Quantum mechanics I

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Contents

I. LITERATURE

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2) C. Cohen-Tannoudji, Quantum Mechanics, Wiley.

3) R. Shankar, Principles of Quantum Mechanics, Plenum.

4) L. D. Landau & E. M. Lifschitz, Lehrbuch der theoretischen Physik, Bd.3, Quantenmechanik, Akademie-Verlag.

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II. HISTORICAL BACKGROUND

A. 1901: Max Planck

In 1901 Max Plank explained blackbody radiation using an assumption of light quanta (photons). Every photon carries energy $E = \hbar\omega$, where $\omega = 2\pi\nu$ is the angular frequency of light (ν is the frequency) and

$$\hbar = 1.05457266 \times 10^{34}\mathrm{J}\cdot\mathrm{s}\ . \tag{1}$$

B. 1905: Albert Einstein

In 1905 Albert Einstein used the concept of light quanta to explain the photo-effect. The maximal kinetic energy of an electron released from a metal is given by

$$E_{kin,max} = \hbar\omega - W\ , \tag{2}$$

where W is the work function, i.e., work needed to extract an electron from the metal.

C. 1911: Ernest Rutherford

Rutherford model of an atom.

D. 1913: Niels Bohr

Formulated a quantization principle, which allowed to explain spectra of atoms (both allowed energies of electrons and the allowed frequency of emitted and absorbed photons).

E. 1923: Arthur Holly Compton

In 1923 the scattering of photons (X-rays) on electrons has been observed by Compton (Compton effect). This is an example of *inelastic* scattering, in which the photon looses a part of its energy to the electron. From the relation $E = \hbar\omega$, the dispersion relations $E = cp$ ($p \equiv |\mathbf{p}|$), and $\omega = ck$ ($k = |\mathbf{k}|$ is the wave vector) one gets the relation $\mathbf{p} = \hbar\mathbf{k}$. The wave vector is further related to the wave length of the photon $\lambda = 2\pi/k$.

We derive here the relation between the scattering angle θ and the change of the wave length of the photon. Relativistic 4-momentum of a photon

$$p^\mu = \begin{pmatrix} E/c \\ \mathbf{p} \end{pmatrix} = \hbar \begin{pmatrix} \omega/c \\ \mathbf{k} \end{pmatrix} = \hbar \begin{pmatrix} k \\ \mathbf{k} \end{pmatrix} \ , \tag{3}$$

where $k \equiv |\mathbf{k}|$. For an electron $E = \sqrt{m^2c^4 + c^2p^2}$

$$p^\mu = \begin{pmatrix} E/c \\ \mathbf{p} \end{pmatrix} = \begin{pmatrix} \sqrt{m^2c^2 + p^2} \\ \mathbf{p} \end{pmatrix} \tag{4}$$

Before the scattering the electron had velocity $\mathbf{v} = 0$. The conservation of the 4-momentum gives

$$\hbar \begin{pmatrix} k \\ \mathbf{k} \end{pmatrix} + \begin{pmatrix} \sqrt{m^2c^2 + p^2} \\ \mathbf{p} \end{pmatrix} = \hbar \begin{pmatrix} k' \\ \mathbf{k}' \end{pmatrix} + \begin{pmatrix} \sqrt{m^2c^2 + p'^2} \\ \mathbf{p}' \end{pmatrix} \tag{5}$$

We choose $\mathbf{p} = 0$ (initially the electron is at rest)

$$\hbar \begin{pmatrix} k \\ \mathbf{k} \end{pmatrix} + \begin{pmatrix} mc \\ \mathbf{0} \end{pmatrix} = \hbar \begin{pmatrix} k' \\ \mathbf{k}' \end{pmatrix} + \begin{pmatrix} \sqrt{m^2c^2 + p'^2} \\ \mathbf{p}' \end{pmatrix} \tag{6}$$

$$\hbar \begin{pmatrix} k - k' \\ \mathbf{k} - \mathbf{k}' \end{pmatrix} + \begin{pmatrix} mc \\ \mathbf{0} \end{pmatrix} = \begin{pmatrix} \sqrt{m^2c^2 + p'^2} \\ \mathbf{p}' \end{pmatrix} \tag{7}$$

We calculate the Minkovski length (norm) of the left and the right sides. On the right side we can use the general property $p_\mu p^\mu = p_0^2 - \mathbf{p}^2 = m^2c^2$ for an electron (for a photon $p_\mu p^\mu = 0$).

$$\left[\hbar(k - k') + mc\right]^2 - \hbar^2 \left(\mathbf{k} - \mathbf{k}'\right)^2 = m^2c^2 \tag{8}$$

$$2\hbar^2(\mathbf{k} \cdot \mathbf{k}' - kk') + 2\hbar mc(k - k') = 0 \tag{9}$$

$$k - k' = \frac{\hbar}{mc} kk'(1 - \cos\theta) \tag{10}$$

$$\frac{1}{k'} - \frac{1}{k} = \frac{\hbar}{mc}\,(1 - \cos\theta) \tag{11}$$

With $\lambda = 2\pi/k$ we get

$$\lambda' - \lambda = \frac{2\pi\hbar}{mc}\,(1 - \cos\theta) \tag{12}$$

Compton wavelength $\lambda\!\!\!^{-}_c \equiv \frac{\hbar}{mc} = 3,86 \times 10^{-11}\text{cm} = 3,86 \times 10^{-13}\text{m}$.

$$\lambda' - \lambda = 2\pi\lambda\!\!\!^{-}_c\,(1 - \cos\theta) = 4\pi\lambda\!\!\!^{-}_c\,\sin^2\frac{\theta}{2} \tag{13}$$

F. 1924: Louis de Broglie

In his PhD thesis in 1924 de Broglie postulated that also electrons have the wave nature (matter waves). The relations

$$E = \hbar\omega \quad , \quad \mathbf{p} = \hbar\mathbf{k} \tag{14}$$

are also valid for the electrons (and other matter particles). This means that an electron with momentum p is characterized by the wave length (de Broglie wave length)

$$\lambda = \frac{2\pi}{k} = \frac{2\pi\hbar}{p}\ . \tag{15}$$

III. SCHRÖDINGER EQUATION

A. Schrödinger equation for a free particle

Schrödinger introduced a complex wave function $\psi(\mathbf{r}, t)$, which satisfies the following wave equation (for a free particle)

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\,\boldsymbol{\nabla}^2\psi\ , \tag{16}$$

where $\boldsymbol{\nabla} = (\partial_x, \partial_y, \partial_z)$ or $\boldsymbol{\nabla} = (\partial_1, \partial_2, \partial_3)$. It is easy to see that a plane wave

$$\psi(\mathbf{r}, t) = Ce^{i(\mathbf{k}\cdot\mathbf{r} - \omega(k)t)}\ , \tag{17}$$

satisfies this equation if

$$E = \hbar\omega(k) = \frac{\hbar^2k^2}{2m} = \frac{p^2}{2m}\ . \tag{18}$$

B. Physical meaning and normalization

The physical meaning is as follows: $\rho(\mathbf{r},t) \equiv |\psi(\mathbf{r},t)|^2$ is the probability density to find the electron at point $\mathbf{r}$ at time t. More precisely $dP(\mathbf{r},t) = \rho(\mathbf{r},t)d^3r$ is the probability to find the particle in a volume element d^3r around $\mathbf{r}$. This interpretation requires the normalization condition

$$\int d^3r\, \rho(\mathbf{r},t) = 1 \ , \tag{19}$$

which means that with probability 1 the particle is located somewhere. The plane wave solution cannot be normalized (we will discuss this problem later). Yet, since the Schrödinger equation is linear, we can build a superposition of plane wave solutions which would be normalizable. A general solution of the free particle Schrödinger equation reads

$$\psi(\mathbf{r},t) = \int \frac{d^3k}{(2\pi)^3} C(\mathbf{k})\, e^{i(\mathbf{k}\cdot\mathbf{r}-\omega(k)t)} \ . \tag{20}$$

With a proper choice of the function $C(\mathbf{k})$ this solution can be made normalizable. We will discuss such solutions (wave packets) in what follows.

C. Momentum operator

We stick to the description of free particles and consider the expectation value of its coordinate and velocity. For the coordinate we obtain

$$\langle \mathbf{r} \rangle = \int d^3r\, \mathbf{r}\rho(\mathbf{r},t) = \int d^3r\, \psi^*(\mathbf{r},t)\mathbf{r}\psi(\mathbf{r},t) \ . \tag{21}$$

For the averaged velocity this gives

$$\langle \mathbf{v} \rangle = \frac{d}{dt}\langle \mathbf{r} \rangle = \int d^3r\, \left([\partial_t \psi^*(\mathbf{r},t)]\, \mathbf{r}\psi(\mathbf{r},t) + \psi^*(\mathbf{r},t)\mathbf{r}\,[\partial_t\psi(\mathbf{r},t)] \right) \ . \tag{22}$$

We use (16) and its complex conjugated version:

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2\psi \ , \tag{23}$$

$$-i\hbar\frac{\partial\psi^*}{\partial t} = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2\psi^* \ , \tag{24}$$

we obtain

$$\langle \mathbf{v} \rangle = \frac{\hbar}{2mi}\int d^3r\, \left(\left[\boldsymbol{\nabla}^2\psi^*\right]\mathbf{r}\psi - \psi^*\mathbf{r}\left[\boldsymbol{\nabla}^2\psi\right] \right) \ . \tag{25}$$

The calculation is simplified in coordinates:

$$\langle v_\beta \rangle = \frac{\hbar}{2mi} \sum_\alpha \int d^3r \, \left([\partial_\alpha \partial_\alpha \psi^*] \, r_\beta \psi - \psi^* r_\beta \, [\partial_\alpha \partial_\alpha \psi] \right) \, . \tag{26}$$

Perform partial integration in the first term

$$\langle v_\beta \rangle = \frac{\hbar}{2mi} \sum_\alpha \int d^3r \, \left(\psi^* \partial_\alpha \partial_\alpha r_\beta \psi - \psi^* r_\beta \partial_\alpha \partial_\alpha \psi \right) \, . \tag{27}$$

In the first term ∂_α can act either on r_β or on ψ. Using $\partial_\alpha r_\beta = \delta_{\alpha,\beta}$ we get

$$\langle v_\beta \rangle = \frac{\hbar}{mi} \int d^3r \, \psi^* \partial_\beta \psi \, . \tag{28}$$

In the vector form this reads

$$\langle \mathbf{v} \rangle = \frac{\hbar}{mi} \int d^3r \, \psi^* \boldsymbol{\nabla} \psi = \frac{1}{m} \int d^3r \, \psi^* \left(\frac{\hbar}{i} \boldsymbol{\nabla} \right) \psi \, . \tag{29}$$

Since classically we would expect

$$\langle \mathbf{v} \rangle = \frac{1}{m} \langle \mathbf{p} \rangle \, , \tag{30}$$

we define the momentum operator as

$$\hat{\mathbf{p}} \equiv \frac{\hbar}{i} \boldsymbol{\nabla} \, . \tag{31}$$

Its expectation value is defined as

$$\langle \hat{\mathbf{p}} \rangle \equiv \int d^3r \, \psi^* \hat{\mathbf{p}} \psi = \int d^3r \, \psi^* \left(\frac{\hbar}{i} \boldsymbol{\nabla} \right) \psi \, . \tag{32}$$

This makes sense also because if we act with $\hat{\mathbf{p}}$ on the plane wave we obtain

$$\hat{\mathbf{p}} e^{i(\mathbf{k}\cdot\mathbf{r} - \omega(k)t)} = \hbar \mathbf{k} e^{i(\mathbf{k}\cdot\mathbf{r} - \omega(k)t)} \, . \tag{33}$$

D. Schrödinger equation for a particle in a potential

The momentum operator introduced above allows to write down the Schrödinger equation for a free particle as

$$i\hbar \frac{\partial \psi}{\partial t} = \frac{\hat{\mathbf{p}} \cdot \hat{\mathbf{p}}}{2m} \psi = \frac{\hat{\mathbf{p}}^2}{2m} \psi \, . \tag{34}$$

If we introduce the operator of the kinetic energy as

$$\hat{T} \equiv \frac{\hat{\mathbf{p}}^2}{2m} \, , \tag{35}$$

the Schrödinger equation for a free particle reads

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{T}\psi \ . \tag{36}$$

This immediately motivates the full Schrödinger equation for a particle of mass m in a potential energy $V(\mathbf{r})$:

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi \ , \tag{37}$$

where the Hamiltonian operator is given by $\hat{H} \equiv \hat{T}+\hat{V}$. The potential energy operator $\hat{V}$ just multiplies the wave function with the potential energy, i.e., $\hat{V}\psi = V(\mathbf{r})\psi(\mathbf{r},t)$ (accordingly the operator $\hat{\mathbf{r}}$ is defined as $\hat{\mathbf{r}}\psi(\mathbf{r},t) = \mathbf{r}\psi(\mathbf{r},t)$). From now on we will investigate the full version of the Schrödinger equation (37).

E. Continuity equation

Consider the time-derivative of the probability density $\rho(\mathbf{r},t)$. Using the Schrödinger equation and its complex conjugate

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi \ , \tag{38}$$

$$-i\hbar\frac{\partial\psi^*}{\partial t} = \hat{H}\psi^* \ , \tag{39}$$

we obtain

$$\partial_t\rho = (\partial_t\psi^*)\psi + \psi^*(\partial_t\psi) = \frac{1}{-i\hbar}(\hat{H}\psi^*)\psi + \frac{1}{i\hbar}\psi^*(\hat{H}\psi) \ . \tag{40}$$

Substituting $\hat{H} = \hat{T} + \hat{V}$ we observe that the potential energy term drops and we get

$$\partial_t\rho = \frac{\hbar}{2mi}(\left[\boldsymbol{\nabla}^2\psi^*\right]\psi - \psi^*\left[\boldsymbol{\nabla}^2\psi\right]) \ . \tag{41}$$

We define the current density of the probability

$$\mathbf{j} = \frac{\hbar}{2mi}(\psi^*\left[\boldsymbol{\nabla}\psi\right] - \left[\boldsymbol{\nabla}\psi^*\right]\psi) \ . \tag{42}$$

It is easy to show that the following equation holds

$$\partial_t\rho + \boldsymbol{\nabla}\cdot\mathbf{j} = 0 \ . \tag{43}$$

This is the continuity equation, which expresses the conservation of the probability.

