Theoretical Biophysics

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Quantum Theory und Molecular Dynamics

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Preface - Aim of the lecture

Provide an introduction into quantum theory with a particular focus on applications in biophysics (molecular QT), it shall provide an entry point for study of a broad range of methods and approaches in quantum biophysics and quantum chemistry. Please note that a full and extensive development of the quantum theory from first principles is beyond the scope of this one-semester lecture. Therefore certain topics might be omitted or addressed only briefly in side-notes, such as the coordinate free formulation using the Dirac-notation ("bra", "ket"). A full understanding of this more elegant formulation requires a much more in-depth development of the mathematical basis of quantum theory (linear Algebra, Hilbert-space), which can not be given in the available time-frame. Nevertheless, the lecture is intended to enable interested students to dive in the more advanced topics on their own.

1 Introduction

Up to begin of 20th century the classical (theoretical) physics consisted of two independent pillars:

Matter	Radiation
particles / trajectories	waves / fields
– classical mechanics (Newton, Lagrange, Hamilton,...) – statistical mechanics (Boltzmann,...) – classical thermodynamics	– classical electrodynamics (Maxwell, Faraday, Hertz...)

However at the end of 19th and begin of 20th century more and more experimental observations accumulated which could not be accounted for by these classical theories.

1. Quantum nature of radiation $\rightarrow$ not explainable by classical electrodynamics where radiation was considered to behave as waves based on multiple experimental observations (e.g. Young two-slit experiment $\rightarrow$ interference)

$$\rightarrow \text{particle-wave dualism.}$$

   - Black body radiation (1900):
   Phenomenological assumption $\rightarrow$ emission and absorption of energy is only possible in packets (quantized)
   $E_n = nh\nu,\ n = 1, 2\ldots,\ h = 6,63 \cdot 10^{-34} Js = 4.14 \cdot 10^{-15} eVs$
   $\rightarrow$ Planck's law agrees with experiments
   - Photoelectric effect (first experiments 1887):
   Experimental observations:
   – number of emitted electrons proportional to the intensity of light
   – kinetic energy of electrons proportional to the frequency of light
   but independent of intensity!
   Theoretical explanation by Einstein (1905):
   Radiation consists of photons with energy $E = h\nu \rightarrow$ provides an explanation
   - Compton Effect (1922):
   X-ray scattering can be understood as inelastic collisions of 'particles'
   energy of a photon: $E = h\nu = pc$
   momentum of a photon: $p = h\nu/c = h/\lambda$

2. Structure and stability of 'fundamental' units of matter (atoms) can not be explained by classical mechanics and electrodynamics

   - Rutherford's scattering (1911) $\rightarrow$ 'planetary model' of an atom:
   radius of nucleus $R_n \approx 5 \cdot 10^{-15} m$ radius of atom (electron orbit)
   $R_n \approx 5 \cdot 10^{-10} m$ Classical electrodynamics: unstable configuration as accelerated charges should (electron rotating around atom) radiate and lose continous energy, classically predicted lifetimes $\approx 10^{-11} s$:
   - Line spectra of elements (emission/absorption) cannot be explained, only empirical description, e.g. for hydrogen Balmer/Rydberg:
   $\nu = R \left(\frac{1}{m^2} - \frac{1}{n^2} \right),\ n, m \in \mathbb{N},\ n < m$
   - Bohr's atom model (1913): classical mechanics + additional postulates
   1) stable quantized orbits (radiation free)
   2) emission + absorption of radiation correspond to transition between two orbits $h\nu = E_n - E_m \rightarrow$ Balmer/Rydberg formula
   Fails for more complicated atoms (He), ad-hoc assumptions without foundations
   - De Broglie's matter waves (1923/24): Particles (Electrons, Protons, etc) can be ascribed a wave length (frequency) following the Planck/Einstein

formulae: $p = mv = h/\lambda$, $E = h\nu$

Combining de Broglie relations with Bohrs first postulate allows the 'interpretation' as quantized orbits as orbits which fulfill the boundary conditions of a standing wave.

