the phys. quantity represented by the oper. A is carried out, i.e. $P(\alpha) = |c_\alpha|^2 = |\langle \psi_\alpha | \phi \rangle|^2$

(ii) In particular: the eigenvalues of A are the only allowed outcomes of a measurement of A.

This is confirmed by experiment.

Note: if the eigenvalue α is degenerate then in more detailed notation

$$P(\alpha) = \sum_{i=1}^{k} |c_{\alpha,i}|^2$$ where $\psi_{\alpha,i}$, $i=1,\dots,k$ are a orthonormal basis of the eigenspace for α.

CASE (B)

* Completeness now means that for any Hermitian operator A on $\mathcal{H}$ with orthogonal eigenstates ψ_α

$$\boxed{\phi(\vec{r}) = \int b_\alpha \, \psi_\alpha(\vec{r}) \, d\alpha}$$

or, if in addition there is a set of discrete eigenvalues α_i

$$\boxed{\phi(\vec{r}) = \sum_i c_{\alpha_i} \psi_{\alpha_i}(\vec{r}) + \int b_\alpha \psi_\alpha(\vec{r}) \, d\alpha}$$

The integration range is over the entire continuous spectrum of A, including implicit summation or integration over degeneracies.

* Each eigenfct. in the continuous spectrum now has only infinitesimal weight in the expansion. This clears the way for fcts. that are not L^2.

However it turns out that we can replace the orthonormality condition in L^2 by

$$\boxed{\langle \psi_{\alpha'} | \psi_\alpha \rangle = \int_{\mathbb{R}^3} \psi_{\alpha'}^*(\vec{r})\, \psi_\alpha(\vec{r})\, d^3r = \delta(\alpha' - \alpha)}$$

"A – normalization" since the δ-fct. is in eigenvalues of A.

* One can check that all the basic properties for L^2-spaces and discrete spectra generalize in a straight forward way.
One way to show this is by taking continuous spectra as the limit of discrete spectra in a box of finite dimension L and let $L \to \infty$ (see Herzbacher p. 61 f)

* In particular we have

$$\boxed{b(\alpha) = b_\alpha = \langle \psi_\alpha | \phi \rangle = \int_{\mathbb{R}^3} \psi_\alpha^*(\vec{r})\, \phi(\vec{r})\, d^3r}$$

and

$$\boxed{\langle f(A) \rangle = \int f(\alpha)\, |b_\alpha|^2\, d\alpha}$$

and the completeness relation

$$\boxed{\int \psi_\alpha^*(\vec{r}')\, \psi_\alpha(\vec{r})\, d\alpha = \delta^{(3)}(\vec{r} - \vec{r}')}$$

I. 11.4 Two Simple Examples

CASE (A): Infinite square well.

* Consider a particle of mass m in a potential

$V(\vec{r}) = 0$ for $0<x<L$, $0<y<L$, $0<z<L$ $\quad (\vec{r}=(x,y,z))$

$V(\vec{r}) = \infty$ elsewhere.

We have to solve $-\frac{\hbar^2}{2m}\Delta\psi(x,y,z) = E\psi(x,y,z)$ in the cube L^3

to obtain the eigenvalues and eigenfcts. of H.

Boundary conditions: outside the cube $\psi = 0$, else the potential energy $\langle V\rangle = \int \psi^* V \psi \, d^3r$ of the particle is infinite. On the walls: from the continuity equation (cf. HW II, [4](a)) current $\vec{j}$ on both sides is equal and zero. $\Rightarrow \psi = 0$ on the walls.

* Solve with separation ansatz: $\psi(x,y,z) = X(x)\,Y(y)\,Z(z)$

$$\Rightarrow \frac{d^2X}{dx^2} = -k_x^2 X \quad , \quad \frac{d^2Y}{dy^2} = -k_y^2 Y \quad , \quad \frac{d^2Z}{dz^2} = -k_z^2 Z$$

with $E = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)$

With the boundary conditions the solutions are sin fcts. with $k_i = \text{integer} \cdot \frac{\pi}{L}$

$$\Rightarrow \boxed{\psi(x,y,z) = C \sin n_x \tfrac{\pi}{L} x \sin n_y \tfrac{\pi}{L} y \sin n_z \tfrac{\pi}{L} z} \qquad n_x, n_y, n_z \in \mathbb{N}$$

with $\boxed{E = \underbrace{\frac{\hbar^2\pi^2}{2mL^2}}_{E_0}(n_x^2 + n_y^2 + n_z^2)}$

The latter are the possible eigenvalues. In 3-dimensions most values are degenerate.