For the probability P for a particle to be inside of a volume V,

$$P = \int_V d^3r\, \rho \ , \tag{44}$$

this gives

$$\partial_t P = -\int_V d^3r \boldsymbol{\nabla} \cdot \mathbf{j} = -\int_{\partial V} d\mathbf{S} \cdot \mathbf{j} \ . \tag{45}$$

F. Ehrenfest theorem

In analogy to the expectation value of the momentum operator (32) we can define the expectation value of an arbitrary operator $\hat{A}$ as

$$\langle \hat{A} \rangle \equiv \int d^3r\, \psi^* \hat{A} \psi \ . \tag{46}$$

Its time derivative can be easily calculated using the Schrödinger equation (37) and its complex conjugate:

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi \ , \tag{47}$$

$$-i\hbar \frac{\partial \psi^*}{\partial t} = \hat{H}\psi^* \ , \tag{48}$$

We obtain

$$i\hbar \frac{d}{dt}\langle \hat{A} \rangle = \int d^3r \, \left[\psi^* \hat{A} \left[\hat{H}\psi \right] - \left[\hat{H}\psi^* \right] \hat{A}\psi \right] \ . \tag{49}$$

In the second term we can use integration by parts (or the fact that H is hermitian as will be defined later) to get

$$i\hbar \frac{d}{dt}\langle \hat{A} \rangle = \int d^3r \, \left[\psi^* \hat{A}\hat{H}\psi - \psi^* \hat{H}\hat{A}\psi \right] \ . \tag{50}$$

This can be rewritten as

$$\frac{d}{dt}\langle \hat{A} \rangle = \frac{i}{\hbar} \langle \left[\hat{H}, \hat{A} \right] \rangle \ , \tag{51}$$

where $\left[\hat{H}, \hat{A} \right] \equiv \hat{H}\hat{A} - \hat{A}\hat{H}$ is the commutator.

In general operators do not commute and commutators play a very important role in quantum mechanics. For example the operators $\hat{r}_\alpha$ and $\hat{p}_\beta = -i\hbar\partial_\beta$ do not commute. Indeed

$$\hat{p}_\beta \hat{r}_\alpha \psi = -i\hbar \partial_\beta r_\alpha \psi = -i\hbar \delta_{\alpha,\beta}\psi - i\hbar r_\alpha \partial_\beta \psi = -i\hbar\delta_{\alpha,\beta}\psi + \hat{r}_\alpha \hat{p}_\beta \psi \ . \tag{52}$$

This gives

$$[\hat{r}_\alpha, \hat{p}_\beta] = i\hbar\delta_{\alpha,\beta} \ . \tag{53}$$

Now we are in a position to recalculate the expectations values of the velocity (time derivative of $\mathbf{r}$) and the time derivative of the momentum. For the velocity we get

$$\langle \mathbf{v} \rangle = \frac{d}{dt}\langle \hat{\mathbf{r}} \rangle = \frac{i}{\hbar}\langle [\hat{H}, \hat{\mathbf{r}}] \rangle = \frac{i}{\hbar}\left\langle \left[\frac{\hat{\mathbf{p}}^2}{2m}, \hat{\mathbf{r}} \right] \right\rangle \ . \tag{54}$$

For the commutator, using $[\hat{r}_\alpha, \hat{p}_\beta] = i\hbar\delta_{\alpha,\beta}$, we get

$$\begin{aligned} \left[\hat{\mathbf{p}}^2, \hat{\mathbf{r}}\right]_\beta &= \sum_\alpha [\hat{p}_\alpha \hat{p}_\alpha, \hat{r}_\beta] = \sum_\alpha (\hat{p}_\alpha \hat{p}_\alpha \hat{r}_\beta - \hat{r}_\beta \hat{p}_\alpha \hat{p}_\alpha) \\ &= \sum_\alpha (\hat{p}_\alpha \hat{p}_\alpha \hat{r}_\beta - \hat{p}_\alpha \hat{r}_\beta \hat{p}_\alpha - i\hbar\delta_{\alpha,\beta}\hat{p}_\alpha) = \sum_\alpha (-2i\hbar\delta_{\alpha,\beta}\hat{p}_\alpha) = -2i\hbar\hat{p}_\beta \ . \end{aligned} \tag{55}$$

This gives

$$\langle \mathbf{v} \rangle = \frac{d}{dt}\langle \hat{\mathbf{r}} \rangle = \frac{1}{m}\langle \hat{\mathbf{p}} \rangle \ . \tag{56}$$

For the time derivative of the momentum we get

$$\frac{d}{dt}\langle \mathbf{p} \rangle = \frac{i}{\hbar}\langle [\hat{H}, \hat{\mathbf{p}}] \rangle = \frac{i}{\hbar}\langle [\hat{V}, \hat{\mathbf{p}}] \rangle \ . \tag{57}$$

We calculate the commutator

$$[\hat{V}, \hat{\mathbf{p}}]_\alpha = V(\mathbf{r})(-i\hbar\partial_\alpha) - (-i\hbar\partial_\alpha)V(\mathbf{r}) = i\hbar\partial V/\partial r_\alpha \ . \tag{58}$$

As a result we obtain

$$\frac{d}{dt}\langle \mathbf{p} \rangle = \langle -\boldsymbol{\nabla}\hat{V} \rangle \ . \tag{59}$$

This relation, together with $\frac{d}{dt}\langle \hat{\mathbf{r}} \rangle = \frac{1}{m}\langle \hat{\mathbf{p}} \rangle$ is called the Ehrenfest theorem. We see that the expectation values of the coordinate and momentum satisfy the usual Hamiltonian equations of motion. Quantum mechanics allows, however, for fluctuations around these expectation values.

G. Stationary solutions

If the potential $V(\mathbf{r})$ is time-independent a special class of solutions of the Schrödinger equation exists. One makes the following Ansatz

$$\Psi(\mathbf{r}, t) = f(t)\psi(\mathbf{r}) \tag{60}$$

and substitutes it to the Schrödinger equation $i\hbar\partial_t\Psi = H\Psi$. One obtains

$$i\hbar(\partial_t f)\psi = (\hat{H}\psi)f \ . \tag{61}$$

On the right hand side the Hamiltonian acts only on ψ since f is independent of $\mathbf{r}$. Then

$$i\hbar(\partial_t f)/f = (\hat{H}\psi)/\psi \ . \tag{62}$$

On the left hand side we have a function of t only and on the right hand side we have a function of $\mathbf{r}$ only. The only possibility is that both give a constant independent of t and $\mathbf{r}$. We call this constant E. Then we obtain

$$i\hbar(\partial_t f) = Ef \quad \text{and} \quad \hat{H}\psi = E\psi \ . \tag{63}$$

The first equation is easy to solve

$$f = e^{-iEt/\hbar} \ . \tag{64}$$

The second equation

$$\hat{H}\psi = E\psi \tag{65}$$

is called the stationary Schrödinger equation. It is an eigenvalue equation for the operator $\hat{H}$.

Assuming we found several solutions, ψ_n, of this equation with eigen-energies E_n, we can build the following time-dependent solution

$$\Psi(t) = \sum_n c_n \psi_n e^{-iE_n t/\hbar} \tag{66}$$

Should ψ_n form a complete basis in the Hilbert space, $\Psi(t)$ would be the most general solution.

H. Wave packets (in 1D)

One of the immediate applications of the expansion of the type (66) is the wave packet solution for a free particle with the Hamiltonian

$$\hat{H} = \hat{T} \ , \tag{67}$$

where

$$\hat{T} \equiv \frac{\hat{\mathbf{p}}^2}{2m} \ . \tag{68}$$

The plane wave solutions $\propto e^{i(\mathbf{k}\cdot\mathbf{r}-\omega(k)t)}$ can now be arrived via the eigenvalue/eigenvectors of H. Indeed the wave functions

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \tag{69}$$

satisfy the stationary Schrödinger equation

$$H\psi_{\mathbf{k}}(\mathbf{r}) = E_{\mathbf{k}}\psi_{\mathbf{k}}(\mathbf{r}) \tag{70}$$

with $E_{\mathbf{k}} = \hbar^2 k^2/2m$. The general solution of the time dependent Schrödinger equation is then (in analogy to (66)) given by

$$\Psi(\mathbf{r},t) = \int \frac{d^3k}{(2\pi)^3}\, g(\mathbf{k})\, \psi_{\mathbf{k}}(\mathbf{r}) e^{-iE_k t/\hbar} \ , \tag{71}$$

where the function $g(\mathbf{k})$ plays the role of the expansion coefficients c_n in (66).

A very special role is played by the solutions in which the function $|g(k)|$ is peaked around a certain wave vector $\mathbf{k}_0$. These are called wave packets.

For simplicity we will continue our consideration in 1D. Then the general solution of the time-dependent Schrödinger equation reads

$$\Psi(x,t) = \int \frac{dk}{2\pi}\, g(k)\psi_k(x) e^{-iE_k t/\hbar} = \int \frac{dk}{2\pi}\, g(k) e^{i(kx-\omega(k)t)} \ , \tag{72}$$

where $\omega(k) = E_k/\hbar$.

Let us first consider the initial state at $t = 0$. The we have

$$\Psi_0(x) = \Psi(x, t=0) = \int \frac{dk}{2\pi}\, g(k) e^{ikx} \ . \tag{73}$$

That is $\Psi_0(x)$ is just the Fourier transform of $g(k)$. We now introduce explicitly the absolute value of $g(k)$ and its phase

$$g(k) = |g(k)| e^{-i\alpha(k)} \ . \tag{74}$$

This gives

$$\Psi_0(x) = \int \frac{dk}{2\pi}\, |g(k)| e^{i(-\alpha(k)+kx)} = \int \frac{dk}{2\pi}\, |g(k)| e^{i\phi(k)} \ , \tag{75}$$

where $\phi(k) \equiv kx - \alpha(k)$. Since $|g(k)|$ is peaked around k_0, that is, it is essentially non-zero only in a small vicinity of k_0 of order Δk (e.g. in the interval $k_0 - \Delta k/2 < k < k_0 + \Delta k/2$) we can expand the phase $\phi(k)$ around k_0:

$$\phi(k) = \phi(k_0) + \frac{\partial\phi(k)}{\partial k}\Big|_{k=k_0} \cdot (k-k_0) + \frac{1}{2}\frac{\partial^2\phi(k)}{\partial k^2}\Big|_{k=k_0} \cdot (k-k_0)^2 + O((k-k_0)^3) \ . \tag{76}$$

Keeping only the lowest orders we obtain

$$\Psi_0(x) = e^{i\phi(k_0)} \int \frac{dk}{2\pi}\, |g(k)| e^{i\left(\frac{\partial\phi}{\partial k}\Big|_{k=k_0} \cdot (k-k_0) + O((k-k_0)^2)\right)} \ . \tag{77}$$

The solution is, thus, a plane wave $e^{i\phi(k_0)} = e^{i(k_0 x - \alpha(k_0))}$ multiplied by an envelope. We employ now the stationary phase approximation. This means the integral in the envelope will be the largest if all the exponents interfere constructively. This happens if

$$\frac{\partial \phi(k)}{\partial k}\Big|_{k=k_0} = 0 \ . \tag{78}$$

This is the stationary phase condition. Substituting $\phi(k) = kx - \alpha(k)$ we see that the stationary phase condition gives

$$x = x_0 \equiv \frac{\partial \alpha(k)}{\partial k}\Big|_{k=k_0} \ . \tag{79}$$

Thus, the wave packet will be centered around $x = x_0$. Substituting this into (77) we obtain

$$\Psi_0(x) = e^{i(k_0 x - \alpha(k_0))} \int \frac{dk}{2\pi} |g(k)| e^{i((k-k_0))(x-x_0)+\ldots)} \ . \tag{80}$$

Now we can estimate the width of the envelope function. Since $k - k_0$ can at most be of order Δk, the destructive interference of different plane waves will start once $|x - x_0|\Delta k \geq 2\pi$. Thus, we estimate the width of the envelope as

$$\Delta x \sim \frac{2\pi}{\Delta k} \ . \tag{81}$$

This is, actually, nothing but the uncertainty relation. The exact inequality will be derived later.