$\rightarrow$ natural question: Can particles behave as waves?

- Experimental demonstration of diffraction with electrons (Davisson+Germer, 1927)

$\rightarrow$ Wave-particle dualism for radiation & matter

- both pillars of theoretical physics are affected.

- similar phenomena & problems, thus the theoretical solution may be similar

In the end a single theory emerges which provides a "synthesis" of the classical theoretical pillars: Quantum Theory (incl. Quantum Field Theory). It provides a highly successful theoretical framework for describing the fundamental building blocks of matter and radiation at small (atomic) scales.

Correspondence principle: All objects obey the laws of quantum mechanics. However for large systems and/or high energies classical mechanics/electrodynamics provide good quantitative predictions $\rightarrow$ classical theories as a limiting case for large systems (many degrees of freedom) or large quantum numbers (high energy).

Quantum Biophysics (Molecular Quantum Physics): Quantum theories of biophysical systems and biomolecules provide a theoretical foundation for:

- biochemistry (quantum chemistry)

- quantitative methods for analysis of biomolecules (e.g. spectroscopy)

- biological function of quantum systems (e.g. photosynthesis, enzymatic activity, etc).

2 Postulates of Quantum Mechanics

We start with the fundamental postulates of quantum theory. A lot of the terms and concepts here will be completely new and abstract (wavefunction, operator, measurement, Schrödinger equation). However this postulates provide the absolute basis of all of quantum theory: **Whatever we do in quantum theory, must make sense in the light of these postulates**. Throughout the lecture and the accompanying exercise all the novel terms should get clarified.

2.1 Quantum states

> The state of a system is fully described by its wave function:
>
> $$\Psi(\mathbf{r_1}, \mathbf{r_2}, \ldots, \mathbf{r_N}, t)$$

- The wave function depends on the coordinates of all particles in the system.

- it is complex and not directly measurable

- motivated by the wave-particle dualism

- for non-interacting particles it can be decomposed into a product of single particle functions:

$$\Psi(\mathbf{r_1}, \mathbf{r_2}, \ldots, \mathbf{r_N}, t) = \psi(\mathbf{r_1}, t)\psi(\mathbf{r_2}, t), \ldots \psi(\mathbf{r_N}, t)$$

- Probabilistic interpretation of wave functions: The square of the wave function $|\psi(\mathbf{r}, t|^2$ is proportional to the probability to find the particle in the time intervall dt at position $\mathbf{r}$, thus it corresponds to a probability density (with correct normalization). The wave function is also referred to as probability amplitude.
  As a consequence:

  - The wave function must be unique: For each value of $\mathbf{r}$ only one value of $\psi(\mathbf{r})$.

  - The wave function must be continuous

  - The first derivative has to be continuous (Exception: points in space with infinite potential)

  - The wave function must be quadratically integrable (in space - not time!)
    $$\int_{\Omega} |\psi(\mathbf{r}, t)|^2 d\mathbf{r} < \infty \tag{1}$$

    with Ω being the space where the wave function is defined, e.g. for the full n-dimensional Cartesian space Ω corresponds to $\mathbb{R}^n$ ($n = 1, 2, 3$).

2.2 Observables

Each quantity A that can be "measured" is described by linear, self-adjoint (hermitian) operator $\hat{A}$.

<u>Definition</u> of an hermetian operator $\hat{A}$: An operator that is its own hermitian conjugate:
$$\hat{A} = \hat{A}^\dagger$$

with $A^\dagger$ being the adjunct operator ("complex conjugated").

$$\langle \phi | A\psi \rangle = \int_{-\infty}^{+\infty} \phi^*(\hat{A}\psi)dx = \int_{-\infty}^{+\infty} (\hat{A}^\dagger \phi^*)\psi dx = \langle \hat{A}^\dagger \phi | \psi \rangle$$

Equivalent formulation of the postulate in bra/ket notation:

$$\langle\phi|\hat{A}\psi\rangle = \left[\langle\psi|\hat{A}\phi\rangle\right]^*$$

An important consequence: Hermitian operators have only real eigenvalues. Thus all allowed expectation values of an observable (see next two postulates below) are real as should be for real physical quantities.