Spectrum:

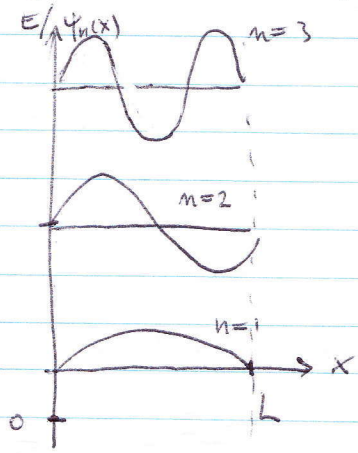
E	$3E_0$	$6E_0$	$9E_0$	$11E_0$	$12E_0$	...
	ground state					
Degeneracy	1	3	3	3	1	
	$(n_x,n_y,n_z)=(1,1,1)$	$(2,1,1)$ $(1,2,1)$ $(1,1,2)$	$(2,2,1)$ $(2,1,2)$ $(1,2,2)$	$(3,1,1)$ $(1,3,1)$ $(1,1,3)$	$(2,2,2)$	

The eigenfcts. $\psi_{n_x n_y n_z} = \frac{8}{L^3} \sin n_x \frac{\pi}{L} x \sin n_y \frac{\pi}{L} y \sin n_z \frac{\pi}{L} z$

form an orthonormal basis of the L^2-fcts on the box L^3 with vanishing values on the boundary. This is a special case of ~~Fourier~~'s Theorem!

* Eigenfcts. in 1-D: $\psi_n(x) = \frac{2}{L} \sin n \frac{\pi}{L} x$, energy $E = \frac{\hbar^2 \pi^2}{2mL^2} n^2$

non-degenerate



CASE (3): Free particle

* We know the solutions to are linear combinations of plane waves

$$\psi_{\vec{p}}(\vec{r}) = C e^{\frac{i}{\hbar} \vec{p} \cdot \vec{r}}$$

They are eigenstates to both the momentum operator $\vec{p} = -i\hbar \nabla_r$

and the Hamiltonian $H = \frac{p^2}{2m}$:

$\hat{\vec{p}}\,\psi_{\vec{p}}(\vec{r}) = \vec{p}\,\psi_{\vec{p}}(\vec{r})$ (more accurately: $\psi_{\vec{p}}$ is eigenfct. to P_x, P_y, P_z simultaneously.

($\hat{\vec{p}}$: op., $\vec{p}$: number)

$$\hat{H}\,\psi_{\vec{p}}(\vec{r}) = \underbrace{\frac{p^2}{2m}}_{E}\,\psi_{\vec{p}}(\vec{r})$$

We will usually prefer to label eigenstates with eigenvalues $\vec{p}$ since there is no degeneracy.

~~For~~ eigenvalues E there is a continuous degeneracy that can be parameterized by points $\hat{n}$ on the unit sphere: $\psi_{\vec{p}} = \psi_{E,\hat{n}}$ $\left(\hat{n} = \frac{\vec{p}}{p}\right)$

(E: eigenvalue, $\hat{n}$: degeneracy label)

* Normalization: $\langle \psi_{\vec{p}'} | \psi_{\vec{p}} \rangle = C^2 \int e^{+\frac{i}{\hbar}(\vec{p}-\vec{p}')\cdot\vec{r}}\, d^3r = C^2 (2\pi\hbar)^3 \delta(\vec{p}-\vec{p}')$

$\Rightarrow C = (2\pi\hbar)^{-3/2}$ in momentum normalization

* The expansion of arbitrary fcts.

$$\psi(\vec{r}) = \frac{1}{(2\pi\hbar)^{3/2}} \int_{\mathbb{R}^3} b_{\vec{p}}\, e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}}\, d^3p$$

is just the ~~Fourier~~ integral, i.e. $b_{\vec{p}} = \phi(\vec{p})$ is the ~~Fourier~~ transform.