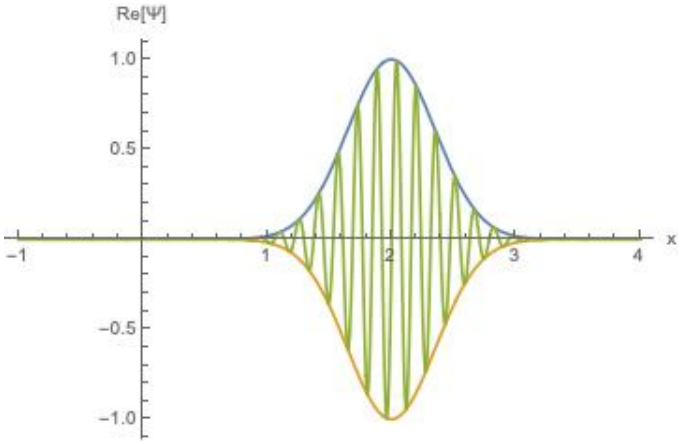

FIG. 1: Wave packet

Now, we consider the evolution in time:

$$\Psi(x,t) = \int \frac{dk}{2\pi} |g(k)| e^{i(-\alpha(k)+kx-\omega(k)t)} = \int \frac{dk}{2\pi} |g(k)| e^{i\phi(k,t)} \ , \tag{82}$$

where we have defined

$$\phi(k,t) = kx - \alpha(k) - \omega(k)t \ . \tag{83}$$

We expand again around k_0:

$$\phi(k,t) \approx \phi(k_0,t) + \frac{\partial\phi}{\partial k}\Big|_{k=k_0} \cdot (k-k_0) + \frac{1}{2}\frac{\partial^2\phi}{\partial k^2}\Big|_{k=k_0} \cdot (k-k_0)^2 + O((k-k_0)^3) \tag{84}$$

We obtain

$$\phi(k_0,t) = k_0 x - \omega(k_0)t - \alpha(k_0) \ , \tag{85}$$

$$\frac{\partial\phi(k)}{\partial k}\Big|_{k=k_0} = -\frac{\partial\alpha(k)}{\partial k}\Big|_{k=k_0} + x - t\frac{\partial\omega(k)}{\partial k} = x - x_0 - t\frac{\partial\omega(k)}{\partial k}\Big|_{k=k_0} \ , \tag{86}$$

$$\frac{\partial^2\phi(k)}{\partial k^2}\Big|_{k=k_0} = -\frac{\partial^2\alpha(k)}{\partial k^2}\Big|_{k=k_0} - t\frac{\partial^2\omega(k)}{\partial k^2}\Big|_{k=k_0} \ . \tag{87}$$

The stationary phase condition

$$\frac{\partial\phi(k)}{\partial k}\Big|_{k=k_0} = 0 \tag{88}$$

gives now

$$x = t\,\frac{\partial\omega(k)}{\partial k}\Big|_{k=k_0} + x_0 \ , \tag{89}$$

We introduce, thus, the group velocity

$$v_g \equiv \frac{\partial\omega(k)}{\partial k}\Big|_{k=k_0} \ , \tag{90}$$

so that the wave packet is peaked around $x = x_0 + v_g t$.

The solution we obtained thus far reads

$$\Psi(x,t) \approx e^{i(k_0 x - \omega(k_0)t - \alpha(k_0))} \int \frac{dk}{2\pi}|g(k)|e^{i(x-x_0-v_g t)(k-k_0)} \ . \tag{91}$$

The plane wave in front of the envelope "runs" with the so called phase velocity, $v_{\rm ph} \equiv \omega(k_0)/k_0$, whereas the envelope moves with the group velocity v_g.

Unfortunately (91) is not the full truth. We have to take into account the second order terms in the expansion of $\phi(k)$ around k_0. This gives then

$$\Psi(x,t) \approx e^{i(k_0 x - \omega(k_0)t - \alpha(k_0))} \int \frac{dk}{2\pi}|g(k)|e^{i(x-x_0-v_g t)(k-k_0)}\, e^{-\frac{i}{2}(\alpha''(k_0)+\omega''(k_0)t)(k-k_0)^2} \ . \tag{92}$$

The term (phase) $\sim \omega''(k_0)t(k-k_0)^2$ "works" agains the interference argument applied above. Once $|\omega''(k_0)t(k-k_0)^2|$ becomes of order 2π the strong oscillations suppress the contributions of such values of k. Effectively then Δk becomes smaller and Δx becomes

larger. The wave packet widens. This is called dispersion. At large t one can estimate the effective width in the k-space as $\Delta k_{\text{eff}} \sim \sqrt{\frac{2\pi}{\omega''(k_0)t}}$. Then, the width of the wave packet should scale as $\Delta x \sim 2\pi/\Delta k_{\text{eff}} \sim \sqrt{2\pi\omega''(k_0)t} \sim \sqrt{2\pi\hbar t/m}$. Of course this behavior would be be only relevant, once $\sqrt{2\pi\omega''(k_0)t}$ has reached the initial width of the wave packet.

IV. BASIC PRINCIPLES OF QUANTUM MECHANICS

A. Hilbert space

Whereas a state of a classical system is a point is the phase space (for a single particle $(\mathbf{r}, \mathbf{p})$), in quantum mechanics a state of a system is described by a wave function, which is a vector in a Hilbert space.

Let us start with the concept of a **vector space**. A vector space is a set of objects (vectors). The vectors can be added to each other. A sum of two vectors is a vector again. If we have two vectors $\mathbf{v}$ and $\mathbf{u}$, then $\mathbf{g} = \mathbf{v} + \mathbf{u}$ is a vector again. This operation is commutative $\mathbf{v} + \mathbf{u} = \mathbf{u} + \mathbf{v}$. In addition vectors can be multiplied by numbers to produce other vectors. If one uses only real numbers this vector space is called a a real vector space. In complex vector space one employs complex numbers[1]. In quantum mechanics we use complex vector spaces. Thus, the most general vector we can construct out of two vectors $\mathbf{v_1}$ and $\mathbf{v_2}$ is $\mathbf{g} = c_1\mathbf{v_1} + c_2\mathbf{v_2}$, where c_1 and c_2 are complex coefficients[2]. Every vector space has a basis (it is not unique). A basis is a set of linearly independent vectors $\mathbf{b_n}$, such that any vector can be represented as $\mathbf{v} = \sum_n c_n \mathbf{b_n}$. The number of vectors in the basis is called dimensionality of the vector space.

In addition to well known d-dimensional vector spaces there are vector spaces of infinite dimensionality. The most relevant for us would be, e.g., the space of all complex functions $\psi(\mathbf{r})$. Assume $\psi_1(\mathbf{r})$ and $\psi_2(\mathbf{r})$ are two complex functions. Clearly, $c_1\psi_1(\mathbf{r}) + c_2\psi_2(\mathbf{r})$ is also a complex function.

Hilbert space is a vector space with a scalar product. The scalar product of two vectors is denoted $(\mathbf{u}, \mathbf{v})$, or in the Dirac notation $\langle \mathbf{u}|\mathbf{v}\rangle$. It has the following properties

1) $(\mathbf{u}, \mathbf{v}) = (\mathbf{v}, \mathbf{u})^*$,

2) $(\mathbf{u}, c_1\mathbf{v_1} + c_2\mathbf{v_2}) = c_1(\mathbf{u}, \mathbf{v_1}) + c_2(\mathbf{u}, \mathbf{v_2})$,

3) $(c_1\mathbf{u_1} + c_2\mathbf{u_2}, \mathbf{v}) = c_1^*(\mathbf{u_1}, \mathbf{v}) + c_2^*(\mathbf{u_2}, \mathbf{v})$,

4) $(\mathbf{v},\mathbf{v}) \geq 0$, if $(\mathbf{v},\mathbf{v}) = 0$ then $\mathbf{v} = 0$,

5) $|(\mathbf{u},\mathbf{v})|^2 \leq (\mathbf{u},\mathbf{u}) \cdot (\mathbf{v},\mathbf{v})$ (Schwarz inequality).

In order to make a Hilbert space out of our complex functions $\psi(\mathbf{r})$ we have to restrict them to the space of quadratically integrable functions, i.e., such that

$$\int d^3r |\psi(\mathbf{r})|^2 < \infty \ . \tag{93}$$

This space is called L^2. The scalar product of two vectors in L^2 is then defined as

$$(\phi,\psi) = \langle\phi|\psi\rangle = \int d^3r \, \phi^*(\mathbf{r})\psi(\mathbf{r}) \ . \tag{94}$$

The norm of the wave function is then given by

$$||\psi|| = \langle\psi|\psi\rangle = \int d^3r \, \psi^*(\mathbf{r})\psi(\mathbf{r}) \ . \tag{95}$$

Every state in L^2 can be normalized. Indeed, defining

$$\psi'(\mathbf{r}) = \frac{\psi(\mathbf{r})}{\sqrt{\langle\psi|\psi\rangle}} \ , \tag{96}$$

we trivially obtain

$$\langle\psi'|\psi'\rangle = 1 \ . \tag{97}$$

B. Dirac notation, dual space

The scalar product allows to define a dual space. For a vector space V the dual space is called V^*. This is a space of all linear maps $V \to \mathbb{C}$. Namely every state $\mathbf{v}$ defines a linear map $\phi_{\mathbf{v}}(\mathbf{u}) = \langle\mathbf{v}|\mathbf{u}\rangle$ in which an arbitrary vector $\mathbf{u}$ is mapped onto the complex number $\langle\mathbf{v}|\mathbf{u}\rangle$. One therefore uses $|v\rangle$ for vectors $\mathbf{v}$ and calls this a "ket" state. The elements of the dual space are denoted as $\langle v|$ and are called the "bra" states. This is the Dirac notation commonly used in quantum mechanics.

C. Orthonormal basis, completeness

In a Hilbert space one can use a special kind of basis, namely an orthonormal basis. The basis states (vectors) $\mathbf{b_n}$ satisfy

$$\langle b_n|b_m\rangle = \delta_{n,m} \ . \tag{98}$$

Every state can be presented as

$$|v\rangle = \sum_n c_n |b_n\rangle \ . \tag{99}$$

The coefficients c_n are unique and can be found by projecting on the state $|b_m\rangle$, i.e., by scalar multiplying (99) from the left by $\langle b_m|$. This gives

$$\langle b_m|v\rangle = \sum_n c_n \langle b_m|b_n\rangle = c_m \ . \tag{100}$$

We have obtained $c_m = \langle b_m|v\rangle$ and

$$|v\rangle = \sum_n c_n |b_n\rangle = \sum_n \langle b_n|v\rangle |b_n\rangle \ . \tag{101}$$

Let us rewrite this relation in a slightly different way

$$|v\rangle = \sum_n c_n |b_n\rangle = \sum_n |b_n\rangle \langle b_n|v\rangle \ . \tag{102}$$

Now we can interpret the combination $P_n = |b_n\rangle \langle b_n|$ as a linear operator. Namely the operator P_n acts on an arbitrary state $|v\rangle$ as

$$P_n |v\rangle = |b_n\rangle \langle b_n|v\rangle = \langle b_n|v\rangle |b_n\rangle \ . \tag{103}$$

The operator P_n is called a projector onto the state $|b_n\rangle$. The relation $|v\rangle = \sum_n |b_n\rangle \langle b_n|v\rangle$ can be now rewritten as

$$|v\rangle = \sum_n |b_n\rangle \langle b_n|v\rangle = \sum_n P_n |v\rangle \ . \tag{104}$$

Since the basis is complete, i.e., every state $|v\rangle$ can be expanded, we conclude that

$$\sum_n P_n = \sum_n |b_n\rangle \langle b_n| = \hat{1} \ , \tag{105}$$

where $\hat{1}$ is the unity operator. This relation is called the completeness relation.

D. Linear operators, matrix representation

A linear operator $\hat{A}$ is a mapping from the Hilbert space to itself $|u\rangle = \hat{A}|v\rangle$, such that $\hat{A}(c_1|v_1\rangle + c_2|v_2\rangle) = c_1\hat{A}|v_1\rangle + c_2\hat{A}|v_2\rangle$.

Consider a linear operator $\hat{A}$. We have the vector $|v\rangle$ and the vector $|u\rangle$, which is the result of $\hat{A}$ acting on $|v\rangle$, i.e. $|u\rangle = \hat{A}|v\rangle$. We can expand the vectors $|v\rangle$ and $|u\rangle$ in the basis $|b_n\rangle$:

$$|v\rangle = \sum_n v_n |b_n\rangle \ , \tag{106}$$

$$|u\rangle = \sum_m u_m |b_m\rangle \ . \tag{107}$$

Then

$$|u\rangle = \sum_m u_m |b_m\rangle = \hat{A} |v\rangle = \hat{A} \sum_n v_n |b_n\rangle \ . \tag{108}$$

We project onto $\langle b_k|$:

$$\langle b_k|u\rangle = u_k = \sum_n v_n \langle b_k| \hat{A} |b_n\rangle \ . \tag{109}$$

We can rewrite this as

$$u_k = \sum_n A_{k,n} v_n \ , \tag{110}$$

where $A_{k,n} = \langle b_k| \hat{A} |b_n\rangle$ is the matrix of matrix elements of $\hat{A}$. This gives the matrix representation of the operator $\hat{A}$ in the basis $|b_n\rangle$.

E. Completeness relation in L^2

For simplicity we consider one dimension (1D). Thus the wave functions are $|\psi\rangle = \psi(x)$. The scalar product reads

$$\langle \psi_2|\psi_1\rangle = \int dx \, \psi_2^*(x)\psi_1(x) \ . \tag{111}$$

What is the unity operator is L^2? We can think of $\psi(x)$ as a complex vector with x being a continuous index. Then every operator $\hat{A}$ in L^2 can be represented as an infinite dimensional matrix $A(x, x')$. Namely we can write $|\phi\rangle = \hat{A} |\psi\rangle$ as

$$\phi(x) = \int dx' A(x, x')\psi(x') \ . \tag{112}$$

The unity operator is clearly represented by the matrix $\delta(x - x')$. Indeed

$$\psi(x) = \int dx' \, \delta(x - x')\psi(x') \ . \tag{113}$$

Assume we have a complete orthonormal basis $|\psi_n\rangle = \psi_n(x)$ in L^2. The dimensionality is of course infinite, but index n can be regarded here as a discrete one running to infinity. The orthonormality means

$$\langle \psi_m|\psi_n\rangle = \int dx \, \psi_m^*(x)\psi_n(x) = \delta_{m,n} \ . \tag{114}$$

The completeness relation then reads

$$\sum_n \psi_n(x)\psi_n^*(x') = \delta(x - x') \ . \tag{115}$$

Let us check once again

$$|\phi\rangle \;=\; \phi(x) = \int dx'\,\delta(x-x')\phi(x') = \sum_n \int dx'\,\psi_n(x)\psi_n^*(x')\phi(x')$$
$$= \sum_n \psi_n(x) \int dx'\,\psi_n^*(x')\phi(x') = \sum_n c_n\psi_n(x) = \sum_n c_n\,|\psi_n\rangle \;\; . \tag{116}$$

Here $c_n = \langle\psi_n|\phi\rangle = \int dx'\,\psi_n^*(x')\phi(x')$.

