Introduction and orientation

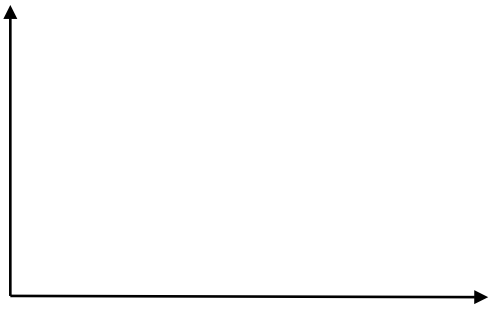
Quantum mechanics

- was needed to interpret and explain new experimental observations
- replaces Newton's equation of motion by Schrödinger equation, which is the "equation of motion" of very small particles

  "replacing zero by Planck's constant h"
- yields classical mechanics for macroscopic objects as a limiting case, if $\mathrm{h} \to 0$.
- leads to the concept ***wave function*** and ***quantization*** of energy, and consequently, particle–wave dualism, uncertainty relation, probability interpretation and quantum state
- all experimental observations, so far, support quantum theory

Quantum theory and relativity are called *modern physics.*

Next, we will briefly consider the "new experimental observations" more than 100 years, ago, which led to the need of formulation of quantum mechanics.



0.1 Black-body radiation

Black body (musta kappale):

- absorbs all radiation
- emits according to *Stefan–Boltzmann law*

$$M = \sigma T^4, \qquad (0.1)$$

where $\sigma = 5.67 \times 10^{-8}\ \mathrm{Wm^{-2}K^{-4}}$

For example 1 cm^2 area at 1000 K temperature emits power of about 6 W.

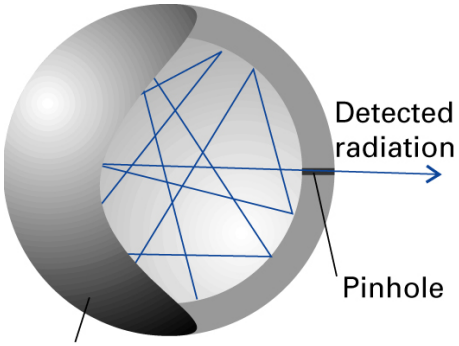


Fig. 0.1.

The power distribution in wave length or frequency cannot be explained in classical physics.

For the maximum of power *Wien's displacement law*

$$\lambda_{\max} T = \text{constant} \qquad (0.2)$$
$$= 2.9 \text{ mmK}.$$

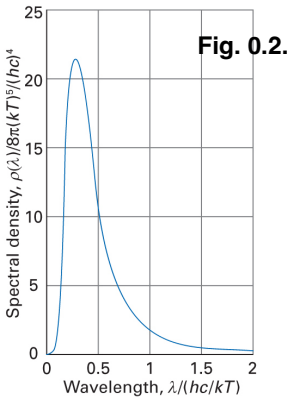
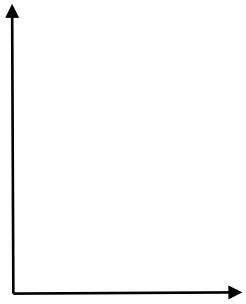


Fig. 0.2.

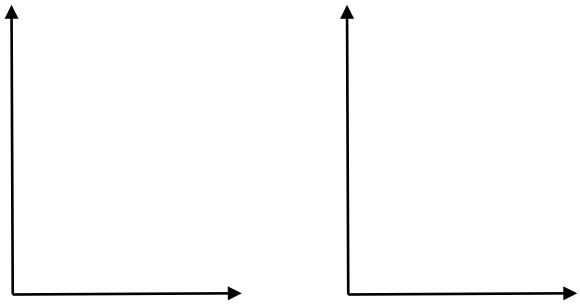
Let us assume that the electromagnetic field is composed of oscillators, whose energy depends on frequency and the energy distribution is continuous for each frequency according to the Boltzmann distribution

$$p(\varepsilon) \propto e^{-\varepsilon/kT}.$$



Planck's quantum hypothesis:

Oscillator energies are multiples of $h\nu$ (plus possible zero point shift), where h is a constant. Thus, $h\nu$ is the *quantum of energy.*



Planck distribution for the spectral density (1900) is

$$dU = \frac{8\pi h\nu^3}{c^3}\left(\frac{e^{-h\nu/kT}}{1-e^{-h\nu/kT}}\right)d\nu, \qquad (0.5)$$

Example. The 2.7 K *cosmic background radiation* contains about 400 photons / cm^3.

0.2 Heat capacities

Dulong and Petit formulated (1819) a theory for the heat capacities of solids. It is based on a hypothesis of atoms being the oscillators, similarly as the EMF, above. This allows classical formulation of internal energy and heat capacity of solids, valid for insulator type solids in room temperature and higher, but not at very low temperatures.

Einstein in 1906 realized the analogy between oscillating matter particles and those of EMF, "quantized" energies of oscillating atoms and derived the theory of heat capacities of solids, valid also at very low temperatures.

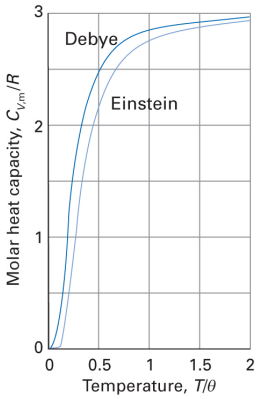


Fig. 0.3.

0.3 Photoelectric and Compton effects

In 1906 Einstein explained the photoelectric effect in terms of quanta $h\nu$ of light given to the emitted electrons from the metal. Therefore, the kinetic energy of an electron becomes as

$$1/2\ m\ v^2 = h\nu - \phi. \qquad (0.7)$$

This implies, that the quanta of light have to be "localized" and the light itself is a stream of particles, *i.e.* the photons.

Compton effect

If photons are particles with energy $h\nu$ and zero restmass, they should carry momentum

$$p = h\nu / c. \qquad (0.9)$$

In 1923 Compton demonstrated by using x-rays that this is the case.

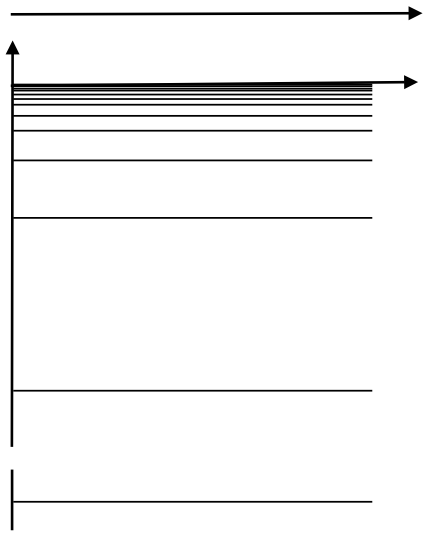
0.4 Atomic spectra

Atomic emission and absoption spectra show discrete "lines", that can be understood only by allowing discrete energy states for atoms, *i.e.* quantization. Balmer noticed in 1885, that spectral lines of hydrogen (in visible region) can be fitted to relation

$$\frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right), \qquad (0.5)$$

where $R_H = 1.09678 \times 10^5$ cm^{-1}, known as Rydberg constant, and $n = 3, 4, 5, \ldots$. Thus, 2 and n correspond different states of hydrogen atom.

Based on this observation Bohr in 1913 developed his atomic model by quantizing the energies of electrons in hydrogen atom.



0.5 Duality of matter

After realizing the analogy between Fermat's principle (in optics) and Hamilton's principle (in mechanics) in 1924 de Broglie suggested, that with a moving body there is an associated wave, whose wave length is

$$\lambda = h / p. \qquad (0.14)$$

Davisson and Germer in 1925 observed diffraction of electrons and verified the above relation (0.14). G. P. Thomson in v. 1927 also found diffraction of electrons as waves.

Uncertainty principle

From *particle–wave dualism* it follows the sc. *uncertainty principle* (epätarkkuusperiaate) or principle of indeterminacy (Heisenberg 1927), according to which, sc. complementary pairs of properties of a system can be known simultaneously with a limited precision, only. For the simultaneous particle position and momentum, *e.g.*, it holds $\Delta x \, \Delta p_x \geq \hbar/2$, where Δx and Δp_x are standard deviations of the quantities.

One should note, that this does not relate to limited accuracy in carrying out the measurement, but the fact that simultaneus exact values do not really exist.

1. Foundations of quantum mechanics

Next, the basic concepts and postulates of quantum mechanics will be briefly presented. Also, the usual notations and direct consequences of postulates are introduced.

Operators in quantum mechanics

In classical mechanics measurable observables are functions (of time, position, ...), whereas in quantum mechanical description observables are operators, whose eigenvalues are measured. Usually the same notation is used for observables and operators, *e.g.*, Ω.

1.1. Linear operators

An operator Ω is a *linear operator,* if for all relevant functions f and g

$$\Omega\,(af+bg) \;=\; a\Omega f + b\Omega g, \tag{1.1}$$

where a and b are some constants.

1.2. Eigenfunctions and eigenvalues

Function f is *the eigenfunction of an operator* Ω (ominaisfunktio), if

$$\Omega\, f = \omega\, f, \tag{1.2}$$

and then, ω is the corresponding *eigenvalue* (ominaisarvo).

Eigenfunctions $\{ f_n \}$ of an operator Ω form *a complete set* (täydellinen joukko)*, a basis,* in which any other function g can be expanded as a linear combination

$$g = \sum_n c_n\, f_n. \tag{1.3}$$

This is useful, if the eigenfunctions and eigenvalues are known, as

$$\Omega g = \Omega \sum_n c_n\, f_n = \sum_n c_n\, \Omega\, f_n = \sum_n c_n\, \omega_n\, f_n. \tag{1.4}$$

If more than one eigenfunction correspond to the same eigenvalue ω, the state is called *degenerate.* Linear combinations of degenerate eigenfunctions correspond to the same ω.