2.3   Measurement Results

In any measurement of the observable associated with operator $\hat{A}$, the only values that will be ever observed are the eigenvalues a, which satisfy

$$\hat{A}\Psi = a\Psi\,.$$

This postulate states a central point of quantum mechanics– values of dynamical variables can be quantized (discrete). However, it is also possible to have a continuum of eigenvalues in the case of unbound states. If the system is in an eigenstate of $\hat{A}$ with eigenvalue a then any measurement of quantity A will yield a.

The state of the quantum system does not have to be an eigenstate of $\hat{A}$ before the measurement. An arbitrary state can be always expanded in the complete set of eigenstates of $\hat{A}$:

$$\Phi = \sum_i^n c_i\Psi_i$$

The eigenvalues a_i will occur during measurement with probability $|c_i|^2$.

Important consequence: The measurement of Ψ which yields the eigenvalue a_i, leads to a "collapse" of the wavefunction into the corresponding eigenstate

Measurement affects the state of the system.

2.4   Expectation Value

If the system is described by a normalized wave function ($\langle\Psi|\Psi\rangle = 1$), then the average value of the observable corresponding to $\hat{A}$ is

$$\langle A\rangle = \langle\Psi|\hat{A}\Psi\rangle = \int_\Omega \Psi^*\hat{A}\Psi d\omega$$

2.5   Schrödinger Equation

> The state function (wavefunction) of a system evolves in time according to the time-dependent Schrödinger equation
>
> $$i\hbar\partial_t\Psi(\mathbf{r_1},\ldots,\mathbf{r_N},t) = \hat{H}\Psi(\mathbf{r_1},\ldots,\mathbf{r_N},t)$$
> $$= -\frac{\hbar^2}{2m}\Delta\Psi(\mathbf{r_1},\ldots,\mathbf{r_N},t) + V\Psi(\mathbf{r_1},\ldots,\mathbf{r_N},t)$$

3   Fundamentals: Wavefunction, Operators and Uncertainty

3.1   A brief excursion to probability theory

<u>Discrete variables</u>

Lets consider $n(j)$ observations of a discrete variable j, with total number of observations $n = \sum_j n(j)$. Examples could be a coin toss experiment (two states, $j = 0, 1$, n throws), or a distribution of ages in years of a sample of n people. The probability to observe a certain state is:

$$p(j) = \frac{n_j}{n}\ .$$

By definition the probability distribution must be normalized: $\sum_j p(j) = 1$. The most probable observation is given by the value $\tilde{j}$ with maximum probabilty: $p(\tilde{j}) = max(p(j))$, whereas the expectation value ("mean") of the discrete variable is given by

$$\langle j\rangle = \sum_j jp(j)\ .$$

For a general function of j we can calculate the expectation value as:

$$\langle f(j)\rangle = \sum_j f(j)p(j)$$

Note: In general,

$$\langle j\rangle \neq \tilde{j} \qquad \text{and} \qquad \langle f(j)\rangle \neq f(\langle j\rangle).$$

For the variance $\sigma^2 = (j - \langle j\rangle)^2$ one can easily show that the following identity holds

$$\sigma^2 = \langle j^2\rangle - \langle j\rangle^2$$

which gives a convenient recipe to calculate the standard deviation as

$$\sigma = \sqrt{\langle j^2\rangle - \langle j\rangle^2}.$$

Note, this directly implies that $\langle j^2 \rangle \geq \langle j \rangle^2$ must hold for all distributions.