F. Hermitian operators, their eigenvectors and eigenvalues

For every operator $\hat{A}$ one can define its Hermitian conjugated $\hat{A}^\dagger$ operator. This is defined by the following relation

$$\left\langle u|\hat{A}v\right\rangle = \left\langle \hat{A}^\dagger u|v\right\rangle \;\; . \tag{117}$$

for any pair of states $|u\rangle$ and $|v\rangle$. The operator $|A\rangle$ is called Hermitian if $\hat{A}^\dagger = A$ [3]. There are two important facts about Hermitian operators.

1) Eigenvalues of Hermitian operators are real. Indeed, assume we have an eigenvector $|v\rangle$ with an eigenvalue a, i.e., $\hat{A}\,|v\rangle = a\,|v\rangle$. Multiplying by $\langle v|$ we get

$$\left\langle v|\hat{A}v\right\rangle = a\,\langle v|v\rangle \;\; . \tag{118}$$

On the other hand

$$\left\langle v|\hat{A}v\right\rangle = \left\langle \hat{A}v|v\right\rangle = \langle av|v\rangle = a^*\,\langle v|v\rangle \;\; . \tag{119}$$

Comparing we conclude that $a = a^*$, i.e., it is real.

2) Two eigenvectors with non-equal eigenvalues are orthogonal. Indeed, assume $|v_1\rangle$ and $|v_2\rangle$ are the eigenvectors. We have

$$\hat{A}\,|v_1\rangle = a_1\,|v_1\rangle \quad , \quad \hat{A}\,|v_2\rangle = a_2\,|v_2\rangle \;\; . \tag{120}$$

We multiply the first equation by $\langle v_2|$ from the left. This gives

$$\left\langle v_2|\hat{A}v_1\right\rangle = a_1\,\langle v_2|v_1\rangle \;\; . \tag{121}$$

On the other hand

$$\left\langle v_2|\hat{A}v_1\right\rangle = \left\langle \hat{A}v_2|v_1\right\rangle = a_2\;\langle v_2|v_1\rangle \;\; . \tag{122}$$

(remember a_1 and a_2 are real). Combining we obtain

$$(a_1 - a_2)\,\langle v_2|v_1\rangle = 0 \;. \tag{123}$$

Thus, if $a_1 \neq a_2$, we have $\langle v_2|v_1\rangle = 0$.

Let us prove that the momentum operator is Hermitian.

$$\langle\phi|\hat{p}\,\psi\rangle = \int dx\phi^*(x)\left[-i\hbar\partial_x\psi(x)\right] \ . \tag{124}$$

In L^2 the wave functions must vanish at $x \to \pm\infty$. Thus, we can use integration by parts without the boundary terms. We obtain

$$\begin{aligned}\langle\phi|\hat{p}\psi\rangle &= \int dx\phi^*(x)\left[-i\hbar\partial_x\psi(x)\right] = \int dx\left[i\hbar\partial_x\phi^*(x)\right]\psi(x) \\ &= \int dx\left[-i\hbar\partial_x\phi(x)\right]^*\psi(x) = \langle\hat{p}\,\phi|\psi\rangle \ .\end{aligned} \tag{125}$$

Assume we have two Hermitian operators. Is their product Hermitian? It is easy to check that for arbitrary $\hat{A}$ and $\hat{B}$ (not necessarily Hermitian)

$$(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger \ . \tag{126}$$

Indeed

$$\left\langle\phi|\hat{A}\hat{B}\psi\right\rangle = \left\langle\hat{A}^\dagger\phi|\hat{B}\psi\right\rangle = \left\langle\hat{B}^\dagger\hat{A}^\dagger\phi|\psi\right\rangle \ . \tag{127}$$

Thus, if $\hat{A}$ and $\hat{B}$ are Hermitian, we obtain

$$(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger = \hat{B}\hat{A} \ . \tag{128}$$

Thus, $\hat{A}\hat{B}$ is Hermitian only if $\hat{A}\hat{B} = \hat{B}\hat{A}$, i.e, if they commute. For example $\hat{x}\,\hat{p}$ is not Hermitian.

We see, thus, that the kinetic energy operator $\hat{\mathbf{p}}^2/2m$ is Hermitian. Also the coordinate operator and, thus, the potential energy operator are Hermitian. We conclude that the Hamiltonian operator

$$H = \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{\mathbf{r}}) \tag{129}$$

is Hermitian.

G. Hermitian operators have a complete, orthonormal basis of eigenstates

See[4]. We have already proven that two eigenstates of a Hermitian operator $\hat{A}$

$$\hat{A}\,|v_1\rangle = a_1\,|v_1\rangle \quad , \quad \hat{A}\,|v_2\rangle = a_2\,|v_2\rangle \ . \tag{130}$$

with $a_1 \neq a_2$ are orthogonal. What happens if $\hat{A}$ has a degenerate subspace, i.e., there are several eigenvectors with the same eigenvalue. These must not be orthogonal. We can, however, find orthogonal combinations of these eigenvectors.

Assume we have N eigenvectors $|v_n\rangle$, where $n \in [1, \ldots, N]$, such that $a_1 = a_2 = \ldots = a_N \equiv a$. Any superposition of $|v_n\rangle$ would be again an eigenvector of $\hat{A}$ with the eigenvalue a. We construct the following matrix

$$C_{n,m} = \langle v_n | v_m \rangle \ . \tag{131}$$

This matrix is Hermitian, $C_{n,m} = C^*_{m,n}$. From linear algebra we know that there exists a unitary matrix U, such that $U^\dagger C U = C^D$, where C^D is diagonal. Then, the states

$$|\phi_k\rangle = \sum_n |v_n\rangle \, U_{n,k} \tag{132}$$

are orthogonal. Indeed,

$$\langle \phi_p | \phi_k \rangle = \sum_{n,m} U^*_{m,p} \, \langle v_m | v_n \rangle \, U_{n,k} = (U^\dagger C U)_{p,k} = C^D_{p,k} \propto \delta_{p,k} \ . \tag{133}$$

What remains is just to normalize the states $|\phi_k\rangle$ and we obtain N orthonormal degenerate eigenstates of $\hat{A}$ with the eigenvalue a. Thus, $\hat{A}$ has a complete orthonormal basis.

H. Uncertainty relations

Consider two Hermitian operators $\hat{A}$ and $\hat{B}$. Let's take an arbitrary state $|\psi\rangle$. The variance of $\hat{A}$ in the state $|\psi\rangle$ is defined

$$\sigma_A^2 = \left\langle \left[\hat{A} - \langle \hat{A} \rangle \right]^2 \right\rangle = \langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2 \ . \tag{134}$$

Here the averaging is in state $|\psi\rangle$, i.e., $\langle \ldots \rangle = \langle \psi | \ldots | \psi \rangle$.

We obtain

$$\sigma_A^2 = \left\langle \psi \right| \left[\hat{A} - \langle \hat{A} \rangle \right]^2 \left| \psi \right\rangle = \left\langle \left[\hat{A} - \langle \hat{A} \rangle \right] \psi \right| \left[\hat{A} - \langle \hat{A} \rangle \right] \left| \psi \right\rangle = \langle f | f \rangle \ , \tag{135}$$

where

$$|f\rangle = \left[\hat{A} - \langle \hat{A} \rangle \right] |\psi\rangle \ . \tag{136}$$

Analogously

$$\sigma_B^2 = \langle g | g \rangle \quad , \quad |g\rangle = \left[\hat{B} - \langle \hat{B} \rangle \right] |\psi\rangle \ . \tag{137}$$

Next we use the Schwarz's inequality:

$$\sigma_A^2 \sigma_B^2 = \langle f|f\rangle \langle g|g\rangle \geq |\langle f|g\rangle|^2 \ . \tag{138}$$

We calculate $z \equiv \langle f|g\rangle$

$$z = \langle f|g\rangle = \langle\psi| \left[\hat{A} - \langle\hat{A}\rangle\right] \left[\hat{B} - \langle\hat{B}\rangle\right] |\psi\rangle = \langle\hat{A}\hat{B}\rangle - \langle\hat{A}\rangle\langle\hat{B}\rangle \ . \tag{139}$$

Analogously

$$z^* = \langle g|f\rangle = \langle\hat{B}\hat{A}\rangle - \langle\hat{A}\rangle\langle\hat{B}\rangle \ . \tag{140}$$

Thus

$$z - z^* = 2i\mathrm{Im}[z] = \langle[\hat{A}, \hat{B}]\rangle \ . \tag{141}$$

Since

$$|\langle f|g\rangle|^2 = |z|^2 = (\mathrm{Re}\,[z])^2 + (\mathrm{Im}\,[z])^2 \geq (\mathrm{Im}\,[z])^2 \ = \frac{1}{4}\left|\left\langle[\hat{A}, \hat{B}]\right\rangle\right|^2, \tag{142}$$

we, finally, obtain

$$\sigma_A \sigma_B \geq \frac{1}{2}\left|\left\langle[\hat{A}, \hat{B}]\right\rangle\right| \ . \tag{143}$$

In particular, for $A = \hat{x}$ and $B = \hat{p}$, using $[\hat{x}, \hat{p}] = i\hbar$, we obtain

$$\sigma_x \sigma_p = \Delta x \Delta p \geq \frac{\hbar}{2} \ . \tag{144}$$

I. Eigenstates of the momentum operator, continuum

The eigenstates of the momentum operator can be formally defined as

$$|p\rangle = \psi_p(x) = e^{ipx/\hbar} \ . \tag{145}$$

These states are not normalizable and thus do not belong to L^2. Yet, as these are the eigenstates of a very important operator $\hat{p} = -i\hbar\partial_x$, one profits very much from using them. Then we need the orthogonality relation for such states. This is given by

$$\int dx\, \psi^*_{p_1}(x)\psi_{p_2}(x) = 2\pi\hbar\, \delta(p_1 - p_2) \ . \tag{146}$$

Also the completeness relation can be formulated

$$\int \frac{dp}{2\pi\hbar}\, \psi_p(x)\psi^*_p(x') = \delta(x - x') \ . \tag{147}$$

Any arbitrary wave function in L^2 can expanded in the basis of states $|p\rangle$ as

$$\psi(x) = \int \frac{dp}{2\pi\hbar}\, \phi(p)\, |p\rangle = \int \frac{dp}{2\pi\hbar}\, \phi(p) e^{ipx/\hbar} \ . \tag{148}$$

Comparing with the discrete expansions of the type $\psi(x) = \sum_m c_m \psi_m(x)$ we see that the following equivalence has to be declared

$$\sum_m \to \int \frac{dp}{2\pi\hbar} \quad , \quad c_m \to \phi(p) \ . \tag{149}$$

The function $\phi(p)$ can be thought of as the wave function in the p-representation.

J. Eigenstates of the coordinate operator

It is also possible to find the eigenstates of the coordinate operator. These are

$$|\xi\rangle = \delta(x - \xi) \ . \tag{150}$$

Indeed

$$\hat{x}\, |\xi\rangle = x\delta(x-\xi) = \xi\delta(x-\xi) = \xi\, |\xi\rangle \ . \tag{151}$$

This states are also not normalizable, but satisfy the following orthogonality relations

$$\langle \xi_2 | \xi_1 \rangle = \int dx\, \delta(x - \xi_2)\delta(x - \xi_1) = \delta(\xi_1 - \xi_2) \ . \tag{152}$$

The completeness relation is

$$\int d\xi \delta(x - \xi)\delta(x' - \xi) = \delta(x - x') \ . \tag{153}$$

Any wave function $\psi(x)$ can be trivially expanded in the basis $|\xi\rangle$:

$$\psi(x) = \int d\xi \psi(\xi)\, |\xi\rangle = \int d\xi \psi(\xi)\delta(x - \xi) = \psi(x) \ . \tag{154}$$

Thus, the function $\psi(x)$ can also be seen as a set of coefficients:

$$\psi(x) = \langle x | \psi \rangle \ . \tag{155}$$

K. Postulates of quantum mechanics (for a single particle)

1) The state of the system is described by a wave function $|\psi\rangle = \psi(\mathbf{r})$, which belongs to the Hilbert space of square integrable functions L^2.

2) The physical observables correspond to Hermitian operators. E.g., coordinate $\hat{x}$, momentum $\hat{p}$, but also $\hat{x}^2$ etc.

3) The expectation value of an observable $\hat{A}$ in a state $|\psi\rangle$ is given by

$$\langle \hat{A} \rangle = \left\langle \psi | \hat{A} \psi \right\rangle \ . \tag{156}$$

4) The state of the system evolves in time according the the Schrödinger equation

$$i\hbar \partial_t |\psi\rangle = \hat{H} |\psi\rangle \ , \tag{157}$$

where $\hat{H}$ is the Hermitian operator called Hamiltonian:

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{\mathbf{r}}) \ . \tag{158}$$

Important consequence: the Hamiltonian, as any Hermitian operator, has a complete orthonormal basis of eigenstates:

$$\hat{H} |\phi_n\rangle = E_n |\phi_n\rangle \quad , \quad \langle \phi_m | \phi_n \rangle = \delta_{m,n} \quad , \quad \sum_n |\phi_n\rangle \langle \phi_n| = \hat{1} \ . \tag{159}$$

(Sometimes index n is continuous and the states $|\phi_n\rangle$ do not belong to L^2). At $t = 0$ any initial state $|\psi_0\rangle = |\psi(t=0)\rangle$ can be expanded in this basis

$$|\psi_0\rangle = \sum_n c_n |\phi_n\rangle \ , \tag{160}$$

where $c_n = \langle \phi_n | \psi_0 \rangle$. At time t the state evolves to

$$|\psi(t)\rangle = \sum_n c_n e^{-iE_n t/\hbar} |\phi_n\rangle \ . \tag{161}$$

5) Measurement postulate. Consider an observable $\hat{A}$. As a Hermitian operator it has an orthonormal complete basis of eigenstates

$$\hat{A} |n\rangle = a_n |n\rangle \quad , \quad \langle n | m \rangle = \delta_{n,m} \quad , \quad \sum_n |n\rangle \langle n| = \hat{1} \ . \tag{162}$$

Assume, the state of the system right before the measurement is $|\psi\rangle = \sum_n c_n |n\rangle$. A single (strong, projective) measurement of the observable $\hat{A}$ leads to a projection (collapse) of the

state into one of the eigenstates $|n\rangle$ whereas the measurement gives the (real) eigenvalue a_n as a result. This happens with probability $|c_n|^2$. This is one of the most controversial postulates, which lead to numerous discussions and controversies. The famous Stern-Gerlach experiment was a strong projective measurement. Most of the measurements performed in experiments are not of this type. Yet, nowadays, strong measurements are routinely performed in quantum bits (qubits).