* Closure relation:

$$\int_{\mathbb{R}^3} \psi^*_{\vec{p}}(\vec{r}')\,\psi_{\vec{p}}(\vec{r})\, d^3p = (2\pi\hbar)^{-3} \int_{\mathbb{R}^3} e^{\frac{i}{\hbar}\vec{p}(\vec{r}-\vec{r}')}\, d^3p = \delta^{(3)}(\vec{r}-\vec{r}')$$

as expected.

I.12 Unitary Operators and Representations

I.12.1 Unitary Operators

* Let $\mathcal{H}$ be a Hilbert space. A linear operator U on $\mathcal{H}$ is called unitary if

$$\boxed{U^\dagger U = U U^\dagger = \mathbb{1}}$$

($\mathbb{1}$: identity operator)

This is equivalent to the condition $\boxed{\langle Uf | Ug\rangle = \langle f|g\rangle}$ (for all $f,g \in \mathcal{H}$)

($\langle Uf|Ug\rangle = \langle f|U^\dagger U g\rangle = \langle f|g\rangle$)

I.e. unitary operators are the ones who preserve scalar products (and norms).

* Recall: in $\mathbb{R}^n$ unitary operators (matrices) are rotations and inversions.

They form a group of matrices called $O(n)$, the orthogonal group.

Generalisation: The unitary operators on $\mathcal{H}$ form a (usually non-abelian) group w.r.t. their "product".

Why? U_1, U_2 unitary, then $(U_1U_2)^\dagger U_1U_2 = U_2^\dagger U_1^\dagger U_1 U_2 = \mathbb{1}$ etc.

$\Rightarrow U_1U_2$ unitary. Unit element: $\mathbb{1}$ is unitary, inverse: $U^{-1} = U^\dagger$ is unitary

* Eigenvalues of unitary operators have modulus 1, i.e. can be written as $e^{i\phi}$, $\phi \in \mathbb{R}$, and eigenfcts. for different eigenvalues are orthogonal.

Why? $U\psi_1 = \alpha_1\psi_1$, $U\psi_2 = \alpha_2\psi_2 \Rightarrow 0 = \int \psi_2^* \psi_1 d^3r - \int \psi_2^* U^\dagger U \psi_1 d^3r$

$= (1 - \alpha_2^*\alpha_1)\int \psi_2^*\psi_1 d^3r$

if $\alpha_1 \neq \alpha_2$ $\int \psi_2^*\psi_1 d^3r = 0$; if $\alpha_1 = \alpha_2 \Rightarrow |\alpha_1|^2 = 1$

I.12.2 Representations and Galilei Group

* Symmetry operations usually form groups.
  - E.g. translations $t_{\vec{a}}: \vec{r} \mapsto \vec{r}+\vec{a}$ with $\vec{a} \in \mathbb{R}^3$; the $t_{\vec{a}}$, $\vec{a} \in \mathbb{R}^3$ form a group w.r.t. to concatenation: $t_{\vec{b}} t_{\vec{a}}: \vec{r} \mapsto (\vec{r}+\vec{a})+\vec{b} = \vec{r}+(\vec{a}+\vec{b})$
  i.e. $t_{\vec{b}} t_{\vec{a}} = t_{\vec{b}+\vec{a}}$. This is obviously an abelian group analogous ("isomorphic") to $\mathbb{R}^3$ and summations of vectors in there.
  - The Galilei group $\mathcal{G}$ of translations, rotations, boosts (with speeds $v<c$) and space and time inversions form a group. The most general transformation is $t \mapsto \lambda t + b$; $\vec{r} \mapsto R\vec{r} + \vec{w}\lambda t + \vec{a}$; $\vec{r} \mapsto \lambda \vec{r} + \vec{w}$
  where $R \in O(3)$, $\lambda = \pm 1$, $b \in \mathbb{R}$, $\vec{a} \in \mathbb{R}^3$, $\vec{w} \in \mathbb{R}^3$.
  Elements with $\det R = +1$, $\lambda = +1$ form the proper orthochronous subgroup $\mathcal{G}_+^+$.