Example. Hydrogen atom p orbitals and d orbitals.

Functions $g_1, g_2, ..., g_n$ are *linearly independent,* if constants $c_1, c_2, ..., c_n$, such that

$$\Sigma_i\, c_i\, g_i \;=\; 0 \tag{1.7}$$

do not exist. Otherwise functions g_i are *linearly dependent* and one of the functions g_i can be presented as a linear combination others.

1.3. Representations

The choice of operators corresponding to the observables is not unique. Also, the formal operators can be chosen different ways, but usually differential operators or matrices are used.

Most often the operator corresponding to position is chosen to be coordinate x (or vector $\mathbf{r}$), as

$$x \rightarrow x \qquad \text{and} \qquad p_x \rightarrow -i\hbar\,\partial/\partial x. \tag{1.8}$$

That is called *position representation.* In *momentum representation* we have

$$x \rightarrow i\hbar\,\partial/\partial p_x \qquad \text{and} \qquad p_x \rightarrow p_x. \tag{1.9}$$

There are also other possible representations.

1.4. Commutation and non-commutation

For the operators A and B generally $AB \neq BA$. If so, the operators do not commute. Operators commute, if $AB = BA$. We define the *commutator* as

$$[A, B] = AB - BA. \tag{1.10}$$

Example 1.3. Find $[x, p_x]$ in position representation.

1.5. Construction of operators

Many other physical operators can be constructed from the position and momentum operators. For the kinetic energy $T = p^2/2m$ we obtain the corresponding operator

$$T = \frac{p_x^2}{2m} = \frac{1}{2m}\left(-i\hbar\frac{d}{dx}\right)^2 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \tag{1.11a}$$

for the one dimensional motion on x-axis. In three dimensions we can derive

(1.11b)

Usually the potential energy depends on the position, only. Thus, the potential energy operator of an electron in the electrostatic field of a nucleus is simply

$$V = -\frac{1}{4\pi\varepsilon_0}\frac{Z\,e^2}{r}, \tag{1.12}$$

where r is the electron–nucleus distance. For the total energy or Hamilton's function

$$H = T + V \tag{1.13}$$

the corresponding *hamiltonian (operator)* becomes as

(1.14)

(1.15)

1.6. Integrals over operators

Often, as matrix elements we need to evaluate integrals

$$I = \int f^* \, \Omega \, g \, d\tau, \tag{1.16}$$

where f^* is the complex conjugate of f and $d\tau$ is volume element for integration over the whole volume. Scalar product of functions f and g

$$S = \int f^* \, g \, d\tau \tag{1.17}$$

is called as *overlap integral.* If functions are *normalized* such, that

$$\int f^* \, f \, d\tau = 1 \quad \text{and} \quad \int g^* \, g \, d\tau = 1, \tag{1.18}$$

the overlap integral is a measure of similarity of the two functions given in range $0 \le S \le 1$. If $S = 0$, the functions f and g are called *orthogonal*.

Functions $g_1, g_2, ..., g_n$ are *orthonormal* to each other, if

$$\int g_n^* \, g_m \, d\tau = \delta_{nm}, \tag{1.19}$$

where δ_{nm} is the *Kronecker delta* function.

Example 1.4. Normalize the function $f_n = N \sin(n\pi x/L)$ in $0 < x < L$. Consider orthogonality of functions f_n.

1.7. Dirac bracket and matrix notation

Let us denote by using angle brackets

$$\langle m|\Omega|n\rangle = \int \psi_m^* \, \Omega \, \psi_n \, d\tau, \tag{1.20}$$

and

$$\langle m|n\rangle = \int \psi_m^* \, \psi_n \, d\tau = \delta_{mn}. \tag{1.21}$$

Thus, the orthonormality condition can be written as

$$\langle m|n\rangle = \delta_{mn}. \tag{1.22}$$

We also denote $\Omega\,|n\rangle = \omega_n\,|n\rangle$, where $|n\rangle = \psi_n$, and furthermore $\langle n| = \psi_n^*$, thus

$$\langle m|n\rangle = \langle n|m\rangle^*. \tag{1.23}$$

Operator and commutation relations can be described also by using matrices as an alternative for differential operators.

A product of matrices $\mathbf{A}$ and $\mathbf{B}$ as $\mathbf{C} = \mathbf{AB}$ can be written in terms of matrix elements

$$C_{rc} = \sum_s A_{rs}\, B_{sc}.$$

Thus, in general $\mathbf{AB} \neq \mathbf{BA}$.

The above integrals $\langle m|\Omega|n\rangle$ are matrix elements of $\mathbf{\Omega}$, as $\Omega_{mn} = \langle m|\Omega|n\rangle$. Thus,

$$\langle r|C|c\rangle = \sum_s \langle r|A|s\rangle\langle s|B|c\rangle = \langle r|AB|c\rangle, \tag{1.24}$$

because $C = AB$. Therefore, we make an interpretation

$$\sum_s |s\rangle\langle s| = 1. \tag{1.25}$$

This is called *completeness relation* or *closure relation,* because these orthogonal functions $|s\rangle$ span the whole functional space. Therefore, any function $|\psi\rangle$ can be expanded as

$$|\psi\rangle = \sum_s c_s\,|s\rangle. \tag{1.3}$$

By multiplying this from left with $\langle r|$, we obtain $\langle r|\psi\rangle = c_r$ and change to position representation

$$\langle r|\psi\rangle = \sum_r \langle r|\psi\rangle\,|r\rangle = \psi(r).$$

Example: Diagonal hamiltonian

Consider Schrödinger equation $H\psi = E\psi$ as a matrix equation. Now, substitute $\psi = \sum_n c_n\,|n\rangle$, which gives $H\sum_n c_n\,|n\rangle = \sum_n c_n\,H\,|n\rangle = E\sum_n c_n\,|n\rangle$.

By multiplying from left with bra vector $\langle m|$, we obtain

$$\sum_n c_n\,\langle m|H|n\rangle = E\sum_n c_n\,\langle m|n\rangle = E\,c_m,$$

and because $\langle m|H|n\rangle = H_{mn}$, we have

$$\sum_n H_{mn}\,c_n = E\,c_m,$$

for the hamiltonian in basis $\{\,|n\rangle\,\}$.

Now, if we find a basis $\{\,|n\rangle\,\}$, which makes hamiltonian diagonal, *i.e.,* $H_{mn} = 0$, if $m \neq n$, it follows that

$$H_{nn}\,c_n = E_n\,c_n\,.$$

This means that the diagonal matrix elements are the eigenvalues, $H_{nn} = E_n$. Furthermore, it can be shown that the eigenvectors are the corresponding eigenfunctions. Thus, we have the solution to the Scrödinger equation, and for this reason, solving the Scrödinger equation is often called *diagonalization* of the hamiltonian.

This procedure is limited by the finite dimension of the hamiltonian or the quality of the finite basis set. However, there are efficient numerical algorithms for diagonalization of high dimensional matrices, *i.e.,* finding the the eigenvalues and eigenvectors of non-singular matrices. Therefore, this is the most popular method in practical numerical and theoretical approaches.

1.8. Hermitian operators

An operator Ω is hermitian, if

$$\int \psi_m^* \, \Omega \, \psi_n \, d\tau = \{ \int \psi_n^* \, \Omega \, \psi_m \, d\tau \}^* \qquad (1.26a)$$

for any two functions ψ_m and ψ_n. Alternatively,

$$\int \psi_m^* \, \Omega \, \psi_n \, d\tau = \int \{\Omega \, \psi_m\}^* \, \psi_n \, d\tau, \qquad (1.26b)$$

where integrations are over the whole space.

With bracket notation the hermiticity condition (1.26a) is (1.26c)

$$\langle m|\Omega|n\rangle = \langle n|\Omega|m\rangle^*.$$

Example 1.5. Show that the operators x and p_x are hermitian.

For x:

$$\langle m|x|n\rangle = x \langle m|n\rangle = x \langle n|m\rangle^* = \langle n|x|m\rangle^*$$

QED.

For p_x:

$$\begin{aligned} \int \psi_m^* \, p_x \, \psi_n \, d\tau &= -i\hbar \int \psi_m^* \, \partial\psi_n/\partial x \, d\tau = -i\hbar \{ / \psi_m^* \psi_n - \int \partial\psi_m^*/\partial x \, \psi_n \, d\tau \} \\ &= -i\hbar \{ 0 - \int \partial\psi_m^*/\partial x \, \psi_n \, d\tau \} = -i\hbar \{ - \int \partial\psi_m^*/\partial x \, \psi_n \, d\tau \} \\ &= -i\hbar \{ - \int \psi_n^* \, \partial\psi_m/\partial x \, d\tau \}^* = \{ -i\hbar \int \psi_n^* \, \partial\psi_m/\partial x \, d\tau \}^* \\ &= \{ \int \psi_n^* \, p_x \, \psi_m \, d\tau \}^* \end{aligned}$$

QED.

By using the hermiticity condition (1.26c) $\langle m|\Omega|n\rangle = \langle n|\Omega|m\rangle^*$ we can derive two important properties:

Property 1: Eigenvalues of an hermitian operator are real.

As $\Omega \, |\omega\rangle = \omega \, |\omega\rangle$, then $\langle\omega| \, \Omega \, |\omega\rangle = \omega \langle\omega|\omega\rangle = \omega$

and $\langle\omega| \, \Omega \, |\omega\rangle^* = \omega^*$.

But (1.26c) => $\langle\omega| \, \Omega \, |\omega\rangle = \langle\omega| \, \Omega \, |\omega\rangle^*$ => $\omega = \omega^*$.

Therefore, ω has to be real!

QED.

Being real, the eigenvalues of an hermitian operator are good for representing measurable values of observables.

Property 2: Eigenfunctions corresponding to different eigenvalues of an hermitian operator are orthogonal.