V. ONE-DIMENSIONAL PROBLEMS

A. Harmonic oscillator (1D)

We follow Schwabl, Chapter 3.1. The Hamiltonian reads

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2\hat{x}^2}{2} \ . \tag{163}$$

The purpose is to find all possible eigenvectors and corresponding eigenvalues of the Hamiltonian, i.e., to solve $\hat{H}\,|\psi\rangle = E\,|\psi\rangle$. This equation, as a differential equation, reads

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{m\omega^2 x^2}{2}\right]\psi(x) = E\psi(x) \ . \tag{164}$$

It is convenient to introduce the following length scale:

$$x_0 \equiv \sqrt{\frac{\hbar}{m\omega}} \tag{165}$$

We define two non-Hermitian operators

$$\hat{a} = \frac{m\,\omega\hat{x} + i\hat{p}}{\sqrt{2m\hbar\omega}} = \frac{1}{\sqrt{2}}\left(\frac{\hat{x}}{x_0} + x_0\frac{\partial}{\partial x}\right) \ , \tag{166}$$

$$\hat{a}^\dagger = \frac{m\,\omega\hat{x} - i\hat{p}}{\sqrt{2m\hbar\omega}} = \frac{1}{\sqrt{2}}\left(\frac{\hat{x}}{x_0} - x_0\frac{\partial}{\partial x}\right) \ . \tag{167}$$

The commutation relation reads

$$[\hat{a}, \hat{a}^\dagger] = 1 \ . \tag{168}$$

The inverted relations are

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}\,(\hat{a} + \hat{a}^\dagger) = \frac{x_0}{\sqrt{2}}\,(\hat{a} + \hat{a}^\dagger) \ , \tag{169}$$

$$\hat{p} = -i\sqrt{\frac{\hbar m\omega}{2}}\,(\hat{a} - \hat{a}^\dagger) = -i\frac{\hbar}{\sqrt{2}\,x_0}\,(\hat{a} - \hat{a}^\dagger) \ . \tag{170}$$

The Hamiltonian can be then rewritten as

$$\hat{H} = \frac{\hbar\omega}{4}\left[(\hat{a}+\hat{a}^\dagger)^2 - (\hat{a}-\hat{a}^\dagger)^2\right] = \frac{\hbar\omega}{2}\left(\hat{a}^\dagger\hat{a} + \hat{a}\hat{a}^\dagger\right) = \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right) = \hbar\omega\left(\hat{n} + \frac{1}{2}\right) \ . \tag{171}$$

We define the (Hermitian) operator $\hat{n} = \hat{a}^\dagger\hat{a}$ (it is called the number operator or the occupation number operator) and try to find its eigenstates. Assume there is one with the eigenvalue ν:

$$\hat{n}\,|\nu\rangle = \nu\,|\nu\rangle \ . \tag{172}$$

Then

$$\nu\,\langle\nu|\nu\rangle = \left\langle\nu|\hat{a}^\dagger\hat{a}\nu\right\rangle = \langle\hat{a}\nu|\hat{a}\nu\rangle \geq 0 \ . \tag{173}$$

Thus $\nu \geq 0$. We can try to find the eigenstate with $\nu = 0$. From (173) with $\nu = 0$ it follows that

$$\hat{a}\,|0\rangle = 0 \ . \tag{174}$$

Assume the state $|0\rangle$ corresponds to the wave function $\psi_0(x)$. Then $\hat{a}\,|0\rangle = 0$ can be written as a differential equation:

$$\left(\frac{d}{dx} + \frac{x}{x_0^2}\right)\psi_0(x) = 0 \ . \tag{175}$$

The solution is a Gaussian

$$\psi_0(x) = \mathcal{N}\exp\left[-\frac{x^2}{2x_0^2}\right] \ , \tag{176}$$

where $\mathcal{N}$ is the normalization constant. To determine $\mathcal{N}$ we calculate the norm

$$\langle 0|0\rangle = \int dx\,|\psi_0|^2 = \mathcal{N}^2\int dx\exp\left[-\frac{x^2}{x_0^2}\right] = \mathcal{N}^2\sqrt{\pi}\,x_0 = 1 \ . \tag{177}$$

This gives

$$\mathcal{N} = \pi^{-\frac{1}{4}}\,x_0^{-\frac{1}{2}} \ . \tag{178}$$

Thus we have found the eigenstate

$$|0\rangle = \psi_0(x) = \pi^{-\frac{1}{4}}\,x_0^{-\frac{1}{2}}\,\exp\left[-\frac{x^2}{2x_0^2}\right] \tag{179}$$

with the lowest possible eigen-energy:

$$\hat{H}\,|0\rangle = \frac{\hbar\omega}{2}\,|0\rangle \ . \tag{180}$$

To find other eigenstates we notice two important commutators:

$$[\hat{n},\hat{a}^\dagger] = \hat{a}^\dagger \quad , \quad [\hat{n},\hat{a}] = -\hat{a} \ . \tag{181}$$

Indeed

$$[\hat{n}, \hat{a}^\dagger] = \hat{n}\,\hat{a}^\dagger - \hat{a}^\dagger\,\hat{n} = \hat{a}^\dagger\,\hat{a}\,\hat{a}^\dagger - \hat{a}^\dagger\,\hat{a}^\dagger\,\hat{a} = \hat{a}^\dagger\,(\hat{a}^\dagger\,\hat{a} + 1) - \hat{a}^\dagger\,\hat{a}^\dagger\,\hat{a} = \hat{a}^\dagger\ . \tag{182}$$

analogously

$$[\hat{n}, \hat{a}] = \hat{n}\,\hat{a} - \hat{a}\,\hat{n} = \hat{a}^\dagger\,\hat{a}\,\hat{a} - \hat{a}\,\hat{a}^\dagger\,\hat{a} = \hat{a}^\dagger\,\hat{a}\,\hat{a} - (\hat{a}^\dagger\,\hat{a} + 1)\,\hat{a} = -\hat{a}\ . \tag{183}$$

1. Creation operator

Assume we have an eigenstate of $\hat{n}$ with the eigenvalue ν, i.e., $\hat{n}\,|\nu\rangle = \nu\,|\nu\rangle$ and it is normalized, i.e. $\langle\nu|\nu\rangle = 1$. Then $|\varphi\rangle \equiv \hat{a}^\dagger\,|\nu\rangle$ is an eigenstate of $\hat{n}$ with the eigenvalue $\nu + 1$. Indeed

$$\hat{n}\ |\varphi\rangle = \hat{n}\hat{a}^\dagger\,|\nu\rangle = (\hat{a}^\dagger\hat{n} + \hat{a}^\dagger)\,|\nu\rangle = (\nu + 1)\hat{a}^\dagger\,|\nu\rangle = (\nu + 1)\ |\varphi\rangle\ . \tag{184}$$

The state $|\varphi\rangle$ is, however, not normalized. Indeed

$$\langle\varphi|\varphi\rangle = \left\langle \hat{a}^\dagger\nu|\hat{a}^\dagger\nu\right\rangle = \left\langle\hat{\nu}|\hat{a}\hat{a}^\dagger\nu\right\rangle = \langle\hat{\nu}|(\hat{n} + 1)\nu\rangle = (\nu + 1)\,\langle\nu|\nu\rangle = \nu + 1\ . \tag{185}$$

The normalized state is then

$$|\nu + 1\rangle = \frac{|\varphi\rangle}{\sqrt{\nu + 1}} = \frac{1}{\sqrt{\nu + 1}}\,\hat{a}^\dagger\,|\nu\rangle\ . \tag{186}$$

Finally

$$\hat{a}^\dagger\,|\nu\rangle = \sqrt{\nu + 1}\ |\nu + 1\rangle\ . \tag{187}$$

2. Annihilation operator

Analogously, we can proceed with the operator $\hat{a}$. We, first show that $|\varphi\rangle \equiv \hat{a}\,|\nu\rangle$ is the eigenvector of $\hat{n}$ with the eigenvalue $\nu - 1$:

$$\hat{n}\,|\varphi\rangle = \hat{n}\hat{a}\,|\nu\rangle = (\hat{a}\hat{n} - \hat{a})\,|\nu\rangle = (\nu - 1)\hat{a}\,|\nu\rangle = (\nu - 1)\ |\varphi\rangle\ . \tag{188}$$

Next, we calculate the norm of $|\varphi\rangle$ assuming $|\nu\rangle$ is normalized:

$$\langle\varphi|\varphi\rangle = \langle\hat{a}\nu|\hat{a}\nu\rangle = \left\langle\hat{\nu}|\hat{a}^\dagger\hat{a}\nu\right\rangle = \langle\hat{\nu}|\hat{n}\nu\rangle = \nu\,\langle\nu|\nu\rangle = \nu\ . \tag{189}$$

The normalized state is then given by

$$|\nu - 1\rangle = \frac{1}{\sqrt{\nu}}\ |\varphi\rangle = \frac{1}{\sqrt{\nu}}\,\hat{a}\,|\nu\rangle\ . \tag{190}$$

and

$$\hat{a}\,|\nu\rangle = \sqrt{\nu}\ |\nu - 1\rangle\ . \tag{191}$$

3. Ladder of eigenstates

We constructed explicitly the state $|0\rangle$ with $\nu = 0$. With help of the creation operator we can now construct the states with $\nu = n$, where n are all non-negative integers:

$$|n\rangle = \frac{(\hat{a}^\dagger)^n}{\sqrt{n!}} |0\rangle \ . \tag{192}$$

The annihilation operator makes $|n-1\rangle$ out of $|n\rangle$. Indeed

$$\hat{a}\,|n\rangle = \frac{\hat{a}(\hat{a}^\dagger)^n}{\sqrt{n!}}\,|0\rangle = \frac{(\hat{a}\hat{a}^\dagger)(\hat{a}^\dagger)^{n-1}}{\sqrt{n!}}\,|0\rangle = \frac{(\hat{n}+1)}{\sqrt{n}}\,|n-1\rangle = \sqrt{n}\,|n\rangle \ . \tag{193}$$

We see that with the help of the operators $\hat{a}$ and $\hat{a}^\dagger$ we can "go up and down" within the ladder of states $|n\rangle$. These are the eigenstates of the Hamiltonian

$$\hat{H}\,|n\rangle = E_n\,|n\rangle \ , \tag{194}$$

where

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \ . \tag{195}$$

4. Absence of other eigenstates

Assume there exists an eigenstate of $\hat{n}$ with a non-integer positive eigenvalue $\nu = n + \alpha$, where $0 < \alpha < 1$. Then acting $n+1$ times with the annihilation operator we would be able to construct a normalized eigenstate with a negative eigenvalue $\alpha - 1$. This, however, contradicts (173). See Schwabl, Chapter 3.1 about not normalizable eigenstates of $\hat{n}$ with negative eigenvalues.

To conclude, we have found all the eigenvectors and the eigenvalues (energies) of the Hamiltonian $\hat{H}$. These are states $|n\rangle$, such that $n \in [0, 1, \ldots, \infty]$ and

$$\hat{H}\,|n\rangle = \hbar\omega\left(n + \frac{1}{2}\right)\,|n\rangle \ . \tag{196}$$

We have found the explicit wave function $\psi_0(x)$ (see Eq. 176) corresponding to the state $|0\rangle$. All the other states can be constructed using

$$\hat{a}^\dagger\,|n\rangle = \sqrt{n+1}\,\,|n+1\rangle \quad \text{and} \quad \hat{a}\,|n\rangle = \sqrt{n}\,\,|n-1\rangle \ . \tag{197}$$

5. Explicit wave functions $\psi_n(x)$ corresponding to $|n\rangle$

The algebraic theory constructed above allows also to construct explicitly all the wave functions $\psi_n(x)$. We have already found $\psi_0(x)$:

$$\psi_0(x) = (\sqrt{\pi}\, x_0)^{-\frac{1}{2}} \, \exp\left[-\frac{1}{2}\,\frac{x^2}{x_0^2}\right] \ . \tag{198}$$

Then

$$\psi_1(x) = \hat{a}^\dagger \psi_0(x) = \frac{1}{\sqrt{2}}\left(\frac{\hat{x}}{x_0} - x_0\frac{\partial}{\partial x}\right)\, \psi_0(x) = (2\sqrt{\pi}\, x_0)^{-\frac{1}{2}} \, \left[2\,\frac{x}{x_0}\right] \exp\left[-\frac{1}{2}\,\frac{x^2}{x_0^2}\right] \ . \tag{199}$$

For arbitrary n one can find

$$\psi_n(x) = \frac{(\hat{a}^\dagger)^n}{\sqrt{n!}}\, \psi_0(x) = (2^n n!)^{-\frac{1}{2}} \, \left(\frac{\hat{x}}{x_0} - x_0\frac{\partial}{\partial x}\right)^n \, \psi_0(x) \ . \tag{200}$$