* In classical mechanics operations of symmetry groups like $\mathcal{G}$ are (usually) straightforward.
In QM symmetry operations have to act on states ψ in Hilbert space $\mathcal{H}$.
How? They need to be represented by operators on $\mathcal{H}$. For simplicity they should be linear (or anti-linear) operators.
Since symmetry transformations leave a system invariant their operators need to preserve probabilities $\hat{=}$ scalar products on $\mathcal{H}$. Thus operators for symmetry transformations are usually unitary.

* For any symmetry group G a set of (linear or anti-linear) operators $D(G)$ on a Hilbert space $\mathcal{H}$ is called a representation of G if there is a unique map $G \to D(G)$, $g \mapsto D_g$ (group element g, operator D_g)

and $D(G)$ has the same group structure as G w.r.t. operator multiplication.

In particular $D_{gh} = D_g D_h$

Sometimes we have to relax this condition to include a (physically unobservable) phase: $D_{gh} = e^{i\phi(g,h)} D_g D_h$ where ϕ real (with certain addl properties)

This is called a projective representation.

* Some symmetry transformations are topologically connected to the identity operator $\mathbb{1}$ (i.e. can be continuously deformed into $\mathbb{1}$). For example the proper orthochronous Galilei group $\mathcal{G}_+^+$ is fully connected to $\mathbb{1}$, the parity transformation $\vec{r} \mapsto -\vec{r}$ can not be deformed into $\mathbb{1}$.

Transformations in the neighborhood of $\mathbb{1}$ can be parameterized by real parameters. For example translations along x: $\vec{r} \to r + a_x \hat{e}_x$ (a_x: real parameter)

In that case operators representing them can be expanded around $\mathbb{1}$:

$$D_g = \mathbb{1} + \frac{i}{\hbar}\varepsilon G + O(\varepsilon^2)$$

(ε: parameter, G: operator)

The operator G is called a generator of the transformation

* D_g is unitary exactly if the generator G is Hermitian.

Why? $\mathbb{1} = D_g^\dagger D_g = (\mathbb{1} - i\varepsilon G)^\dagger (\mathbb{1} - i\varepsilon G) = \mathbb{1} + i\varepsilon G^\dagger - i\varepsilon G + O(\varepsilon^2)$

$\Rightarrow G^\dagger = G$

I. 12.3 Translations

* The time translation operator $\mathcal{D}_b = T(b) = e^{-\frac{i}{\hbar}Hb}$ (cf. I.9.2) is a unitary operator and represents time translations $t \mapsto t+b$ for a system with Hamilton op. H.

Why: $\mathcal{D}_b \psi(\vec{r},t) = \psi(\vec{r},t+b)$ (I.9.2) for all ψ in the Hilbert space.

$\mathcal{D}_{b_2}\mathcal{D}_{b_1} = e^{-\frac{i}{\hbar}H(b_2+b_1)} = \mathcal{D}_{b_2+b_1}$ (group structure); $\mathcal{D}_b^\dagger \mathcal{D}_b = e^{-\frac{i}{\hbar}H(b-b)} = \mathbb{1}$ (unitarity)

$(-)H$ is the generator of time translations.

* The effect of spatial translations is $\psi(\vec{r},t) \mapsto \psi(\vec{r}+\vec{a},t)$

$$\psi(\vec{r}+\vec{a},t) = \sum_{n=0}^{\infty} \frac{1}{n!}(\vec{a}\cdot\nabla_r)^n \psi(\vec{r},t) \quad \text{Taylor expansion}$$

$$= e^{\vec{a}\cdot\nabla_r}\psi(\vec{r},t) = e^{\frac{i}{\hbar}\vec{a}\cdot\vec{p}}\psi(\vec{r},t)$$

($\vec{p}$: momentum operator.)

I.e. the generators of translations in x, y, z are the operators p_x, p_y, p_z

$[p_i, p_j] = 0 \quad \forall i,j = 1,2,3 \Rightarrow$ translations in arbitrary directions commute

$[H, p_i] \neq 0$ except for free particles $\Rightarrow$ time and spatial directions don't commute.

I.12.4 Galilei Boosts

* Consider a change to another coordinate system moving with velocity $-\vec{w}$ w.r.t. the original one: $\vec{r} \mapsto \vec{r} + \vec{w}t$, $\vec{v} \mapsto \vec{v} + \vec{w}$

Thus $\vec{p} \mapsto \vec{p} + m\vec{w}$, $E \mapsto E + \vec{p}\cdot\vec{w} + \frac{mw^2}{2}$ for particle of mass m.