Assume $\Omega \, | \, \omega\rangle = \omega \, | \, \omega\rangle$, $\Omega \, | \, \omega' \rangle = \omega' \, | \, \omega' \rangle$ and $\omega \neq \omega'$.

Now, $\langle\omega' \, | \, \Omega \, | \, \omega\rangle = \omega \langle \omega' \, | \, \omega \rangle = \omega \langle \omega \, | \, \omega' \rangle$

and $\langle\omega' \, | \, \Omega \, | \, \omega\rangle = \langle\omega \, | \, \Omega \, | \, \omega' \rangle^* = \omega' \langle \omega \, | \, \omega' \rangle$

subtract ----------

$0 = (\omega - \omega') \langle \omega \, | \, \omega' \rangle$

Now, because $\omega \neq \omega'$ => $\langle \omega \, | \, \omega' \rangle = 0$ QED.

Postulates of quantum mechanics

1.9. States and wavefunctions

Postulate1: The state of a system is fully described by its wave function $\Psi_{m,n,\ldots}(\mathbf{r}_1, \mathbf{r}_2, \ldots ; t) \equiv |m, n, \ldots ; t\rangle$.

With bracket notation $|\mathbf{K}\rangle = \Psi_{\mathbf{K}}$ and $\langle \mathbf{L}| = \Psi_{\mathbf{L}}^*$, where $\mathbf{K}$ and $\mathbf{L}$ are sets of quantum numbers.

1.10. Fundamental prescription

Postulate 2: Observables are represented by hermitian operators chosen to satisfy certain commutation relations

For example $xp_x - p_x x = i\hbar$, $yp_x - p_x y = 0$, $xp_y - p_y x = 0$, *etc.*

1.11. Outcome of measurements

Postulate 3: For a system in state ψ, repeated measurements of an observable Ω amounts to the expectation value $\langle\Omega\rangle$:

The expectation value of Ω in state ψ is

$$\langle\Omega\rangle = \frac{\int \psi^* \, \Omega \, \psi \, d\tau}{\int \psi^* \, \psi \, d\tau}, \qquad (1.28a)$$

or, if ψ is normalized

$$\langle\Omega\rangle = \int \psi^* \, \Omega \, \psi \, d\tau \, . \qquad (1.28b)$$

From now on we assume that ψ is normalized.

In case ψ is an eigenfunction of Ω, *i.e.*, $\Omega \, \psi = \omega \, \psi$, then

$\langle\Omega\rangle$ = (1.29)

If ψ is not an eigenfunction of Ω, then $\psi = \Sigma_n \, c_n \, \psi_n$, where $\Omega \, \psi_n = \omega_n \, \psi_n$. Then,

$\langle\Omega\rangle$ = (1.30)

Thus, the expectation value is a weighted sum of eigenvalues with weigths $|c_n|^2$.

Postulate 3': When ψ is an eigenfunction of the operator Ω, determination of the value of the observable yields the correspondig eigenvalue ω. When ψ is not an eigenfunction, then a single measurement yields one of the eigenvalues ω_n with the probability $|c_n|^2$.

1.12. Interpretation of the wavefunction

Born interpretation:

Postulate 4: Probability, that the particle will be found in the volume element $d\tau$ at the position $\mathbf{r}$ is $|\psi(\mathbf{r})|^2 \, d\tau$, if ψ is normalized – otherwise propotional to $|\psi(\mathbf{r})|^2 \, d\tau$.

Wavefunction ψ is the *probability amplitude* and $|\psi|^2 = \psi^* \, \psi$ is the *probability density.* In order to define probability density, the wave function needs to be normalizable.

1.13. Equation for the wavefunction

Postulate 5: The wavefunction $\Psi_{m,n,\ldots}(\mathbf{r}_1, \mathbf{r}_2, \ldots ; t)$ evolves in time according to the equation

$$i\hbar \frac{\partial \Psi}{\partial t} = T\Psi + V\Psi \tag{1.33}$$

This is the *Schrödinger equation* (1926), where $H = T + V$ is the hamiltonian (1.11). In one dimensional space (x-axis) and in external potential $V(x)$ for a particle with mass m this becoms as

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V(x,t)\Psi \tag{1.34}$$

1.14. Separation of the Schrödinger equation

The Schrödinger equation can be separated into time and space parts by using a trial solution

$$\Psi(x,t) = \psi(x)\ \theta(t)\ , \tag{1.35}$$

if the potential function is independent of time, *i.e.* $V \neq V(t)$. We obtain

$$-\frac{\hbar^2}{2m}\left(\frac{1}{\psi}\frac{\partial^2 \psi}{\partial x^2}\right) + V(x)\psi = i\hbar \frac{1}{\theta}\frac{d\theta}{dt},$$

where the left-hand depends on space and the right-hand side on time, only. Therefore, both sides have to remain constant E always and everywhere and we can write

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + V(x)\psi = E\psi \tag{1.36a}$$

and

$$i\hbar \frac{d\theta}{dt} = E\ \theta\ . \tag{1.36b}$$

Solution to the latter is

$$\theta(t) = C\ e^{-iEt/\hbar} \tag{1.37}$$

and if the solution to the former is time-independent $\psi(x)$, the full solution to Eq. (1.34) is

$$\Psi(x,t) = \psi(x)\ e^{-iEt/\hbar}\ . \tag{1.38}$$

Equation (1.36a) is sc. *time-independent Schrödinger equation*

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\ \psi = E\ \psi$$

and its solutions ψ are called *stationary states*. Time dependence of stationary states is, according to (1.38), modulation by a complex phase factor $\exp(-iEt/\hbar)$, but the probability density

$$\Psi^*\ \Psi\ =\ \psi^*\ \psi \tag{1.41}$$

is time-independent – therefore the state is called "stationary".

In three dimensional space the Schrödinger

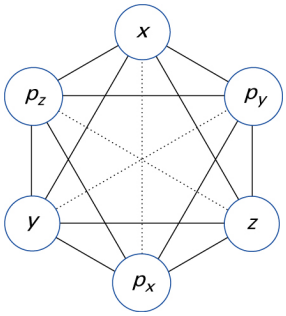
$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(x,y,z)\right)\psi(x,y,z) = E\ \ \psi(x,y,z),$$

where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\ .$$

Complementarity and time evolution

1.15 Simultaneous observables



Property 2: If two observables have simultaneously precisely defined values, then their corresponding operators commute.

In case the two operators do not commute, the observables are *complementary*. The complementary pairs of operators can be found by inspecting the corresponding commutators, *e.g.*, $[x,p_x] = i\hbar \neq 0$.

1.16. Uncertainty principle

Complementary pairs of observables obey sc. Heisenberg (1927) uncertainty relation, *e.g.*

$$\Delta x\ \Delta p_x \geq \hbar/2. \tag{1.42}$$

General form:

If the two operators A and B do not commute, but

$$[A, B] = i\,C,$$

then $$\Delta A\ \Delta B \geq |\langle C\rangle| / 2, \tag{1.43a}$$

where $$\Delta A = \{\langle A^2\rangle - \langle A\rangle^2\}^{1/2}. \tag{1.43b}$$

1.17. Consequences of uncertainty principle

Example 1.8. Consider the uncertainty relation of x and p_x in state $\psi = N \exp(-x^2 / 2\sigma)$.

1.18. Uncertainty in energy and time

In quantum mechanics there is no operator corresponding to time. Thus, time is not an observable, but a "classical" parameter. Thus, the time and energy are not complementary observables the usual way, as often expressed.

Later, in section 6.11, we shall learn the relation between the lifetime τ and uncertainty of the energy δE of an excited state, who are related as $\delta E\,\tau \approx \hbar$.

1.19. Time-evolution and conservation laws

It can be shown that

$$\frac{d}{dt}\langle\Omega\rangle = \frac{i}{\hbar}\langle[H,\Omega]\rangle \tag{1.44}$$

and Ω is called as *constant of motion,* if $\frac{d}{dt}\langle\Omega\rangle = 0$.

Thus, an operator corresponding to a constant of motion commutes with the hamiltonian.

It is easy to show that

$$[H,p_x] = -\frac{\hbar}{i}\frac{dV}{dx} \tag{1.45}$$

and according to Eq. (1.44)

$$\frac{d}{dt}\langle p_x\rangle = \frac{i}{\hbar}\langle[H,p_x]\rangle = -\left\langle\frac{dV}{dx}\right\rangle, \tag{1.46a}$$

thus

$$\frac{d}{dt}\langle p_x\rangle = \langle F\rangle\ . \tag{1.46b}$$

This is *Newton's II law.* Similarly, it can be shown that

$$m\frac{d}{dt}\langle x\rangle = \langle p_x\rangle\ . \tag{1.47}$$

These two relations form the sc. *Ehrenfest's theorem.*

2. Linear motion and harmonic oscillator

Consider next briefly first the general properties of the wave equation, translational motion, tunneling, and then, particle in a box and parabolic confinement as examples of confinement.

Characteristics of the wavefunction

2.1. "Well-behaving" wavefunctions

The wavefunction should be normalized

$$\int \Psi^* \Psi \, d\tau = 1 \qquad (2.1)$$

and it has to be single valued and finite (except for single points) to allow probablity interpretation of $\psi^*\psi$, it has to be continuous and possess first and second derivatives. Also, the first derivative should be continuous, except for some model potentials.

2.2. Some general remarks on the Schrödinger equation

Some general conclusions can be easily made from the differential equation

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}(V-E)\,\psi \qquad (2.2)$$

like the curvature of its solution and relation to high or low potential function, *i.e.* the kinetic energy.

Fig. 2.4.

In case the potential function confines a single particle into some region of space, it defines boundary conditions, which allow a certain set of solutions and corresponding discrete energies, only, *i.e. QUANTIZATION.*

In the matrix mechanics formalism the boundary conditions and quantization come in implicitly hidden in the basis functions.