One finds

$$\psi_n(x) = (2^n n!\sqrt{\pi}\, x_0)^{-\frac{1}{2}}\, H_n\left(\frac{x}{x_0}\right) \, \exp\left[-\frac{1}{2}\,\frac{x^2}{x_0^2}\right] \ , \tag{201}$$

where H_n are the so-called Hermit polynomials. For the Hermit polynomials there exists the following formula:

$$H_n(x) = (-1)^n \, e^{x^2} \, \frac{d^n}{dx^n}\, e^{-x^2} \ . \tag{202}$$

Here are several first Hermit polynomials:

$$H_0(x) = 1 \ , \tag{203}$$

$$H_1(x) = 2x \ , \tag{204}$$

$$H_2(x) = 4x^2 - 2 \ , \tag{205}$$

$$H_3(x) = 8x^3 - 12x \ . \tag{206}$$

6. Zero-point motion

The fact that the ground state energy $E_0 = (1/2)\hbar\omega$ is not zero is consistent with the fact that both $\hat{x}$ and $\hat{p}$ have non-zero variations in the ground state $|0\rangle$. Indeed, using

$$\hat{x} = \frac{x_0}{\sqrt{2}}\,(\hat{a} + \hat{a}^\dagger) \ , \tag{207}$$

we get

$$\hat{x}^2 = \frac{x_0^2}{2}\left(\hat{a}+\hat{a}^\dagger\right)\left(\hat{a}+\hat{a}^\dagger\right) = \frac{x_0^2}{2}\left(\hat{a}^2+\hat{a}\hat{a}^\dagger+\hat{a}^\dagger\hat{a}+(\hat{a}^\dagger)^2\right) \tag{208}$$

This gives

$$\langle 0|\,\hat{x}^2\,|0\rangle = \frac{x_0^2}{2}\,\langle 0|\,\hat{a}\hat{a}^\dagger\,|0\rangle = \frac{x_0^2}{2}\ . \tag{209}$$

The expectation value of $\hat{x}$ is zero:

$$\frac{x_0}{\sqrt{2}}\,\langle 0|\left(\hat{a}+\hat{a}^\dagger\right)|0\rangle = 0\ . \tag{210}$$

Thus,

$$\Delta x^2 = \langle\hat{x}^2\rangle - \langle\hat{x}\rangle^2 = \frac{x_0^2}{2}\ . \tag{211}$$

Analogously $\langle 0|\,\hat{p}\,|0\rangle = 0$ and $\langle 0|\,\hat{p}^2\,|0\rangle = \hbar^2/2x_0^2$. Thus

$$\Delta p^2 = \langle\hat{p}^2\rangle - \langle\hat{p}\rangle^2 = \frac{\hbar^2}{2x_0^2} \tag{212}$$

We see that in the ground state the uncertainty inequality becomes an equality:

$$\Delta x\Delta p = \frac{\hbar}{2}\ . \tag{213}$$

The energy stored in the kinetic part of the Hamiltonian

$$\langle 0|\,\frac{\hat{p}^2}{2m}\,|0\rangle = \frac{\hbar^2}{4mx_0^2} = \frac{\hbar\omega}{4}\ . \tag{214}$$

is equal to the energy stored in the potential part

$$\langle 0|\,\frac{m\omega^2\hat{x}^2}{2}\,|0\rangle = \frac{m\omega^2x_0^2}{4} = \frac{\hbar\omega}{4}\ . \tag{215}$$

Together they give the zero point energy $E_0 = (1/2)\hbar\omega$.

It is easy to generalize these result for the state $|n\rangle$. We get, using (208)

$$\langle n|\,\hat{x}^2\,|n\rangle = \frac{x_0^2}{2}\,(2n+1) \quad , \quad \langle n|\,\hat{x}\,|n\rangle = 0\ , \tag{216}$$

and similarly

$$\langle n|\,\hat{p}^2\,|n\rangle = \frac{\hbar^2}{2x_0^2}\,(2n+1) \quad , \quad \langle n|\,\hat{p}\,|n\rangle = 0\ . \tag{217}$$

7. Coherent states

We now look for states with $\langle x\rangle \neq 0$. For all eigenstates we have $\langle n|\,\hat{x}\,|n\rangle = 0$. Let us try to find states, which are eigenstates of the annihilation operator $\hat{a}$:

$$\hat{a}\,|\alpha\rangle = \alpha\,|\alpha\rangle \ . \tag{218}$$

The eigenvalue α may be a complex number, since $\hat{a}$ is not Hermitian. It is easy to expand $|\alpha\rangle$ in the basis of the eigenstates of the Hamiltonian $|n\rangle = \frac{1}{\sqrt{n!}}(\hat{a}^\dagger)^n\,|0\rangle$. Indeed

$$\langle n|\alpha\rangle = \frac{1}{\sqrt{n!}}\left\langle (\hat{a}^\dagger)^n 0|\alpha\right\rangle = \frac{1}{\sqrt{n!}}\,\langle 0|\hat{a}^n\alpha\rangle = \frac{\alpha^n}{\sqrt{n!}}\,\langle 0|\alpha\rangle \ . \tag{219}$$

The matrix element $C \equiv \langle 0|\alpha\rangle$ becomes a coefficient independent of n. Thus we conclude that

$$|\alpha\rangle = \sum_n |n\rangle\,\langle n|\alpha\rangle = C\sum_{n=0}^{\infty}\frac{\alpha^n}{\sqrt{n!}}\,|n\rangle \ . \tag{220}$$

The coefficient C well be chosen to be real and so that the state $|\alpha\rangle$ is normalized. Namely

$$\langle\alpha|\alpha\rangle = C^2\sum_{n=0}^{\infty}\frac{|\alpha|^{2n}}{n!} = C^2 e^{|\alpha|^2} = 1 \ . \tag{221}$$

We obtain

$$C = e^{-|\alpha|^2/2} \ , \tag{222}$$

$$|\alpha\rangle = e^{-|\alpha|^2/2}\sum_{n=0}^{\infty}\frac{\alpha^n}{\sqrt{n!}}\,|n\rangle \ . \tag{223}$$

Let us consider $|\psi_\alpha(t=0)\rangle = |\alpha\rangle$ to be the initial state at $t = 0$ and find its time evolution. We obtain

$$|\psi_\alpha(t)\rangle = e^{-|\alpha|^2/2}\sum_{n=0}^{\infty}\frac{\alpha^n}{\sqrt{n!}}\,e^{-iE_n t/\hbar}\,|n\rangle \ . \tag{224}$$

Using $E_n/\hbar = \omega(n+\frac{1}{2})$ we obtain

$$|\psi_\alpha(t)\rangle = e^{-|\alpha|^2/2}\,e^{-i\omega t/2}\sum_{n=0}^{\infty}\frac{\alpha^n e^{-in\omega t}}{\sqrt{n!}}\,|n\rangle = e^{-|\alpha|^2/2}\,e^{-i\omega t/2}\sum_{n=0}^{\infty}\frac{(\alpha e^{-i\omega t})^n}{\sqrt{n!}}\,|n\rangle \ . \tag{225}$$

We introduce now $\alpha(t) = \alpha e^{-i\omega t}$ and obtain

$$|\psi_\alpha(t)\rangle = e^{-i\omega t/2}\ |\alpha(t)\rangle \ . \tag{226}$$

We obtain a very simple time dependence. The state remains a coherent state with the complex number α replaced by $\alpha(t)$ and gets an extra phase factor $e^{-i\omega t/2}$.

Now we can calculate the expectation value of $\hat{x}$ in the state $|\psi_\alpha(t)\rangle$. Let us first start at $t = 0$. We obtain

$$\langle\psi_\alpha(0)|\,\hat{x}\,|\psi_\alpha(0)\rangle = \langle\alpha|\,\hat{x}\,|\alpha\rangle = \frac{x_0}{\sqrt{2}}\,\langle\alpha|\,(\hat{a}+\hat{a}^\dagger)\,|\alpha\rangle \ . \tag{227}$$

We use

$$\langle\alpha|\,\hat{a}\,|\alpha\rangle = \langle\alpha|\,\alpha\,|\alpha\rangle = \alpha \ , \tag{228}$$

$$\langle\alpha|\,\hat{a}^\dagger\,|\alpha\rangle = \langle\hat{a}\,\alpha|\alpha\rangle = \alpha^* \ . \tag{229}$$

Thus, we obtain

$$\langle\psi_\alpha(0)|\,\hat{x}\,|\psi_\alpha(0)\rangle = \frac{x_0}{\sqrt{2}}(\alpha+\alpha^*) \ . \tag{230}$$

Assuming the complex number α to have the form $\alpha = |\alpha|e^{i\delta}$ we get

$$\langle\psi_\alpha(0)|\,\hat{x}\,|\psi_\alpha(0)\rangle = \sqrt{2}\,x_0\,|\alpha|\cos(\delta) \ . \tag{231}$$

At $t > 0$ we just obtain

$$\langle\psi_\alpha(t)|\,\hat{x}\,|\psi_\alpha(t)\rangle = \frac{x_0}{\sqrt{2}}(\alpha(t)+\alpha^*(t)) = \sqrt{2}\,x_0\,|\alpha|\cos(\omega t-\delta) \ . \tag{232}$$

We, thus, finally obtain a quantity, which oscillates with frequency ω.

B. Piecewise constant potentials in one dimension

The stationary Schrödinger equation in 1D reads

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi = E\psi \ , \tag{233}$$

or

$$\frac{\partial^2\psi}{\partial x^2} = \frac{2m}{\hbar^2}\,(V(x)-E)\,\psi \ . \tag{234}$$

If $V(x)$ is a constant, the equation is simply solved by plane waves. That is the equation

$$\frac{\partial^2\psi}{\partial x^2} = \frac{2m}{\hbar^2}\,(V-E)\,\psi \tag{235}$$

is solved by

$$\psi(x) = e^{ikx} \ , \tag{236}$$

where

$$k^2 = \frac{2m}{\hbar^2}\,(E-V) \ . \tag{237}$$

For $E > V$ the solutions are

$$\hbar k = \pm\sqrt{2m(E-V)} \ . \tag{238}$$

So we have two plane waves. For $E < V$ the solutions are imaginary

$$\hbar k = \pm i\sqrt{2m(V-E)} \ . \tag{239}$$

Such solutions diverge at either $x \to \infty$ or $x \to -\infty$. However, they are still possible if $E < V$ only in part of the x-axis.

1. Boundary conditions

What if $V(x)$ is piecewise constant and jumps abruptly between? E.g., $V(x) = V_1$ for $x < x_0$ and $V(x) = V_2$ for $x > x_0$. We need a boundary condition for the wave function at $x = x_0$. We look again at the equation

$$\frac{\partial^2\psi}{\partial x^2} = \frac{2m}{\hbar^2}(V-E)\,\psi \ . \tag{240}$$

Due to the jump of $V(x)$ the right hand side is discontinuous. Assume $\psi(x)$ is discontinuous, i.e., $\psi(x_0^-) \neq \psi(x_0^+)$ (these notations stand for $\psi(x_0^{\mp}) \equiv \lim_{\epsilon>0,\epsilon\to 0}\psi(x_0 \mp \epsilon)$). Then the left hand side of (240) would contain the derivative of the delta function $\delta'(x-x_0)$ whereas the right hand side does not contain such a singularity. Similarly, if $\psi'(x)$ is discontinuous, the l.h.s. of (240) would contain a delta function $\delta(x-x_0)$ whereas the r.h.s. does not have it. Thus, we arrive at the boundary condition: both $\psi(x)$ and $\psi'(x)$ must be continuous at $x = x_0$. Namely

$$\psi(x_0^-) = \psi(x_0^+) \ , \tag{241}$$

and

$$\frac{\partial\psi}{\partial x}\Big|_{x_0^-} = \frac{\partial\psi}{\partial x}\Big|_{x_0^+} \ . \tag{242}$$

These boundary conditions are consistent also with the requirement that the current density of the probability is continuous. Indeed, as we have seen above (Eq. 42) the current density is given in 1D by

$$j = \frac{\hbar}{2mi}(\psi^*\,[\partial_x\psi] - [\partial_x\psi^*]\,\psi) \ . \tag{243}$$

This is definitely continuous if both $\psi(x)$ and $\partial_x\psi(x)$ are continuous.