Continuous variables

For variables which can assume continuous values $x \in \mathbb{R}$ (e.g. the age of sample of people given not in years but up to arbitrary fraction of a second), we define a probability density function, which gives us the probability to observe a value of x in a infinitesimally small interval dx: $\rho(x)dx$. We can assign a finite probability only to an interval of x:

$$p_{ab} = \int_a^b \rho(x)dx.$$

Analogous to the discrete variables we have:

$$1 = \int_\Omega \rho(x)dx \stackrel{\text{e.g. } \Omega=\mathbb{R}}{=} \int_{-\infty}^{+\infty} \rho(x)dx$$

$$\langle x \rangle = \int_\Omega x\rho(x)dx$$

$$\langle f(x) \rangle = \int_\Omega f(x)\rho(x)dx$$

$$\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2$$

3.2 Wave function and Operators

Normalization of the wave function

Based on the statistic interpretation of quantum mechanics, we identify $|\Psi(x,t)|^2$ with a probability density. Thus the wavefunction must fulfill the following equation (normalization):

$$\int_\Omega |\Psi(x,t)|^2 dx = \int_\Omega \Psi^*(x,t)\Psi(x,t)dx = 1. \tag{2}$$

But if the wave equation evolves according to the Schrödinger equation, does it stay normalized at all times?

Starting from

$$\frac{d}{dt} \int_{-\infty}^{+\infty} |\Psi(x,t)|^2 dx = \int_{-\infty}^{+\infty} \frac{\partial}{\partial t} |\Psi(x,t)|^2 dx \tag{3}$$

with

$$\frac{\partial}{\partial t}|\Psi|^2 = \frac{\partial}{\partial t}\Psi^*\Psi = \Psi^*\frac{\partial \Psi}{\partial t} + \Psi\frac{\partial \Psi^*}{\partial t} \tag{4}$$

as well as the Schrödinger equation for Ψ and its complex conjugated version for Ψ^*:

$$\frac{\partial}{\partial t}\Psi = +\frac{i\hbar}{2m}\frac{\partial^2}{\partial x^2}\Psi - \frac{i}{\hbar}V\Psi \tag{5}$$

$$\frac{\partial}{\partial t}\Psi^* = -\frac{i\hbar}{2m}\frac{\partial^2}{\partial x^2}\Psi^* + \frac{i}{\hbar}V\Psi^* \tag{6}$$

we eventually arrive at:

$$\frac{\partial}{\partial t}|\Psi(x,t)|^2 = \frac{i\hbar}{2m}\left(\Psi^*\frac{\partial^2}{\partial x^2}\Psi - (\frac{\partial^2}{\partial x^2}\Psi^*)\Psi\right)$$
$$= \frac{\partial}{\partial x}\left[\frac{i\hbar}{2m}\left(\Psi^*\frac{\partial}{\partial x}\Psi - (\frac{\partial}{\partial x}\Psi^*)\Psi\right)\right] \qquad (7)$$

With the pulling-out of the derivative ($\partial_x^2\Psi = \partial_x(\partial_x\Psi)$ above, we can perform partial integration, and eventually write the time evolution of the normalization as

$$\frac{d}{dt}\int_{-\infty}^{+\infty}|\Psi(x,t)|^2 dx = \frac{i\hbar}{2m}\left[\Psi^*\frac{\partial}{\partial x}\Psi - (\frac{\partial}{\partial x}\Psi^*)\Psi\right]_{-\infty}^{+\infty} \qquad (8)$$

As $\Psi(x,t)$ must vanish for $x \rightarrow \pm\infty$ (normalization!) the right hand size is equal zero:

$$\frac{d}{dt}\int_{-\infty}^{+\infty}|\Psi(x,t)|^2 dx = 0 \qquad (9)$$

$\rightarrow$ The normalization is independent on time (constant). A once normalized wave function remains normalized - conservation of probability! QM version of conservation of mass.