For a plane wave (we expect) $\psi(\vec{r},t) = (2\pi\hbar)^{-3/2} e^{\frac{i}{\hbar}(\vec{p}\cdot\vec{r} - Et)} \mapsto (2\pi\hbar)^{-3/2} e^{\frac{i}{\hbar}\left((\vec{p}+m\vec{w})\vec{r} - (\omega + \vec{p}\vec{w} + \frac{mw^2}{2})t\right)}$

On the other hand: $\psi(\vec{r}-\vec{w}t, t) = (2\pi\hbar)^{-3/2} e^{\frac{i}{\hbar}(\vec{p}\cdot\vec{r} - \vec{w}\cdot\vec{p}t - \omega t)}$

$$\Rightarrow \Psi(\vec{r},t) \xrightarrow[\text{boost}]{\text{Galilei}} e^{\frac{i}{\hbar}(m\vec{w}\cdot\vec{r} - \frac{mw^2}{2}t)} \psi(\vec{r}-\vec{w}t, t) \qquad (\square)$$

(corrections to energy and momentum)

Since momentum and energy to be linear we expect $(\square)$ to hold for all wave fcts. ψ, not just plane waves

* The (unitary) operator $e^{\frac{i}{\hbar}\vec{w}\cdot\vec{K}}$ represents boosts by a velocity $\vec{w}$ on the Hilbert space $\mathcal{H}$ as given by $(\square)$, where

$$\boxed{\vec{K} = m\vec{r} - \vec{p}t}$$

$\vec{r}, \vec{p}$: position, momentum operators

is the (Hermitian) generator of boosts.

The representation of $\mathcal{G}_+^\uparrow$ discussed here is projective, i.e. phases can appear upon concatenation of these unitary operators.

More details and why: HW VI

* Rotations in the Galilei group: later

I.13 The Schrödinger Equation with Electromagnetic Fields

* Recall: the magnetic force can usually not be expressed with the help of a (scalar) potential. But there is a vector potential $\vec{A}(\vec{r},t)$, how does it enter the S.E.

Remember $\vec{E} = -\nabla\phi - \frac{\partial \vec{A}}{\partial t}$ el. field, $\vec{B} = \nabla \times \vec{A}$ magn. field.

(ϕ: scalar pot.)

* Recall: $H = \frac{1}{2m}\left(\vec{p} - q\vec{A}\right)^2 + q\phi$ is the class. Hamilton fct. for a particle of mass m, charge q in potentials $\vec{A}(\vec{r},t)$, $\phi(\vec{r},t)$

We find: the Schrödinger equation with el. magn. fields

$$\boxed{i\hbar \frac{\partial \psi}{\partial t} = \frac{1}{2m}\left(-i\hbar\nabla - q\vec{A}\right)^2 \psi + q\phi\psi}$$

reduces to the classical Hamilton-Jacobi eqn. for the phase of the wave fct. and the classical continuity equation in the limit $\hbar \to 0$.

Why? HW IX, [3]

* In particular: the Hamiltonoperator corresponding to the Hamilton fct. above is

$$\boxed{H = \frac{1}{2m}\left(\vec{p} - q\vec{A}\right)^2 + q\phi}$$

where $\vec{p}$ is the usual momentum operator.

* The S.E. above is invariant under simultaneous gauge transformations

$$\vec{A} \mapsto \vec{A} + \nabla f \;, \quad \phi \mapsto \phi - \frac{\partial f}{\partial t} \;, \quad \psi \mapsto e^{\frac{i}{\hbar} q f} \psi \;,$$

$f(\vec{r}, t)$ arbitrary fct., of el. magn. potentials and the wave fct.

Why? HW ~~V~~, [4](a)

* The expectation value of the velocity operator

$$\vec{v} = \frac{1}{m}\left(\vec{p} - q\vec{A}\right)$$

($\vec{p}$ = mom. op.) moves according to

$$m \frac{d\langle \vec{v} \rangle}{dt} = \frac{q}{2}\left\langle \vec{v} \times \vec{B} - \vec{B} \times \vec{v} \right\rangle + q\langle \vec{E} \rangle \,.$$

(Lorentz force)