2. Potential step at $x = 0$

Consider the case $V(x) = 0$ for $x < 0$ and $V(x) = V_0 > 0$ at $x > 0$. On the left side (domain I) there are solutions with $E \geq 0$ and wave vectors $\pm k$, where $\hbar k = \sqrt{2mE}$. We will consider an incoming wave with amplitude A and the outgoing (reflected) wave with amplitude B:

$$\psi_{\rm I} = Ae^{ikx} + Be^{-ikx} \ . \tag{244}$$

Consider first the case $E > V_0$. Then, there are solutions on the right side (domain II) with wave vectors $\pm q$, where $\hbar q = \sqrt{2m(E - V_0)}$. The most general solution reads

$$\psi_{\rm II} = Ce^{iqx} + De^{-iqx} \ . \tag{245}$$

The coefficients A, B, C, D are not arbitrary. They are restricted by the boundary conditions:

$$A + B = C + D \quad , \quad ik(A - B) = iq(C - D) \ . \tag{246}$$

The waves with coefficients A and D are incoming. That is if we would construct wave packets out of these waves located initially far from the potential step, these wave packets would move towards the potential step. The waves with coefficients B and C are outgoing. Since there are two equations but four unknowns, we can choose freely two out of four. It is physically the most convenient and meaningful to choose the amplitudes of the incoming waves, i.e., A and D. Here we analyze the case in which there is only one incoming wave from the left, i.e., $D = 0$. We also choose $A = 1$, which can be interpreted such that there is one particle per unit of length in the incoming wave. Substituting $D = 0$ and $A = 1$ we obtain

$$C = \frac{2k}{k+q} \quad , \quad B = \frac{k-q}{k+q} \ . \tag{247}$$

We calculate the current density on both sides:

$$\begin{aligned} j_{\rm I} &= \frac{\hbar}{2mi}\left[(e^{-ikx} + B^* e^{ikx})(ik)(e^{ikx} - Be^{-ikx}) - c.c.\right] \\ &= \frac{\hbar}{2mi}\left[(ik)(1 - |B|^2 - Be^{-2ikx} + B^* e^{2ikx}) - c.c.\right] \\ &= \frac{\hbar k}{m}\left[1 - |B|^2\right] \ . \end{aligned} \tag{248}$$

$$j_{\rm II} = \frac{\hbar}{2mi}\left[C^* e^{-iqx}(iq)Ce^{iqx} - c.c.\right] = \frac{\hbar q}{m}|C|^2 \ . \tag{249}$$

We observe that as expected $j_{\rm I} = j_{\rm II}$. This results can be interpreted as $j_{\rm I} = j_{\rm i} - j_{\rm r}$, where $j_{\rm i} = \hbar k/m$ is the incoming current and $j_{\rm r} = |B|^2\hbar k/m$ is the reflected current. The current $j_{\rm II}$ can be now called the transmitted current $j_{\rm t} = |C|^2\hbar q/m$. Thus we have

$$j_{\rm t} = j_{\rm i} - j_{\rm r} \ . \tag{250}$$

One can define, thus, the reflection and the transmission probabilities:

$$r = \frac{|j_{\rm r}|}{|j_{\rm i}|} = |B|^2 \ , \tag{251}$$

$$t = \frac{|j_{\rm t}|}{|j_{\rm i}|} = |C|^2 \, \frac{q}{k} \ . \tag{252}$$

Consider now the case $E < V_0$. For $x < 0$ we still have

$$\psi_{\rm I} = Ae^{ikx} + Be^{-ikx} \ . \tag{253}$$

with $\hbar k = \sqrt{2mE}$. For $x > 0$ the only possible solution is

$$\psi_{\rm II} = Ce^{iqx} = Ce^{-\eta x} \ , \tag{254}$$

where $q = i\eta$ and $\hbar\eta = \sqrt{2m(V_0 - E)}$. Indeed the other solution $\propto e^{\eta x}$ diverges at $x \to +\infty$. The boundary conditions read

$$A + B = C \quad , \quad ik(A - B) = -\eta C \ . \tag{255}$$

One unknowns can be chosen. We choose $A = 1$, as above. We obtain

$$C = \frac{2k}{k+q} = \frac{2k}{k+i\eta} \quad , \quad B = \frac{k - i\eta}{k + i\eta} \ . \tag{256}$$

In contrast to the previous case $|B| = 1$. Thus the incoming current $j_{\rm i} = \hbar k/m$ and the reflected current $j_{\rm r} = |B|^2\hbar k/m$ are equal and, thus, the total current on the left side vanishes $j_{\rm I} = 0$. Of course also $j_{\rm II} = 0$. Indeed

$$j_{\rm II} = \frac{\hbar}{2mi}\left[C^* e^{-\eta x}(-\eta) C e^{-\eta x} - c.c.\right] = 0 \ . \tag{257}$$

Although the wave if fully reflected we observe an interesting phenomenon. There is an evanescent wave penetrating under the potential step to a distance of order $1/\eta$. Later we will see that this leads to the phenomenon of tunneling.

Let us consider the limit $V_0 \to \infty$. In this case $\eta \to \infty$, and thus $B \to -1$. In addition $C \to 0$ but so that $C\eta \to -2ik$. Thus, we observe that the wave function on the left side $\psi_{\rm I} = e^{ikx} - e^{-ikx}$ vanishes at $x \to 0$. Also $\psi_{\rm II}$ vanishes for all $x > 0$. Yet, the derivative $\partial\psi_{\rm II}/\partial x|_{x\to 0} = -C\eta \to 2ik$ is finite. All this shows that the appropriate boundary condition for $V_0 \to \infty$ is $\psi_{\rm I}(x = 0) = 0$.

3. Potential barrier, tunneling

We now consider a potential barrier

$$V(x) = V_0\theta(a - |x|) \ . \tag{258}$$

Consider, first, the case $E > V_0$. Then the solution looks like

$$\begin{aligned}
\psi(x) &= Ae^{ikx} + Be^{-ikx} \quad \text{for} \quad x < -a \ , \\
\psi(x) &= Ce^{iqx} + De^{-iqx} \quad \text{for} \quad -a < x < a \ , \\
\psi(x) &= Fe^{ikx} + Ge^{-ikx} \quad \text{for} \quad x > a \ .
\end{aligned} \tag{259}$$

Here $\hbar k = \sqrt{2mE}$ and $\hbar q = \sqrt{2m(E - V_0)}$. The boundary conditions read for $x = -a$

$$\begin{aligned}
Ae^{-ika} + Be^{ika} &= Ce^{-iqa} + De^{iqa} \ , \\
ik(Ae^{-ika} - Be^{ika}) &= iq(Ce^{-iqa} - De^{iqa}) \ ,
\end{aligned} \tag{260}$$

and for $x = a$

$$\begin{aligned}
Fe^{ika} + Ge^{-ika} &= Ce^{iqa} + De^{-iqa} \ , \\
ik(Fe^{ika} - Ge^{-ika}) &= iq(Ce^{iqa} - De^{-iqa}) \ .
\end{aligned} \tag{261}$$

We have 4 equations and 6 unknown variables. It means we can choose 2 of them freely. Physically it makes sense to choose the amplitudes of the incoming waves A and G. Let us choose the situation in which the incoming wave comes only from the left, i.e., $A = 1$ and $G = 0$. Then from the second pair of equations we get

$$\begin{aligned}
Ce^{iqa} + De^{-iqa} &= Fe^{ika} \ , \\
Ce^{iqa} - De^{-iqa} &= \frac{k}{q} Fe^{ika} \ .
\end{aligned} \tag{262}$$

Thus we find the coefficients C and D:

$$\begin{aligned}
Ce^{iqa} &= \frac{F}{2}\left(1 + \frac{k}{q}\right) e^{ika} \ , \\
De^{-iqa} &= \frac{F}{2}\left(1 - \frac{k}{q}\right) e^{ika} \ .
\end{aligned} \tag{263}$$

We substitute these results into the first pair of equations (260) and obtain

$$\begin{aligned}
e^{-ika} + Be^{ika} &= \frac{Fe^{ika}}{2}\left[\left(1 + \frac{k}{q}\right) e^{-2iqa} + \left(1 - \frac{k}{q}\right) e^{2iqa}\right] \ , \\
e^{-ika} - Be^{ika} &= \frac{q}{k}\frac{Fe^{ika}}{2}\left[\left(1 + \frac{k}{q}\right) e^{-2iqa} - \left(1 - \frac{k}{q}\right) e^{2iqa}\right] \ .
\end{aligned} \tag{264}$$

These can be simplified to

$$e^{-ika} + Be^{ika} = Fe^{ika}\left[\cos(2qa) - \frac{ik}{q}\sin(2qa)\right] \ ,$$
$$e^{-ika} - Be^{ika} = Fe^{ika}\left[\cos(2qa) - \frac{iq}{k}\sin(2qa)\right] \ . \tag{265}$$

Adding and subtracting we get

$$F = \frac{e^{-2ika}}{\cos(2qa) - i\frac{k^2+q^2}{2kq}\sin(2qa)} \ . \tag{266}$$

$$B = \frac{iF}{2}\,\frac{q^2-k^2}{kq}\,\sin(2qa) \ . \tag{267}$$

It is straightforward to calculate the transmission probability

$$t = |F|^2 = \frac{1}{1 + \left[\frac{k^2-q^2}{2kq}\right]^2 \sin^2(2qa)} = \frac{1}{1 + \frac{1}{4}\,\frac{V_0^2}{E(E-V_0)}\,\sin^2(2qa)} \ . \tag{268}$$

In the last equality we have used

$$k^2 - q^2 = \frac{2mV_0}{\hbar^2} \ , \tag{269}$$

and

$$kq = \frac{2m\sqrt{E(E-V_0)}}{\hbar^2} \ . \tag{270}$$

We observe resonances at $\sin(2qa) = 0$ and $q \neq 0$ (actually $q > 0$). Namely $t = 1$ for such values of q. This happens for

$$q = \frac{n\pi}{2a} \quad , \quad n = 1, 2, \ldots \tag{271}$$

In terms of the wave length of the waves above the barrier this means ($\lambda = 2\pi/q$)

$$n\,\frac{\lambda}{2} = 2a \ . \tag{272}$$

It is easy to find the energies at which the resonances occur:

$$E_n = V_0 + \frac{\hbar^2}{2m}\left(\frac{\pi n}{2a}\right)^2 \ . \tag{273}$$

We now switch to the most interesting case $E < V_0$. The solution above still holds if we make q imaginary. Namely $q = i\eta$, where

$$\hbar\eta = \sqrt{2m(V_0 - E)} \ . \tag{274}$$

Using $\cos(i\alpha) = \cosh(\alpha)$ and $\sin(i\alpha) = i\sinh(\alpha)$ we obtain for the transmission probability

$$t = |F|^2 = \frac{1}{1 + \left[\frac{k^2+\eta^2}{2k\eta}\right]^2 \sinh^2(2\eta a)} = \frac{1}{1 + \frac{1}{4}\frac{V_0^2}{E(V_0-E)} \sinh^2(2\eta a)} \ . \tag{275}$$

Consider the limit of sufficiently wide and high barrier, such that $2\eta a \gg 1$. Then

$$\sinh^2(2\eta a) \approx \frac{1}{4}\exp\left[4\eta a\right] \gg 1 \ . \tag{276}$$

Therefore

$$t \approx \frac{16E(V_0-E)}{V_0^2} \exp\left[-4\eta a\right] = \frac{16E(V_0-E)}{V_0^2} \exp\left[-\frac{4a}{\hbar}\sqrt{2m(V_0-E)}\right] \ . \tag{277}$$

We obtain an exponentially weak tunneling effect.

4. Potential well

We now consider a potential well

$$V(x) = -V_0\theta(a - |x|) \ . \tag{278}$$

The eigenstates with $E > 0$ are found similarly to the case of energies above the barrier above. The most interesting is the case $-V_0 < E < 0$. The solution looks like

$$\begin{aligned}
&\psi(x) = Ae^{\eta x} \quad \text{for} \quad x < -a \ , \\
&\psi(x) = Ce^{iqx} + De^{-iqx} \quad \text{for} \quad -a < x < a \ , \\
&\psi(x) = Fe^{-\eta x} \quad \text{for} \quad x > a \ .
\end{aligned} \tag{279}$$

Here $\hbar\eta = \sqrt{-2mE}$ and $\hbar q = \sqrt{2m(E-(-V_0))} = \sqrt{2m(E+V_0)}$. The boundary conditions read

$$\begin{aligned}
&Ae^{-\eta a} = Ce^{-iqa} + De^{iqa} \ , \\
&\eta Ae^{-\eta a} = iq(Ce^{-iqa} - De^{iqa}) \ , \\
&Fe^{-\eta a} = Ce^{iqa} + De^{-iqa} \ , \\
&-\eta Fe^{-\eta a} = iq(Ce^{iqa} - De^{-iqa}) \ .
\end{aligned} \tag{280}$$

There are no free parameters to choose. We rewrite

$$\begin{aligned} Ae^{-\eta a} &= Ce^{-iqa} + De^{iqa} \ , \\ -i\frac{\eta}{q}Ae^{-\eta a} &= Ce^{-iqa} - De^{iqa} \ , \\ Fe^{-\eta a} &= Ce^{iqa} + De^{-iqa} \ , \\ i\frac{\eta}{q}Fe^{-\eta a} &= Ce^{iqa} - De^{-iqa} \ . \end{aligned} \tag{281}$$

The first two equations give

$$\begin{aligned} 2Ce^{-iqa} &= Ae^{-\eta a}\left(1 - i\,\frac{\eta}{q}\right) \ , \\ 2De^{iqa} &= Ae^{-\eta a}\left(1 + i\,\frac{\eta}{q}\right) \ . \end{aligned} \tag{282}$$

Analogously

$$\begin{aligned} 2Ce^{iqa} &= Fe^{-\eta a}\left(1 + i\,\frac{\eta}{q}\right) \ , \\ 2De^{-iqa} &= Fe^{-\eta a}\left(1 - i\,\frac{\eta}{q}\right) \ . \end{aligned} \tag{283}$$

We further obtain

$$\frac{C}{D}e^{-2iqa} = \frac{\left(1 - i\,\frac{\eta}{q}\right)}{\left(1 + i\,\frac{\eta}{q}\right)} \ , \tag{284}$$

and

$$\frac{C}{D}e^{2iqa} = \frac{\left(1 + i\,\frac{\eta}{q}\right)}{\left(1 - i\,\frac{\eta}{q}\right)} \ . \tag{285}$$

Further

$$\frac{C}{D} = \frac{q - i\eta}{q + i\eta}e^{2iqa} = \frac{q + i\eta}{q - i\eta}e^{-2iqa} \ . \tag{286}$$

We obtain the quantization condition, i.e., the condition that a solution exists

$$\left(\frac{q + i\eta}{q - i\eta}\right)^2 = e^{4iqa} \ . \tag{287}$$

Here one can distinguish two cases:

1) Symmetric solutions. If one takes

$$\left(\frac{q + i\eta}{q - i\eta}\right) = +e^{2iqa} \ , \tag{288}$$

this immediately leads to $C = D$ and $A = F$. The solution is symmetric, i.e., it satisfies $\psi(x) = \psi(-x)$. Inside the well $\psi(x) \propto \cos(qx)$.

2) Antisymmetric solutions. If one takes

$$\left(\frac{q+i\eta}{q-i\eta}\right) = -e^{2iqa} \ , \tag{289}$$

this immediately leads to $C = -D$ and $A = -F$. The solution is antisymmetric, i.e., it satisfies $\psi(x) = -\psi(-x)$. Inside the well $\psi(x) \propto \sin(qx)$.