Operators & Observables

The expectation value from many (independent!) measurements of position (ensemble average) for a given quantum state is given by

$$\langle x \rangle = \langle \Psi | x \Psi \rangle = \int_{-\infty}^{+\infty}\Psi^* x(x,t) x \Psi(x,t) dx = \int_{-\infty}^{+\infty} x|\Psi(x,t)|^2 dx \qquad (10)$$

The time evolution of the expectation value of the position is given by (see Eq. 8):

$$\frac{d\langle x \rangle(t)}{dt} = \int_\Omega x\frac{\partial}{\partial t}|\Psi(x,t)|^2 dx \qquad (11)$$
$$= \frac{i\hbar}{2m}\int_\Omega x\frac{\partial}{\partial x}\left(\Psi^*\frac{\partial}{\partial x}\Psi - (\frac{\partial}{\partial x}\Psi^*)\Psi\right) dx \qquad (12)$$

This can be simplified again using partial integration and using $\partial x/\partial x = 1$ to

$$\frac{d\langle x \rangle(t)}{dt} = -\frac{i\hbar}{m}\int_\Omega \Psi^*(\frac{\partial}{\partial x}\Psi) dx \qquad (13)$$

which can be compared to the "classical" equation:

$$\frac{d\langle x \rangle(t)}{dt} = \langle v \rangle, \qquad (14)$$

where the change of the expectation value of position is given by the expectation value of the velocity (ensemble average).

In quantum mechanics, it is better to work with momentum instead of the velocity, and for the momentum expectation value we obtain:

$$\langle p \rangle(t) = m \frac{d\langle x \rangle}{dt} = -i\hbar \int_{\Omega} \Psi^* \frac{\partial}{\partial x} \Psi \, dx \tag{15}$$

We recall the postulate in 2.4: $\langle A \rangle = \int_{\Omega} \Psi^* \hat{A} \Psi dx$, and by comparing we immediately obtain the definitions of the position operator and the momentum operator, especially which we use additional (suggestive) brackets:

$$\langle x \rangle = \int_{\Omega} \psi^* \left\{ x \right\} \psi \, dx \qquad = \langle \psi | \hat{x} \psi \rangle$$

$$\langle p \rangle = \int_{\Omega} \psi^* \left\{ \frac{\hbar}{i} \frac{\partial}{\partial x} \right\} \psi \, dx = \langle \psi | \hat{p} \psi \rangle$$

Using similar approach we can "construct" all possible operators for physical observables. Here are examples of (classical) observables and the corresponding operators in vector form for $\mathbb{R}^n$:

Name	Observable	Operator	Operation
position	$\mathbf{r}$	$\hat{\mathbf{r}}$	multiply with $\mathbf{r}$
momentum	$\mathbf{p}$	$\hat{\mathbf{p}}$	$-i\hbar \nabla_{\mathbf{r}}$
kinetic energy	T	$\hat{T}$	$-\frac{i\hbar}{2m} \Delta_{\mathbf{r}}$
potential energy	$V(\mathbf{r})$	$\hat{V}(\mathbf{r})$	multiply with $\hat{V}(\mathbf{r})$
total energy	E	$\hat{H}$	$-\frac{i\hbar}{2m} \Delta_{\mathbf{r}} + V(\mathbf{r})$
angular momentum	$\mathbf{L}$	$\hat{\mathbf{L}}$	$\hat{r} \times \hat{\mathbf{p}} = -i\hbar(\mathbf{r} \times \nabla_{\mathbf{r}})$
ang. momentum x-component	l_x	$\hat{l}_x$	$-i\hbar(y\partial_z - z\partial_y)$

3.3   Uncertainty principle

We recall the de-Broglie relation from the introduction for matter waves:

$$p = \frac{h}{\lambda} = \frac{2\pi\hbar}{\lambda} = \hbar k \tag{16}$$

with λ being the wavelength of a matter wave, and k being the wave number. This immediately implies if I uncertain about the wavelength of a matter wave λ, I am also uncertain about its momentum. However by simple consideration one realizes that for wave packets (see below) we can either determine the wavelength accurately only in cases where the wave is spread out. On the other hand for strongly localized wavepackets it is not possible to find a single wavelength, so the wavelength is uncertain (see schematic figure in lecture).