The wave function and probablility density $\psi^*\psi$ typically penetrates to classically forbidden region, where the classical kinetic energy is negative. This is called (quantum) *tunneling.*

Translational motion

Hamiltonian of the *free particle* ($V(x) \equiv 0$) is

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \qquad (2.3)$$

and the Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\,\psi\,, \qquad (2.4)$$

whose solution is

$$\psi(x) = A\,e^{ikx} + B\,e^{-ikx}\,, \qquad (2.5)$$

where $k = (2mE/\hbar^2)^{1/2}$,

or alternatively

$$\psi(x) = C\cos(kx) + D\sin(kx)\,. \qquad (2.6)$$

2.3. Energy and momentum

Because $E = \frac{(k\hbar)^2}{2m}$ and classically $E = \frac{p^2}{2m}$, we can write

$$\boxed{p = \hbar k\ .} \qquad (2.7a)$$

In Eq. (2.6) for the wave length λ of sin and cos functions applies $k\lambda = 2\pi$, from which we get the magnitude of the *wave vector* $\mathbf{k}$ as

$$\boxed{k = \frac{2\pi}{\lambda}\ .} \qquad (2.7b)$$

Substituting this to (2.7a) the de Broglien relation results in,

$$p = h/\lambda\ . \qquad (2.8)$$

Note, that the energy of the free particle is not quantized!

2.4. Traveling waves and standing waves

Let us determine momentum from the free particle wavefunction $\psi(x)$ using the momentum operator $p_x = -i\hbar\,\partial/\partial x$. Thus, for $\psi = A\,e^{ikx}$

$$\hat{p}\psi = \frac{\hbar}{i}\frac{d}{dx}\left(Ae^{ikx}\right) = \frac{\hbar}{i}ikAe^{ikx} = \hbar k\psi \qquad (2.9)$$

and we get $p = \hbar k$, and thus, $A\,e^{ikx}$ is a traveling wave to the direction of positive x-axis. Similarly, $B\,e^{-ikx}$ is a traveling wave in direction of negative x-axis.

Consider the "standing wave" free particle wavefunctions $C\cos(kx)$ and $D\sin(kx)$.

2.5. Flux density (virtatiheys)

(2.10)

(2.11)

2.6. Wavepackets

A complete wavefunction of a momentum eigenstate is $\Psi_k(x,t) = A\ e^{ikx}\,e^{-iEt/\hbar}$ (2.12)

and for a *wavepacket* propagating on x-axis

$$\Psi(x,t) = \int_{-\infty}^{\infty} g(k)\,\Psi_k(x,t)\,dk\ , \qquad (2.13)$$

where $g(k)$ is the *shape or spectral function.*

Fig 2.11.

Penetration into and through barriers

2.7.–2.9. Potential barriers and tunneling

Particle in a box

2.10.–2.13. 1D and 2D confinements

The particle-in-a-box is very useful confining model potential for nanostructures, such as *quantum dots (QD)*, and in particular, for non-spherical parallel piped geometries.

The *quantum well (QW)* is a modified case: A thin layer with an attractive potential for charge carriers.

We consider here an infinite square-well potential, only. Its solutions are those of the free particle waves, which fit to the boundary conditions

(2.31)

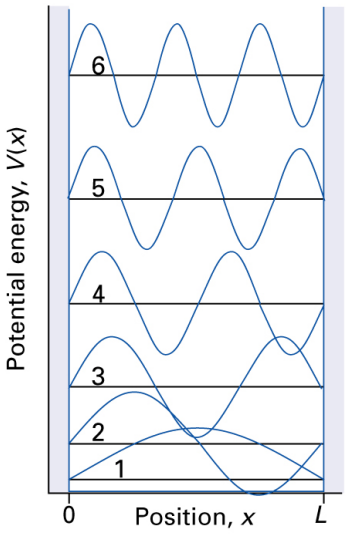


Fig. 2.19.

The energies are the corresponding free particle energies

(2.30)

The two and three dimensional problems trivially separate to one dimensional problems.

We will consider the particle in a spehre, later.

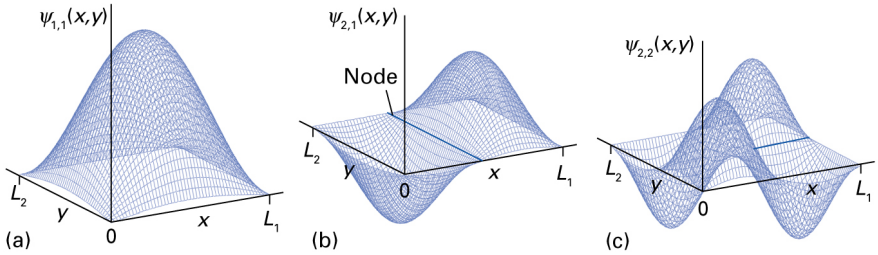


Fig. 2.22.

Harmonic oscillator

2.14 Solutions

The harmonic oscillator is another, even more useful model potential, not only for nanostructures but also for many vibrational phenomena in nature. For example, atoms in molecules and solids can be successfully modelled as harmonic oscillators.

The harmonic force $F = -kx$ arises from the harmonic (or parabolic) potential

$$V(x) = \tfrac{1}{2}\, k\, x^2 , \qquad (2.37)$$

because

$$-\frac{dV}{dx} = F.$$

Thus, hamiltonian becomes as

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \tfrac{1}{2} k\, x^2 \qquad (2.38)$$

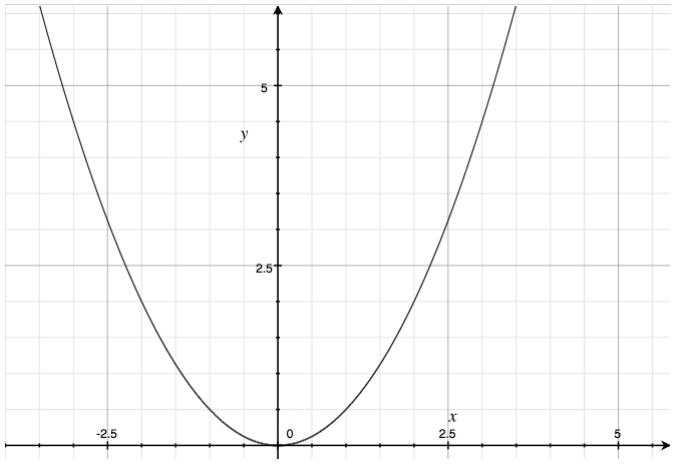
and the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \tfrac{1}{2} k\, x^2\, \psi = E\, \psi , \qquad (2.39)$$

whose *eigenvalues* are

$$E_\nu = (\nu + \tfrac{1}{2})\hbar\omega ; \quad \nu = 0, 1, 2, 3, \ldots \qquad (2.40)$$

where $\omega = (k/m)^{1/2}$. The two lowest energy eigenfunctions are



$\psi_0(x) = N_0\, e^{-y^2/2}$ and

$\psi_1(x) = N_1\, 2y\, e^{-y^2/2}$, where $y = (m\omega/\hbar)^{1/2}\, x$. This is easy to verify by substitution to (2.39).

The lowest eigenvalue is called as *zero-point energy* (nollapiste-energia).

The general form of the wave function of one-dimensional harmonic oscillator (ODHO) is

$$\psi_v(x) = N_v\, H_v(y)\, e^{-y^2/2}\,, \qquad (2.41a)$$

where $H_v(y)$ are Hermite polynomials, for which

$H_0(y) = 1$, $\quad H_1(y) = 2y$ and we have a recursion formula $\quad H_{v+1} = 2y\, H_v - 2v\, H_{v-1}$.

The wavefunctions are eigenstates, and therefore, *orthogonal* and by using the normalization factor

$$N_v = \left(\frac{1}{2^v}\, v!\, \pi^{1/2} \right)^{-1/2} \qquad (2.41b)$$

the eigenfunctions (2.41a) become *orthonormal*

$$\int_{-\infty}^{\infty} \psi_v^*(x)\, \psi_\tau(x)\, dx = \delta_{v\tau}\,.$$

2.15. Properties of solutions

The level spacing of harmonic oscillator is constant $\hbar\omega$, *i.e.*

$$E_{v+1} - E_v = \hbar\omega, \qquad (2.42)$$

which is a consequence of hidden x^2–p^2 symmetry. Another consequence is that for the ground state the uncertainty principle gives the least for $\Delta x\, \Delta p_x = \hbar/2$.

Furthermore, the two and three dimensional harmonic oscillators are trivially separable to ODHOs, and consequently, the multidimensional wavefunction is a product of one-dimensionals, and similarly, the eigenenergies sum up to the multidimensional case. Because of this the three and two dimensional HO are popular models for circular, ellipsoidal, spherical and parabolic quantum dots (QD).

The hidden x^2–p^2 symmetry can also be seen in the following:

Virial theorem: If the potential energy can be written as $V(x) \propto a\, x^s$, *where* a *is a constant, the mean kinetic and potential energies are related by*

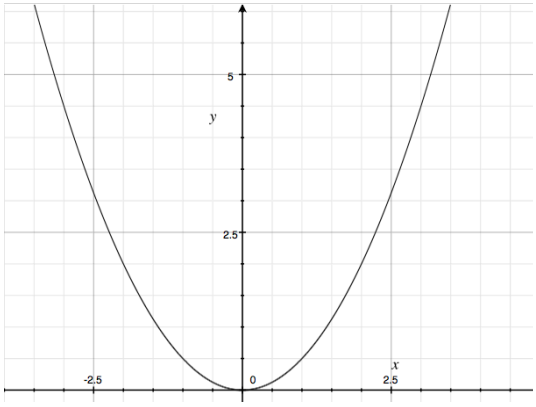
$$2\,\langle T\rangle = s\,\langle V\rangle. \qquad (2.43)$$

This theorem originally comes from classical mechanics, but applies also to quantum mechanics.