This uncertainty is a fundamental consequence of the description of particles by wave functions. It can be derived and quantified more rigorously with the so called Heisenberg's uncertainty principle.

$$\sigma_x \sigma_p \geq \frac{\hbar}{2} \tag{17}$$

with σ_x and σ_p being the standard deviation of the position and momentum, respectively.

4 Time-independent Schrödinger equation

In the last postulate 2.5 we introduced the Schrödinger equation, which describes the evolution of the wave function. In principle, we just need to know how to solve this equation and we can solve all quantum mechanical problems. Unfortunately it is often not that easy, but there some problems of where analytical solutions of the Schrödinger equationare possible. Furthermore, we can also approximations to simplify complex problems to provide approximate solutions for of real-world problems.

In this section we will consider specifically the case where the potential is independent on time $V = V(x)$. The Schrödinger equation reads,

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = -\frac{\hbar^2}{2m} \Delta \Psi(\mathbf{r}, t) + V(\mathbf{r}) \Psi(\mathbf{r}, t)$$

with the Laplace operator $\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$. using the definition of the Hamilton operator in a short form as:

$$i\hbar \Psi(\mathbf{r}, t) = \hat{H} \Psi(\mathbf{r}, t) \tag{18}$$

Please note that with an time-independent potential, also the Hamilton operator is independ on time.

Side note: In the Dirac-notation with bra/kets it reads:

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{H} |\Psi\rangle \tag{19}$$

Although the difference to the Eq. 18 appears tiny, it is actually a pretty significant one: Here $|\Psi\rangle$ corresponds to the quantum state in a general coordinate-free representation, whereas in 18, the quantum state is described by a wave function in specific (space) representation.

For simplicity, we will consider now the Schrödinger equation in one dimension. Nevertheless all the following discussion and results can be extended without problems to more spatial dimensions. In 1d we have:

$$i\hbar \frac{\partial}{\partial t} \Psi(x, t) = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + V(x) \Psi(x, t) \tag{20}$$

The above equation can be solved with so called *separation of variables* approach, because the potential does not depend on t. We assume that the wave function solving the equation can be written as a product of a purely space dependent function and a purely time depenent function:

$$\Psi(x,t) = \phi(t)\psi(x)$$

As a consequence our partial derivative read:

$$\frac{\partial}{\partial t}\Psi = \psi\frac{d\phi}{dt}, \quad \frac{\partial^2\Psi}{\partial x^2} = \phi\frac{d^2\psi}{dt^2} \tag{21}$$

Inserting this into the Eq. 20 and dividing by $\phi(t)\psi(t)$ yields:

$$i\hbar\frac{1}{\phi(t)}\frac{\partial\phi(t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{\partial^2\psi(x)}{\partial x^2} + V \tag{22}$$

Please note that the left hand side depends only on time and the right hand side depends only on position. This two sides can only be equal if they are constant (do not change if we change t or x). Otherwise, one could change the position, which would change the right hand side, without changing the left-hand side which clearly would mean that both sides are not equal anymore. We will name this constant E, as it will turn out that it corresponds to the total energy of the quantum state.

$$i\hbar\frac{1}{\phi(t)}\frac{\partial\phi(t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{\partial^2\psi(x)}{\partial x^2} + V = E = const. \tag{23}$$

So we end up effectively with two ordinary differential equations. Lets take a look first at the time-dependent part, from which we obtain the following differential equation:

$$\frac{d}{dt}\phi = -\frac{i}{\hbar}E\phi \tag{24}$$

The general solution of the above equation ($d\phi/dt = -\lambda\phi$ with $\lambda = -iE/\hbar$) reads

$$\phi(t) = Ce^{-i\frac{E}{\hbar}t} \tag{25}$$

Here, without loss of generality we can set $C = 1$ as we can normalize the full wave function Ψ via the spatial part ψ.

The second equation (spatial part) reads:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi = E\psi \tag{26}$$

$$\hat{H}\psi = E\psi \tag{27}$$

This is the so-called time-independent Schrödinger equation. Its solution, the spatial wave function $\psi(x)$, depends on the form of the potential $V(x)$.

The full wave function $\Psi = \psi\phi$ is time dependent:

$$\Psi(x,t) = \psi(x)e^{-\frac{iE}{\hbar}t} \tag{28}$$

but the probability density turns out to be time-independent:

$$|\Psi(x,t)|^2 = \Psi^*\Psi = \psi^*e^{+\frac{iE}{\hbar}t}\psi e^{-\frac{iE}{\hbar}t} = |\psi(x)|^2 \tag{29}$$

Thus all separable solutions of Eq. 20 are stationary quantum states, with all observables being time independent:

$$\langle A \rangle = \int_\Omega \Psi^* \hat{A} \Psi \, dx = const. \tag{30}$$

In particular:

$$\langle x \rangle = const., \quad \langle p \rangle = 0$$

. Thus, nothing moves in a pure stationary quantum state.

Any linear combination of stationary solutions of the Schrödinger equation is also a solution. Thus we can write any solution as an superposition of all possible separable solutions:

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n\psi_n(x)e^{-\frac{iE_n}{\hbar}t} = \sum_{n=1}^{\infty} c_n\Psi_n(x,t) \tag{31}$$

It corresponds to a superposition (or mixture) of quantum states with different (allowed) energies. The full temporal evolution is set by the initial condition at time $t = 0$:

$$\Psi(x,0) = \sum_{n=1}^{\infty} c_n\psi_n(x) \tag{32}$$

In contrast to a pure stationary state the probability density of a mixed state is not constant. It can be shown for the simplest case of the superposition of only two states, with the initial condition:

$$\Psi(x,0) = c_1\psi_1(x) + c_2\psi_2(x) \tag{33}$$

The time-dependent solution reads:

$$\Psi(x,t) = c_1\psi_1(x)e^{-\frac{iE_1}{\hbar}t} + c_2\psi_2(x)e^{-\frac{iE_2}{\hbar}t} \tag{34}$$

Using the Euler formula, $e^{i\theta} = \cos(\theta) + i\sin(\theta)$, we can calculate the corresponding probability density to:

$$|\Psi(x,t)|^2 = c_1^2\psi_1^2 + c_2^2\psi_2^2 + 2c_1c_2\psi_1\psi_2\cos\left(\frac{E_2 - E_1}{\hbar}t\right) \tag{35}$$

The final term is time dependent and apparently corresponds to a periodic oscillation with the angular frequency

$$\omega = \frac{E_2 - E_1}{\hbar}$$

directly proportional to the difference of the energy level of the two quantum states.

4.1 The free particle

For the potential free case, $V(x) = 0$, the Schrödinger equation simplifies to:

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} = E\psi \tag{36}$$

or

$$\frac{\partial^2 \psi}{\partial x^2} = -k^2\psi, \text{ with } k = \frac{\sqrt{2mE}}{\hbar} \tag{37}$$

The solution of the above quation reads:

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \tag{38}$$

The full time-dependent solutions are plane waves

$$\Psi(x,t) = Ae^{i(kx-\frac{\hbar k^2}{2m}t)} + Be^{-i(kx+\frac{\hbar k^2}{2m}t)} \tag{39}$$

Where the first term corresponds to a wave running to the right and the second term corresponds to wave running to the left in 1d. We can write the "stationary" solutions for a free particle also q bit shorter if we allow for the wave number k to assume both positive and negative values:

$$\Psi_k(x,t) = Ae^{i(kx-\omega t)}, \quad k = \pm\frac{\sqrt{2mE}}{\hbar}, \ \omega = \frac{E}{\hbar}$$

this plane wave solution can be discussed in full analogy to classical waves (see e.g. electrodynamics).