Example for the harmonic oscillator $\quad s = 2 \;\Rightarrow$

for Coulomb potential $\quad s = -1 \;\Rightarrow$

2.16. Classical limit



At high quantum numbers the probability density of quantum harmonic oscillator approaches that of the classical. This is one example of the sc. *correspondence principle* (vastaavaisuusperiaate).

Time evolution of a wavepacket follows classical oscillation. The simplest classical like oscillation is that of a sc. Glauber or coherent state (1963), the "ground state wavefunction oscillation".

Generally, in harmonic oscillation classical and quantum behavior are closely similar, the only difference being quantization, which may not be always essential.

3. Rotational motion and hydrogen atom

Particle on a ring and in a circle

Let us consider particle dynamics on a ring in a plane. This is equivalent with rotation around a fixed axis. As another case, consider a particle in an "infinitely deep circular well", where the wavefunction can be separated to the angular and radial motions. Then, the dynamical states are determined by the *moment of inertia* I, which in case of a mass on a ring is $I = m r^2$, where m and r are particle mass and radius of gyration, respectively.

3.1. Hamiltonian and Schrödinger equation (particle on a ring)

In free rotation around z-axis ($V(x,y)=0$) the hamiltonian is (with $r^2 = x^2 + y^2 =$ constant)

$$H = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right) \tag{3.1}$$

and in *polar coordinates* $x = r\cos\phi$ and $y = r\sin\phi$

$$H = -\frac{\hbar^2}{2mr^2}\frac{d^2}{d\phi^2} = -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}. \tag{3.3}$$

Denote the wavefunction as $\Phi(\phi)$, and the Schrödinger equation and its solutions are

$$\frac{d^2\Phi}{d\phi^2} = -\frac{2IE}{\hbar^2}\Phi\,. \tag{3.4}$$

$$\Phi(\phi) = Ae^{im_\ell\phi} + Be^{-im_\ell\phi}, \tag{3.5}$$

where m_ℓ is only a short hand notation, like the one in free particle case.

This short hand notation is a dimensionless number $m_\ell = (2IE/\hbar^2)^{1/2}$, and similarly as for the free particle, it defines the wave length of the wavefunction, which should be "well-behaving".

Therefore, the boundary condition for the wavefunction (3.5) is uniqueness $\Phi(\phi) = \Phi(\phi+2\pi)$, which implies

$$Ae^{im_\ell\phi} + Be^{-im_\ell\phi} = Ae^{im_\ell\phi}e^{i2\pi m_\ell} + Be^{-im_\ell\phi}e^{-i2\pi m_\ell}$$

and thus, $e^{i2\pi m_\ell} = 1$ and $m_\ell = 0, \pm1, \pm2, \ldots$.
Therefore, the quantized energy is

$$E = m_\ell^2\frac{\hbar^2}{2I}. \tag{3.6}$$

Thus we see, that the energies are doubly degenerate except for the lowest one with $m_\ell = 0$, and there is no zero-point energy.

3.2. Angular momentum

The classical rotation energy is $\ell_a^2 / 2I$ and based on the above $\ell_a^2 = m_\ell^2\hbar^2$, where ℓ_a is the *angular momentum* around a given axis a. Classically, for the rotation around z-axis we have (3.7)

$$\ell_z = x\,p_y - y\,p_x, \tag{3.8}$$

and thus, the corresponding operator is

$$\ell_z = x\frac{\hbar}{i}\frac{\partial}{\partial y} - y\frac{\hbar}{i}\frac{\partial}{\partial x} = \frac{\hbar}{i}\frac{\partial}{\partial\phi}. \tag{3.9–10}$$

Application on $\Phi_A = A\,e^{im_\ell\phi}$ gives the eigenvalue equation

$$\ell_z\Phi_A = A\frac{\hbar}{i}\frac{\partial}{\partial\phi}e^{im_\ell\phi} = m_\ell\hbar Ae^{im_\ell\phi} = m_\ell\hbar\Phi_A \tag{3.11}$$

3.3. Shape of the wavefunction

Thus, Φ_A has an angular momentum $m_\ell \hbar$, which indicates rotation. Similarly, $\Phi_B = B\, e^{-im_\ell \phi}$ has an angular momentum $-m_\ell \hbar$ and rotates to the opposite direction. Wavefunctions Φ_A (or Φ_B) are orthonormal with different values of m_ℓ with the normalization constant

$$A = B = \sqrt{\frac{1}{2\pi}} \,. \qquad (3.12)$$

It should be noted that these states are stationary with constant probability density, but the angle (or position on the ring) is not defined at all, *i.e.,* fully uncertain.

3.4. Classical limit

3.5. Circular well (particle in a circle)

Let us consider particle in a 2D circle of radius a, a typical nanostructure in semiconductor interfaces or surfaces.

Again, we have the hamiltonian (3.1), now with a constraint $r \le a$. We can separate the radial and angular motion by $\psi(\mathbf{r}) = R(r)\,\Phi(\phi)$, the latter being the same as above, $\Phi_C = C\, e^{\pm im_\ell \phi}$ (3.3–12).

Then, the radial equation becomes as

(3.23)

where $z = kr$ and $k^2 = 2mE/\hbar^2$. As m_ℓ are integer numbers, solutions to this Bessel's equation are *Bessel functions* $J_{m_\ell}(kr)$, also called as *cylindrical harmonics* and can be presented as series expansion

(3.24)

With the boundary condition

$$J_{m_\ell}(ka) = 0 \qquad (3.25)$$

the total energy eigenvalues and the shapes of some Bessel functions are shown in Figs. (3.8–10).

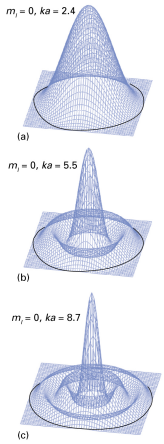
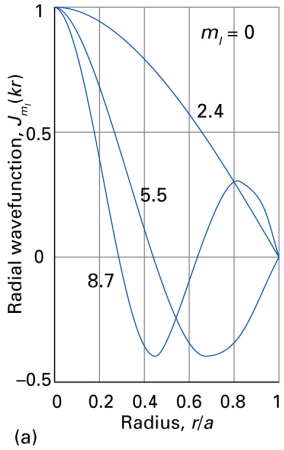


Fig. 3.10.



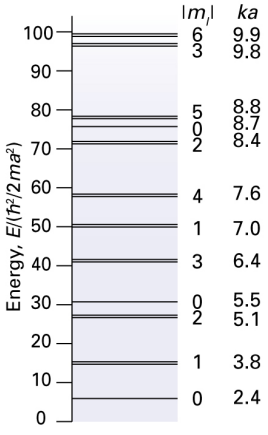


Fig. 3.8.

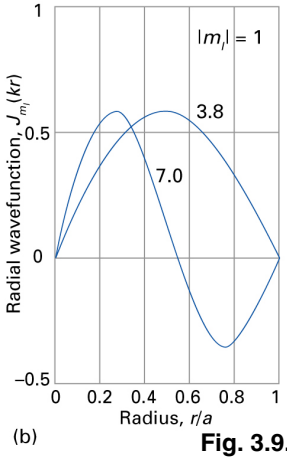


Fig. 3.9.

Particle on a sphere

Consider now the particle motion with a constant radius of rotation r. This is also the quantum dynamics of rotation of a solid uniform sphere with a radius $a = (2/5)^{-1/2}\, r$.

3.6. Schrödinger equation and its solution

As the external potential is zero, the hamiltonian is

$$H = -\frac{\hbar^2}{2m}\nabla^2 . \qquad (3.26)$$

Writing the Laplace operator in spherical coordinates

$$x = r\sin\theta\cos\phi\,,\quad y = r\sin\theta\sin\phi \quad \text{and} \quad z = r\cos\theta \qquad (3.27)$$

we have

$$\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2} r + \frac{1}{r^2}\Lambda^2\,, \qquad (3.28)$$

where

$$\Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} \qquad (3.29)$$

is the angular part of laplacian, sc. *Legendre operator.*

Thus, the rotational hamiltonian is

$$H = -\frac{\hbar^2}{2mr^2}\Lambda^2 \qquad (3.30)$$

and because $mr^2 = I$ is the moment of inertia, the related Schrödinger equation is

$$\Lambda^2\psi = -\frac{2IE}{\hbar^2}\psi\,. \qquad (3.31)$$

Solutions to this are *spherical harmonics* $Y_{\ell m_\ell}(\theta,\phi)$, which are eigenfunctions of legendrian

$$\Lambda^2 Y_{\ell m_\ell} = -\ell(\ell+1)Y_{\ell m_\ell}\,, \qquad (3.33)$$

where $\ell = 0, 1, 2, \ldots$ and $m_\ell = \ell, \ell-1, \ell-2, \ldots, -\ell$.