Side note: A brief excursion to classical wave functions
The classical wave functions are solution of the (classical) wave equation:

$$\Delta\phi - \frac{1}{v^2}\frac{\partial^2}{\partial t^2}\phi = 0$$

Can you spot the difference to the Schrödinger equation?
The solution of the above equations are also plane waves:

$$\phi(\mathbf{r},t) = Ae^{i(\mathbf{kr}\pm\omega t)}$$
$$\omega(k) = vk \ \text{ (dispersion relation)}$$

Electromagnetic waves in vacum $v = c = 3 \cdot 10^8 m/s$

Phase of plane wave:
$$\phi(\mathbf{r},t) = \mathbf{kr} \pm \omega t$$

$\rightarrow$ points in space corresponding to equal phase $\mathbf{kr} = $ const. define planes perpendicular to wave vector $\mathbf{k}$ in 3d (or lines in 2d).

At time t_0:
$$\mathbf{kr} \pm \omega t_0 = \phi_0$$
For $t > t_0$, for all points along the equal phase plane by definition:
$$\phi(\mathbf{r}, t) = \mathbf{kr} \pm \omega t_0 = \phi_0$$
which yields for points with the same phase (Note: in 1d its only a single point):
$$r_\parallel = \frac{\phi_0}{k} \mp \frac{\omega}{k} t \quad \text{with} \quad r_\parallel = \frac{\mathbf{kr}}{k} \ .$$
This provides directly a definition of phase velocity:
$$v_p = \frac{\omega}{k} \ .$$

——————————————————————————————————— Considering plane wave functions as solutions for free particles leads to fundamental problems:

1. One can easily show that if we identify the phase velocity with the quantum mechanical velocity $v = qm$, this leads to a conflict with the classical limit:
$$v_{qm} = \frac{\omega}{k} = \sqrt{\frac{E}{2m}} = \frac{v_{class}}{2}$$
where we used $E = mv_{class}^2/2$.

2. The plane wave functions are not normalizable in open space as
$$\lim_{b \to \infty} \iiint_{-b}^{b} |\psi(\mathbf{r}, t)|^2 \, dx\, dy\, dz = \infty$$

Particles must be localized in space - not possible with plane waves in open space!

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Side note: "Plane wave" solutions may exist in bounded space. Furthermore, they are useful for simple analytical approach to scattering at potential barriers and tunneling in 1d system.

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4.1.1 Wave packets

However as in the general case we can use a superposition of plane waves to describe a free particle:
$$\Psi(\mathbf{r}, t) = \frac{1}{(2\pi)^{3/2}} \int A(\mathbf{k}) e^{i(\mathbf{kr} - \omega t)} d^3 k$$

Note $A(\mathbf{k})$ and $\phi(\mathbf{r}, t)$ are connected via a Fourier transform, i.e
$$A(\mathbf{k}) = \frac{1}{(2\pi)^{3/2}} \int \Psi(\mathbf{r}, t = 0) e^{-i\mathbf{kr}} d^3 r$$

This wave packets can be normalized and thus correspond to solutions which can be "localized" at time $t = 0$

One dimensional wave packets

Example 1:

$$A(k) = \begin{cases} A_0 & \text{for } |k| < \Delta k/2 \\ 0 & \text{otherwise} \end{cases}$$

yields

$$\Psi(x,0) = \frac{A_0}{\sqrt{2\pi}} \int_{-\Delta k/2}^{\Delta k/2}$$
$$= \sqrt{\frac{2}{\pi}} A_0 \frac{\sin(\frac{\Delta kx}{2})}{x}$$

with the approximate width $\Delta x \approx 4\pi/\Delta k \rightarrow \Delta x \Delta k \approx 4\pi$ "classical uncertainty" emerging from the properties of the Fourier transform.