TABLE 3.2
Some Spherical Harmonics

Symbol	Polar	Cartesian	Normalization Constant
Y_{00}	1	1	$\frac{1}{2}(1/\pi)^{1/2}$
Y_{10}	$\cos\theta$	z/r	$\frac{1}{2}(3/\pi)^{1/2}$
$Y_{1\pm1}$	$\mp(\sin\theta)e^{\pm i\phi}$	$\mp(x \pm iy)/r$	$\frac{1}{2}(3/2\pi)^{1/2}$
Y_{20}	$(3\cos^2\theta - 1)$	$(3z^2 - r^2)/r^2$	$\frac{1}{4}(5/\pi)^{1/2}$
$Y_{2\pm1}$	$\mp(\sin\theta)(\cos\theta)e^{\pm i\phi}$	$\mp z(x \pm iy)r^2$	$\frac{1}{2}(15/2\pi)^{1/2}$
$Y_{2\pm2}$	$(\sin^2\theta)e^{\pm 2i\phi}$	$(x \pm iy)^2/r^2$	$\frac{1}{4}(15/2\pi)^{1/2}$
Y_{30}	$(5\cos^3\theta - 3\cos\theta)$	$z(5z^2 - 3r^2)/r^3$	$\frac{1}{4}(7/\pi)^{1/2}$
$Y_{3\pm1}$	$\mp\sin\theta(5\cos^2\theta - 1)e^{\pm i\phi}$	$\mp(x \pm iy)(5z^2 - r^2)/r^3$	$\frac{1}{8}(21/\pi)^{1/2}$
$Y_{3\pm2}$	$(\sin^2\theta)(\cos\theta)e^{\pm 2i\phi}$	$z(x \pm iy)^2/r^3$	$\frac{1}{4}(105/2\pi)^{1/2}$
$Y_{3\pm3}$	$\mp(\sin^3\theta)e^{\pm 3i\phi}$	$\mp(x \pm iy)^3/r^3$	$\frac{1}{8}(35/\pi)^{1/2}$

Douglas, Bodie E. and Hollingsworth, Charles A. *Symmetry in Bonding and Spectra – An Introduction* (Orlando, Florida: Academic Press, Inc., 1985), p. 88.

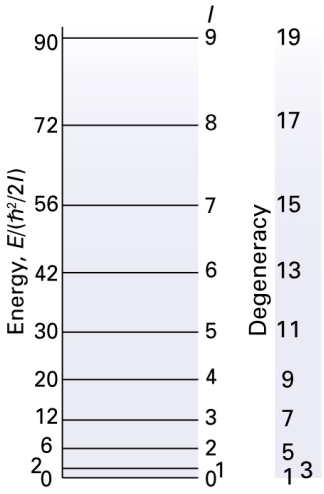


Fig. 3.13.

(3.34)

Comparison of Eqs. (3.31) and (3.33) shows the quantization

$$E = \frac{\hbar^2}{2I}\ell(\ell+1); \qquad \ell = 0,1,2,... \qquad (3.35)$$

and the degeneracy $(2\ell+1)$ of each eigenenergy: $m_\ell = \ell, \ell-1, ..., -\ell$.

3.7. Angular momentum of the particle

Comparison with $E_{class} = \ell^2 / 2I$ shows that

$$\ell \to \hbar\sqrt{\ell(\ell+1)} \qquad (3.36)$$

and that the angular momentum is quantized with ℓ being also the quantum number. Thus, we give two meanings for ℓ.

The spherical harmonics are also eigenfunctions of ℓ_z

$$\ell_z\, Y_{\ell m_\ell}(\theta,\phi) \;=\; m_\ell\, \hbar\, Y_{\ell m_\ell}(\theta,\phi), \qquad (3.37)$$

where $m_\ell = -\ell, -\ell{+}1, \ldots, \ell$.

The spherical harmonics are not, however, eigenfunctions of ℓ_x and ℓ_y, because these do not commute with ℓ_z.

Fig. 3.14–15.

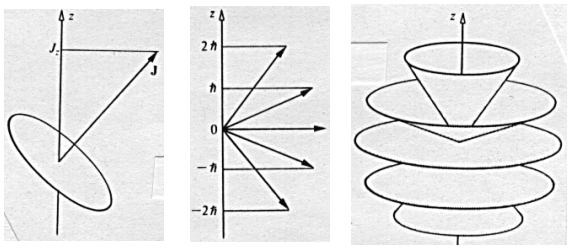
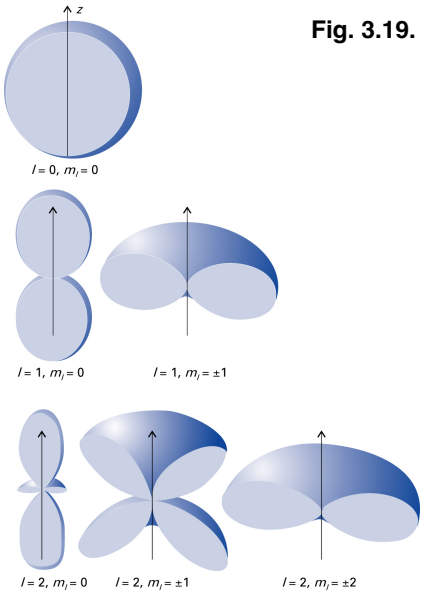


Fig. 3.19.



3.8. Properties of the solutions

Notice that, again, there is no zero-point energy related with rotation. Kind of centrifugal effect is seen as $m_\ell \to \ell$.

The cartesian p-orbitals:

3.9. Rigid rotor

For two particles m_1 and m_2 with a constant separation r, but otherwise, in free motion

$$H \;=\; -\hbar^2/2m_1\, \nabla^2_1 - \hbar^2/2m_2\, \nabla^2_2\,, \qquad (3.39)$$

which can be separated to center of mass (CM) and relative motion. Then

$$1/m_1\nabla^2_1 + 1/m_2\nabla^2_2 = 1/m\nabla^2_{CM} + 1/\mu\nabla^2,$$

where $m = m_1 + m_2$ and

$$1/\mu = 1/m_1 + 1/m_2. \qquad (3.40)$$

where μ is *reduced mass.*

Thus, the Schrödinger equation is

$$-\hbar^2/2m\, \nabla^2_{CM}\Psi - \hbar^2/2\mu\, \nabla^2\Psi \;=\; E_{tot}\Psi \qquad (3.41)$$

and with the trial $\Psi = \psi_{CM}\,\psi$ we get

$$-\hbar^2 / 2m\, \nabla^2_{CM}\psi_{CM} \;=\; E_{CM}\,\psi_{CM} \qquad (3.42a)$$

$$-\hbar^2 / 2\mu\, \nabla^2\psi \;=\; E\,\psi, \qquad (3.42b)$$

where $E_{tot} = E_{CM} + E$. The former equation describes the free-particle dynamics (2.5–6), which is in 3D $\psi_{CM}(\mathbf{R}) = A\, \exp(i\mathbf{k}\cdot\mathbf{R})$.

Based on (3.28) with $r = |\mathbf{r}| =$ constant $\nabla^2 \to \Lambda^2/r^2$ and the latter takes the form

$$-\hbar^2 / 2\mu r^2\, \Lambda^2\psi \;=\; E\,\psi \qquad (3.43)$$

With $I = \mu r^2$ this becomes (3.31, 33), whose solutions are spherical harmonics and energies are given in (3.35)

$$E_{J\,M_J} \;=\; J(J{+}1)\, \hbar^2 / 2I. \qquad (3.44)$$

3.10. Particle in a spherical well, *e.g.,* an electron in a spherical deep quantum dot

Now the Schrödinger equation takes the form

(3.45)

which separates with

$$\psi(r,\theta,\varphi) = R(r)\, Y(\theta,\varphi), \qquad (3.46)$$

where $Y_{\ell m_\ell}(\theta,\varphi)$ is a spherical harmonic in (3.33) and the radial wavefunction is a solution to

(3.47a)

or

(3.47b)

with $k^2 = 2mE/\hbar^2$ and $z = kr$. Solutions to that are *spherical Bessel functions* $j_\ell(kr)$, such as

$$j_0(kr) = \sin(kr)/(kr) \quad \text{and} \qquad (3.48)$$
$$j_1(kr) = \sin(kr)/(kr)^2 - \cos(kr)/(kr).$$

For the infinitely deep well with radius a we apply the boundary condition

$$j_\ell(ka) = 0, \qquad (3.49)$$

which leads to eigen energies

$$E_{n\ell} = F_{n\ell}\, \hbar^2/(2ma^2). \qquad (3.50)$$

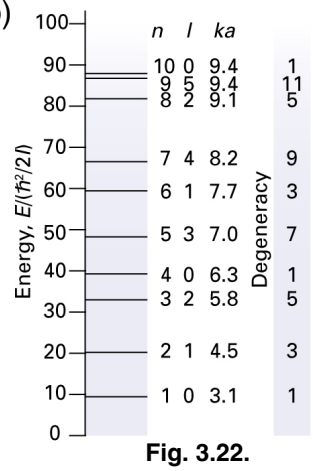


Fig. 3.22.

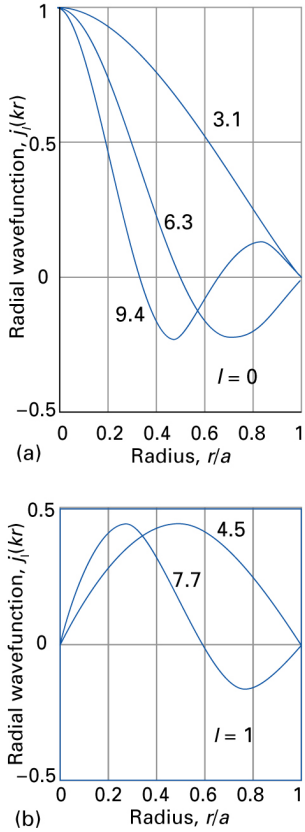


Fig. 3.21.

Motion in Coulombic field

The Coulombic potential $\pm 1/r$ is spherical, and thus, the above considered angular motion is valid as such. We just need to find solutions to the radial part of full stationary states.

3.11. Schrödinger equation for hydrogenic atoms

The hamiltonian for the electron and nucleus under their attractive Coulomb field is

(3.51)

which can be separated as before, leading to the reduced mass $\mu = \dfrac{m_e\, m_p}{m_e + m_p} \approx m_e$

(3.52)

The center-of-mass is free particle as before and we obtain for the relative motion

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi - \frac{1}{4\pi\varepsilon_o}\frac{e^2}{r}\psi = E\,\psi \qquad (3.53)$$

or

$$\frac{1}{r}\frac{\partial^2}{\partial r^2} r\,\psi + \frac{1}{r^2}\Lambda^2\psi + \frac{\mu e^2}{2\pi\varepsilon_o\hbar^2 r}\psi = -\frac{2\mu E}{\hbar^2}\psi\,. \qquad (3.54)$$

3.12. Separation of radial and angular coordinates

Separation goes with the trial wavefunction

$$\psi(r,\theta,\varphi) = R(r)\, Y(\theta,\varphi), \tag{3.55}$$

which leads to the angular equation and quantization $\Lambda^2 Y_{\ell m_\ell}(\theta,\varphi) = -\ell(\ell+1)\, Y_{\ell m_\ell}(\theta,\varphi)$ and the equation

$$\frac{1}{r}\frac{\partial^2}{\partial r^2} r R Y - \frac{1}{r^2}\ell(l+1) R Y + \frac{\mu e^2}{2\pi\varepsilon_0 \hbar^2 r} R Y = -\frac{2\mu E}{\hbar^2} R Y . \tag{3.56}$$

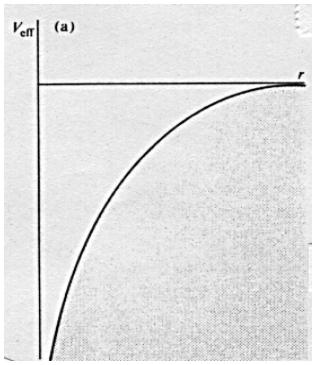
The function Y can be cancelled throughout and we are left with radial equation

$$-\frac{\hbar^2}{2\mu}\frac{d^2u}{dr^2} + V_{eff}(r)\, u = Eu , \tag{3.58}$$

where $u(r) = r R(r)$. Thus, we have an 1D Schrödinger equation for the radial motion with an *effective potential*

$$V_{eff}(r) = -\frac{1}{4\pi\varepsilon_o}\frac{e^2}{r} + \frac{\ell(l+1)\hbar^2}{2\mu r^2} \tag{3.59}$$

The effective potential depends on the angular momentum, that with the classical analogy can be assingned with the centrifugal force of rotation. Thus, the Coulomb attraction contributes to the singularity for the $\ell = 0$ state, only.



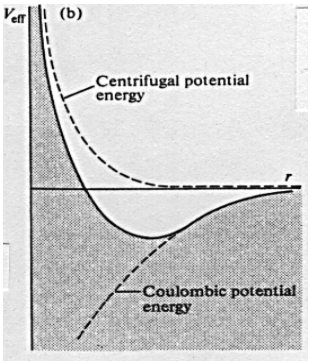


Fig. 3.24.

3.13. Solutions of the radial equation

For $\ell = 0$, the solution of equation (3.58) behaves as $u \sim Ar + Br^2$, when $r \to 0$, and then $R = u/r \to A$, which means that the probability density of the electron at nucleus is $A^2 \neq 0$.

For $\ell \neq 0$, $u \to A\, r^{\ell+1}$ and $R = u/r \to A\, r^{\ell}$, when $r \to 0$.

The wavefunctions of the hydrogen atom can be written in terms of associated Laguerre functions:

TABLE 3.4 Radial functions for hydrogen

$n = 1$	$l = 0$	$R_{10} = \frac{2}{\sqrt{a_0^3}} e^{-r/a_0}$
$n = 2$	$l = 0$	$R_{20} = \frac{1}{\sqrt{2a_0^3}}\left(1 - \frac{r}{2a_0}\right)e^{-r/2a_0}$
	$l = 1$	$R_{21} = \frac{1}{2\sqrt{6a_0^3}}\frac{r}{a_0} e^{-r/2a_0}$
$n = 3$	$l = 0$	$R_{30} = \frac{2}{3\sqrt{3a_0^3}}\left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right)e^{-r/3a_0}$
	$l = 1$	$R_{31} = \frac{8}{27\sqrt{6a_0^3}}\frac{r}{a_0}\left(1 - \frac{r}{6a_0}\right)e^{-r/3a_0}$
	$l = 2$	$R_{32} = \frac{4}{8\sqrt{30a_0^3}}\frac{r^2}{a_0^2} e^{-r/3a_0}$

The unit of length, sc. *Bohr radius*

$$a_0 = (4\pi\varepsilon_0\hbar^2)/(m_e e^2), \tag{3.65}$$

is the radius of the electron in Bohr atomic model (infinite nuclear mass).

For the hydrogenic atoms, in general, it is often used

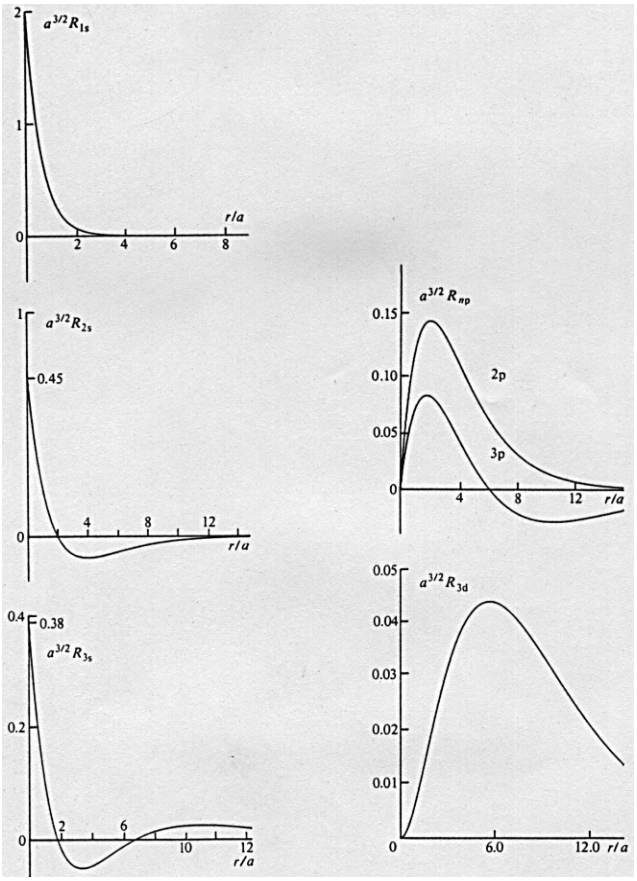
$$a = (4\pi\varepsilon_0\hbar^2)/(\mu e^2)$$

and

$$\varrho = (2Z/na)\, r.$$

(replace $-r/na_0$ by $-\varrho/2$)

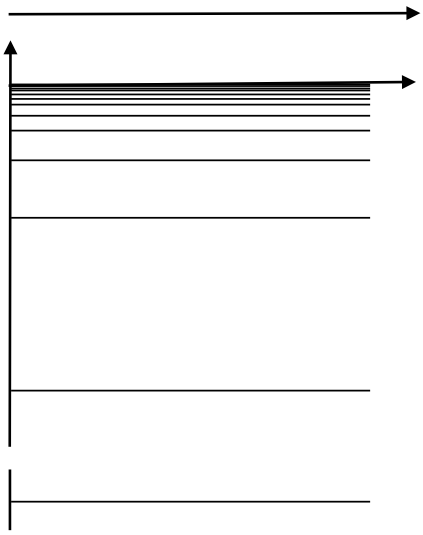
The radial wavefunctions hydrogen atom:



Eigenenergies of the hydrogenic atoms are

$$E_n = -\frac{1}{2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{\mu}{\hbar^2}\frac{1}{n^2}\,;\; n = 1, 2, \ldots \;. \qquad (3.66)$$

$|E_1| = 1$ Ry (Rydberg) $= 13.6$ eV
$= 1/2$ Ha (Hartree).



Cf. 0.4 on p. 5.

3.14. Probabilities and radial distribution function

$P(r) = 4\pi r^2 \langle|\psi(r)|^2\rangle$ is called the *radial distribution function.* It is the particle probability density as a function of r. For a spherical wavefunction $\psi(r)$

$$P(r) = u^2(r) = R^2(r)\, r^2 = 4\pi r^2 |\psi(r)|^2 \qquad (3.69)$$

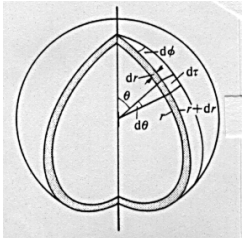


Fig. 4.16. The volume element in spherical polar coordinates.

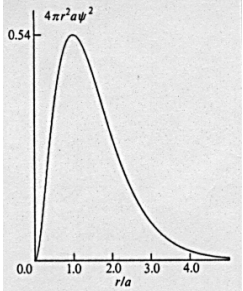


Fig. 4.17. The radial distribution function for the hydrogen 1s-orbital.

3.15. Atomic orbitals

The hydrogenic wavefunctions

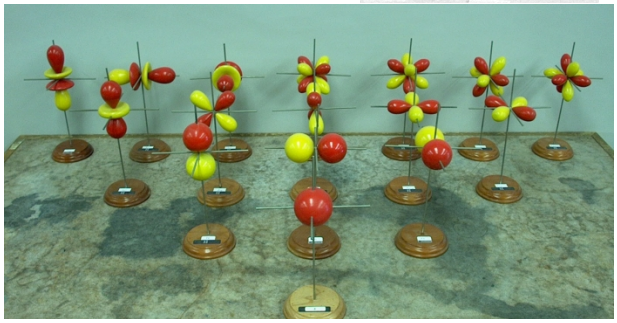
$$\psi_{n\ell m_l}(r,\theta,\phi) = R_{nl}(r)\, Y_{l m_l}(\theta,\phi)$$

are called orbitals. Their degeneracy is n^2 and including the spin $2n^2$.

The $(2\ell+1)$ degeneracy arises from symmetry, but n degeneration is accidental.

ℓ =	0	1	2	3	(0, 1, ..., n–1)
deg.	1	3	5	7	$(2\ell+1)$
n = 1	1s				
2	2s	2p			
3	3s	3p	3d		
4	4s	4p	4d	4f	

The s orbitals are spherical. The p_0 orbital is a real function and the same as p_z orbital. The p_{+1} and p_{-1} are complex combinations of real p_x and p_y, $p_{+1} = (p_x - i\, p_y)/\sqrt{2}$ and $p_{-1} = i\,(p_x + i\, p_y)/\sqrt{2}$, see also the example on p. 8.



The hydrogenic orbitals are simplified models for atomic orbitals. They are used for classification in the periodic table of elements.

TABLE 4.1
Angular Factors of Conventional Atomic Orbitals

Symbol	Polar	Cartesian	Normalizing factor
s	1	1	$\frac{1}{2}\left(\frac{1}{\pi}\right)^{1/2}$
p_x	$\sin\theta\cos\phi$	x/r	$\frac{1}{2}\left(\frac{3}{\pi}\right)^{1/2}$
p_y	$\sin\theta\sin\phi$	y/r	$\frac{1}{2}\left(\frac{3}{\pi}\right)^{1/2}$
p_z	$\cos\theta$	z/r	$\frac{1}{2}\left(\frac{3}{\pi}\right)^{1/2}$
d_{z^2}	$(3\cos^2\theta - 1)$	$(3z^2 - r^2)/r^2$ $(2z^2 - x^2 - y^2)/r^2$	$\frac{1}{4}\left(\frac{5}{\pi}\right)^{1/2}$
d_{xz}	$\sin\theta\cos\theta\cos\phi$	xz/r^2	$\frac{1}{2}\left(\frac{15}{\pi}\right)^{1/2}$
d_{yz}	$\sin\theta\cos\theta\sin\phi$	yz/r^2	$\frac{1}{2}\left(\frac{15}{\pi}\right)^{1/2}$
$d_{x^2-y^2}$	$\sin^2\theta\cos 2\phi$	$(x^2 - y^2)/r^2$	$\frac{1}{4}\left(\frac{15}{\pi}\right)^{1/2}$
d_{xy}	$\sin^2\theta\sin 2\phi$	xy/r^2	$\frac{1}{4}\left(\frac{15}{\pi}\right)^{1/2}$
f_{z^3}	$(5\cos^3\theta - 3\cos\theta)$	$z(5z^2 - 3r^2)/r^3$ $[2z^3 - 3z(x^2 + y^2)]/r^3$	$\frac{1}{4}\left(\frac{7}{\pi}\right)^{1/2}$
f_{xz^2}	$(5\cos^2\theta - 1)\sin\theta\cos\phi$	$x(5z^2 - r^2)/r^3$ $[4xz^2 - x(x^2 + y^2)]/r^3$	$\frac{1}{8}\left(\frac{42}{\pi}\right)^{1/2}$
f_{yz^2}	$(5\cos^2\theta - 1)\sin\theta\sin\phi$	$y(5z^2 - r^2)/r^3$ $[4yz^2 - y(x^2 + y^2)]/r^3$	$\frac{1}{8}\left(\frac{42}{\pi}\right)^{1/2}$
f_{xyz}	$\sin^2\theta\cos\theta\sin 2\phi$	xyz/r^3	$\frac{1}{4}\left(\frac{105}{\pi}\right)^{1/2}$
$f_{z(x^2-y^2)}$	$\sin^2\theta\cos\theta\cos 2\phi$	$z(x^2 - y^2)/r^3$	$\frac{1}{4}\left(\frac{105}{\pi}\right)^{1/2}$
$f_{x(x^2-3y^2)}$	$\sin^3\theta\cos 3\phi$	$x(x^2 - 3y^2)/r^3$	$\frac{1}{8}\left(\frac{70}{\pi}\right)^{1/2}$
$f_{y(3x^2-y^2)}$	$\sin^3\theta\sin 3\phi$	$y(3x^2 - y^2)/r^3$	$\frac{1}{8}\left(\frac{70}{\pi}\right)^{1/2}$

Douglas, Bodie E. and Hollingsworth, Charles A. *Symmetry in Bonding and Spectra – An Introduction* (Orlando, Florida: Academic Press, Inc., 1985) p. 123.

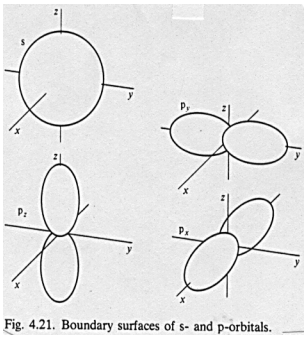


Fig. 4.21. Boundary surfaces of s- and p-orbitals.

$p_x = (p_{+1} + p_{-1})/\sqrt{2}$

$p_y = i\,(p_{+1} - p_{-1})/\sqrt{2}$

$p_z = p_0$

$d_{+2} =$

$d_{+1} =$

$d_0 =$

$d_{-1} =$

$d_{-2} =$

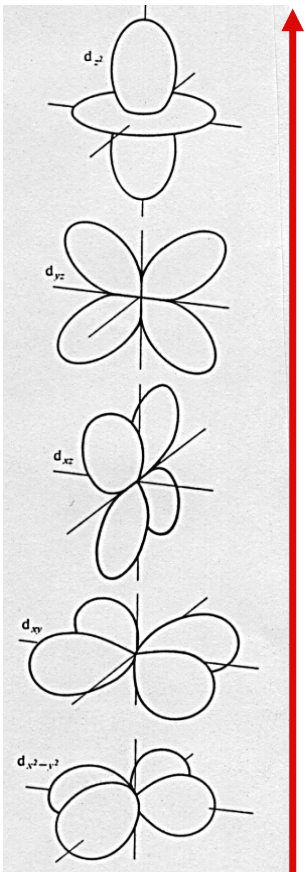


Fig. 4.22. Boundary surfaces for d-orbitals.

Example The ground state wavefunction of hydrogen atom is
where $a_0 = 0.5292$ Å.
a) Where is the most probable position of the electron?
b) What is the probability to find the electron in a volume 1 fm^3, when (i) $r = 0$ and (ii) $r = a_0$?
c) What is the probability to find the electron in a sphere of radius a_0 around the nucleus?

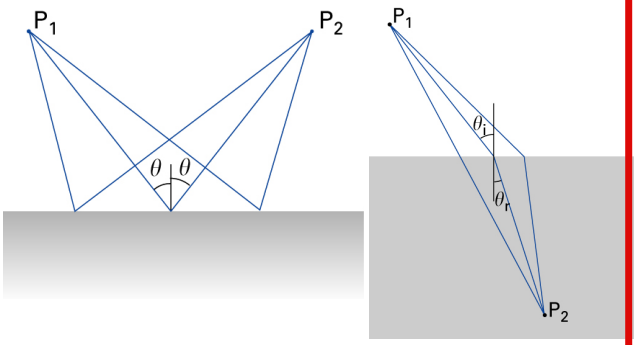
Schrödingerin yhtälö ja etenevät aallot

Vaikka Schrödingerin yhtälö voidaan postuloida kvanttimekaniikkaan, voidaan sitä myös "perustella" aalto–hiukkas-dualismin perusteella.

Valoaallon eteneminen

Geometrisessa optiikassa valoaallot etenevät suoraviivaisesti ns. *Fermat'n periaatteen* mukaisesti: valonsäde kulkee tietä, jonka optinen matka on lyhin (tai saa ääriarvon).

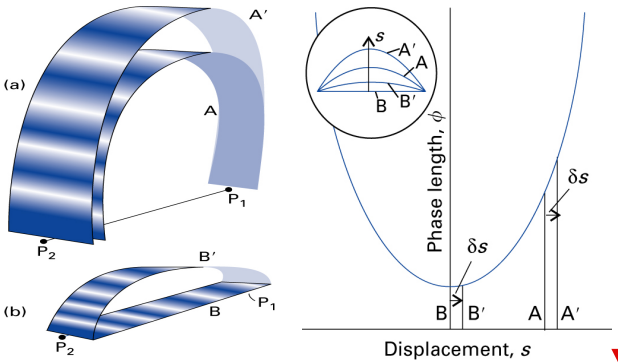
Fysikaalisessa optiikassa tämä voidaan selittää Huygensin periaatteen ja *interferenssin* avulla: lähekkäiset valoaallot interferoivat konstruktiivisesti siellä missä optinen matka saa ääriarvonsa.



1.23. Hiukkasten eteneminen

Klassillisessa mekaniikassa hiukkaset etenevät Newtonin liikeyhtälöiden mukaisesti. Ne voidaan kuitenkin johtaa ns. *Hamiltonin periaatteesta,* joka on analoginen Fermat'n periaatteen kanssa.

Olettamalla etenevälle hiukkaselle aaltoluonne, voidaan koko kvanttimekaniikka johtaa siitä Feynmanin polkuintegraaliformalismia käyttäen.



Hiukkasten eteneminen aaltoina

Kun hiukkaseen liitetään (aallon) amplitudi samoin kuin valoon fysikaalisessa optiikassa ja sovelletaan sitten Hamiltonin periaatetta, saadaan ajasta riippuva Schrödingerin aaltoyhtälö. Siten Schrödingerin aaltoyhtälö voidaan johtaa aineaaltohypoteesista lähtien.

Alkeishiukkasten, esim. elektronien, spin ei ole johdettavissa näistä oletuksista vaan se on postuloitava kokeellisten havaintojen selittämiseksi tai yleistettävä kvanttimekaniikka relativistiseksi, jolloin elektronin spinit tulevat teoriasta omina kvanttitiloinaan.

Schrödingerin aaltoyhtälön suorassa yleistämisessä suhteellisuusteoreettiseksi on ongelmana se, että aika- ja paikkakoordinaattien "rooli" on erilainen: yhtälössä paikan suhteen esiintyy 2. kertaluvun derivaattoja, mutta ajan suhteen vain 1. kertaluvun derivaatta. Schrödingerin aaltoyhtälö

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

onkin itseasiassa diffuusioyhtälön

$$\frac{\partial f}{\partial t} = D\ \nabla^2 f$$

kaltainen.