To proceed further we introduce the angle $0 < \theta < \pi/2$ so that

$$\frac{q+i\eta}{q-i\eta} = e^{2i\theta} \tag{290}$$

or, equivalently, $\tan\theta = \eta/q$. Then, for symmetric solutions this means

$$e^{2i\theta} = e^{2iqa} \rightarrow 2\theta = 2qa + 2\pi N \rightarrow \theta = qa + \pi N \ . \tag{291}$$

This, in turn, means

$$\tan\theta = \tan(qa) \ . \tag{292}$$

Using $\eta^2 + q^2 = \frac{2mV_0}{\hbar^2} \equiv k_0^2$ we obtain $\tan\theta = \eta/q = \sqrt{k_0^2 - q^2}/q$. Thus, we obtain the following transcendental equation

$$\frac{\sqrt{k_0^2 - q^2}}{q} = \frac{\sqrt{(ak_0)^2 - (aq)^2}}{aq} = \tan(qa) \ . \tag{293}$$

This equation can be solved graphically (Fig. 2).

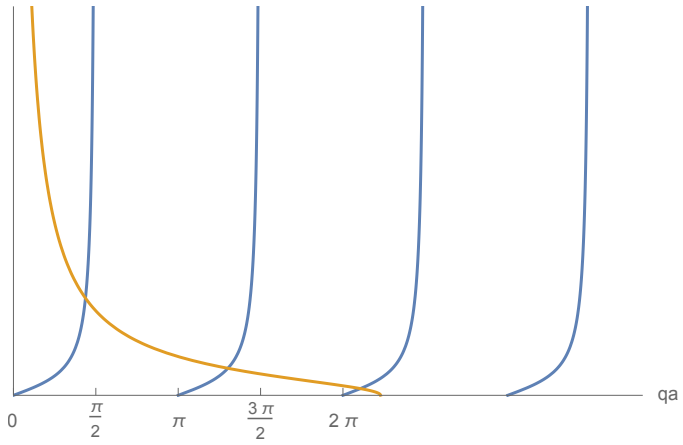

FIG. 2: Graphic solution for the symmetric bound states.

Analogously, for the antisymmetric case

$$e^{2i\theta} = -e^{2iqa} \rightarrow 2\theta = 2qa + \pi(2N+1) \rightarrow \theta = qa + \pi N + \frac{\pi}{2} \ . \tag{294}$$

Therefore

$$\tan\theta = \tan(qa + \pi/2) = -\cot(qa) \ , \tag{295}$$

and

$$\frac{\sqrt{(ak_0)^2 - (aq)^2}}{aq} = -\cot(qa) \ . \tag{296}$$

The graphical solution of this equation is presented in Fig. 3

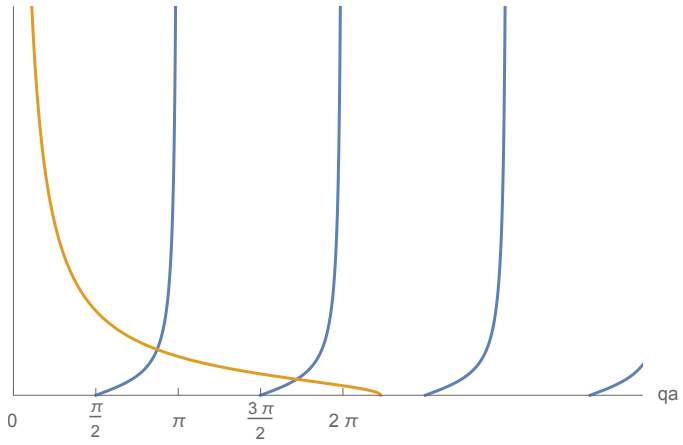

FIG. 3: Graphic solution for the antisymmetric bound states.

Shallow well limit. From the graphical solution we observe that in the limit of very shallow potential well, i.e., when $ak_0 \ll 1$ there is only one symmetric solution. The shallow well condition reads

$$V_0 \ll \frac{\hbar^2}{2ma^2} \ . \tag{297}$$

In this case Eq. (293) can be approximately solved. Indeed this equation can be rewritten as

$$\cos(aq) = \frac{aq}{ak_0} \quad \text{and} \quad 0 < aq < ak_0 \ll 1 \ . \tag{298}$$

We denote $x \equiv aq$ and $x_0 \equiv ak_0$:

$$x = x_0 \cos x \ . \tag{299}$$

Since $x_0 \ll 1$ we can iterate. The first iteration gives $x \approx x_0$. The second:

$$x \approx x_0 \cos x_0 \approx x_0 \left(1 - \frac{x_0^2}{2}\right) \ . \tag{300}$$

For the energy of this state we get

$$E = -V_0 + \frac{\hbar^2 q^2}{2m} = -V_0 + \frac{\hbar^2 x^2}{2ma^2} \ . \tag{301}$$

Substituting $x^2 \approx x_0^2 - x_0^4$ (recall $x_0^2 = (ak_0)^2 = \frac{2mV_0a^2}{\hbar^2}$) we obtain

$$E \approx -\frac{2mV_0^2a^2}{\hbar^2} \ . \tag{302}$$

Scattering states (continuum). For $E > 0$ one can obtain the scattering states similar to the problem of the scattering states with energies above the potential barrier. Thus, for the potential well, the spectrum consists of both bound states (discrete energy levels $E_n < 0$) and continuum of scattering states ($E > 0$).

5. Parity operator

In the last problem (potential well) we have obtained two kinds of bound states - symmetric (also called even), $\psi(x) = \psi(-x)$, and antisymmetric (odd), $\psi(x) = -\psi(-x)$. Is there a mathematical reason why only these two kinds of eigenstates appear? The answer is positive. It has to do with the fact that the potential energy and the whole Hamiltonian is symmetric. Indeed $V(x) = -V_0\theta(a - |x|)$ satisfies $V(x) = V(-x)$. We define the parity operator $\hat{P}$ as follows

$$\hat{P}\psi(x) = \psi(-x) \ . \tag{303}$$

This is a Hermitian operator. Indeed

$$\left\langle \phi|\hat{P}\psi \right\rangle = \int dx\, \phi^*(x)\psi(-x) = \int dx\, \phi^*(-x)\psi(x) = \left\langle \hat{P}\phi|\psi \right\rangle \ . \tag{304}$$

All symmetric wave functions are eigenstates of $\hat{P}$ with eigenvalue 1, all antisymmetric wave functions are eigenstates with eigenvalue -1. There are no other eigenvalues since any function can be written as a sum of a symmetric and an antisymmetric ones:

$$\psi(x) = \frac{\psi(x) + \psi(-x)}{2} + \frac{\psi(x) - \psi(-x)}{2} \ . \tag{305}$$

$$\hat{P}\psi(x) = \frac{\psi(x) + \psi(-x)}{2} - \frac{\psi(x) - \psi(-x)}{2} \ . \tag{306}$$

The operator $\hat{P}$ commutes with our Hamiltonian (because $V(x) = V(-x)$). Indeed

$$\hat{P}\hat{H}\,|\psi\rangle = \hat{P}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\psi(x) = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(-x)\right)\psi(-x)$$
$$= \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\psi(-x) = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\hat{P}\psi(x) = \hat{H}\hat{P}\,|\psi\rangle \ . \tag{307}$$

The property $[\hat{H}, \hat{P}] = 0$ just expresses the fact that the potential energy is symmetric.

Later we will prove the fact that two commuting Hermitian operators share a mutual basis of eigenstates. Here we prove this only for non-degenerate states. Indeed, assume $\hat{H}\,|\psi_n\rangle = E_n\,|\psi_n\rangle$ and E_n is not degenerate. That is there is only one eigenstate with energy E_n. Then

$$\hat{H}\hat{P}\,|\psi_n\rangle = \hat{P}\hat{H}\,|\psi_n\rangle = E_n\hat{P}\,|\psi_n\rangle \ . \tag{308}$$

From this we observe that $\hat{P}\,|\psi_n\rangle$ is also the eigenstate of $\hat{H}$ with eigenvalue E_n. But only one such state exists. Thus $\hat{P}\,|\psi_n\rangle \propto |\psi_n\rangle$ and, therefore, $|\psi_n\rangle$ is also an eigenstate of $\hat{P}$. Since the only possible eigenvalues of $\hat{P}$ are ± 1 we obtain

$$\hat{P}\,|\psi_n\rangle = \pm\,|\psi_n\rangle \ . \tag{309}$$

This explains why all (non-degenerate) eigenstates of $\hat{H}$ are either even or odd.

VI. CENTRAL POTENTIAL AND ANGULAR MOMENTUM

We now switch to a very important class of 3D problems: central potential problems. Central potential is a potential that depends on the radius only $V(\mathbf{r}) = V(|\mathbf{r}|) = V(r)$. The Hamiltonian is then

$$H = \frac{\mathbf{p}^2}{2m} + V(r) \ . \tag{310}$$

Important examples: 1) Coulomb potential $V = -\frac{1}{4\pi\epsilon_0}\,\frac{e^2}{r}$. Solving this problem one can describe the hydrogen atom; 2) 3D oscillator $V = \frac{m\omega^2 r^2}{2}$.

A. Spherical coordinates

The potential energy $V(r)$ depends only on one of the spherical coordinates r. It would therefore be nice to express $\mathbf{p}^2 = -\hbar^2\boldsymbol{\nabla}^2$ is spherical coordinates. These are defined via

$$\begin{aligned} x &= r\sin\theta\cos\phi \ , \\ y &= r\sin\theta\sin\phi \ , \\ z &= r\cos\theta \ . \end{aligned} \tag{311}$$

Evidently $r \in [0, +\infty]$, $\theta \in [0, \pi]$, and $\phi \in [0, 2\pi]$.

First, we find the operator $\boldsymbol{\nabla} = (\partial/\partial x, \partial/\partial y, \partial/\partial z)$ in spherical coordinates (see Appendix A or Appendix C):

$$\boldsymbol{\nabla}^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) . \tag{312}$$

Using further the results of Appendix B one observes that the following relation holds

$$\hat{\boldsymbol{L}}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] , \tag{313}$$

where

$$\hat{\boldsymbol{L}} \equiv \hat{\mathbf{r}} \times \hat{\mathbf{p}} \tag{314}$$

is the angular momentum operator with three components $\hat{L}_x$, $\hat{L}_y$, $\hat{L}_z$.

We, thus, get for the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\hat{\boldsymbol{L}}^2}{2mr^2} + V(r) . \tag{315}$$

B. Angular momentum, algebraic results

For the components of $\hat{\boldsymbol{L}}$ one obtains

$$\begin{aligned}
\hat{L}_x &= -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) = i\hbar\left[\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right] , \\
\hat{L}_y &= -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) = i\hbar\left[-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right] , \\
\hat{L}_z &= -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = -i\hbar\frac{\partial}{\partial\phi} .
\end{aligned} \tag{316}$$

Very important are the commutation relations between $\hat{L}_x$, $\hat{L}_y$, $\hat{L}_z$:

$$\begin{aligned}
[\hat{L}_x, \hat{L}_y] &= [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}\hat{p}_x - \hat{x}\hat{p}_z] = [\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] - [\hat{z}\hat{p}_y, \hat{z}\hat{p}_x] - [\hat{y}\hat{p}_z, \hat{x}\hat{p}_z] + [\hat{z}\hat{p}_y, \hat{x}\hat{p}_z] \\
&= \hat{y}\hat{p}_x[\hat{p}_z, z] + \hat{p}_y\hat{x}[\hat{z}, \hat{p}_z] = i\hbar(\hat{x}\hat{p}_y - \hat{y}\hat{p}_x) = i\hbar\hat{L}_z .
\end{aligned} \tag{317}$$

Analogously we get

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z , \tag{318}$$

$$[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x , \tag{319}$$

$$[\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y . \tag{320}$$

It is easy to show that $[\hat{\boldsymbol{L}}^2, \hat{L}_x] = 0$, $[\hat{\boldsymbol{L}}^2, \hat{L}_y] = 0$, $[\hat{\boldsymbol{L}}^2, \hat{L}_z] = 0$. Indeed

$$\begin{aligned}
&[\hat{\boldsymbol{L}}^2, \hat{L}_x] = [\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \hat{L}_x] = [\hat{L}_y^2 + \hat{L}_z^2, \hat{L}_x] \\
&= \hat{L}_y [\hat{L}_y, \hat{L}_x] + [\hat{L}_y, \hat{L}_x] \hat{L}_y + \hat{L}_z [\hat{L}_z, \hat{L}_x] + [\hat{L}_z, \hat{L}_x] \hat{L}_z \\
&= i\hbar \left(-\hat{L}_y \hat{L}_z - \hat{L}_z \hat{L}_y + \hat{L}_z \hat{L}_y + \hat{L}_y \hat{L}_z \right) = 0 \ . \qquad (321)
\end{aligned}$$

We use now the fact that two commuting Hermitian operators have a mutual basis of eigenstates (for proof see Appendix D). We try to find such a basis for the commuting pair $\hat{\boldsymbol{L}}^2$ and $\hat{L}_z$. We will call such states $|l, m\rangle$ so that

$$\hat{\boldsymbol{L}}^2 |l, m\rangle = \hbar^2 l(l+1) |l, m\rangle \ , \qquad (322)$$

and

$$\hat{L}_z |l, m\rangle = \hbar m |l, m\rangle \ . \qquad (323)$$

Here l and m just parametrize the eigenvalues. Since the eigenvalues of $\hat{\boldsymbol{L}}^2$ must be non-negative, we should demand $l \geq 0$. Thus far this is the only restriction. Indeed the combination $l(l+1)$ can parametrize any real non-negative number if l is taken to be real and non-negative. Also m is an arbitrary (real) number at this stage.

We now define

$$\hat{L}_\pm \equiv \hat{L}_x \pm i\hat{L}_y \ . \qquad (324)$$

We investigate the commutation relations of $\hat{L}_\pm$:

$$[\hat{L}_z, \hat{L}_+] = i\hbar \hat{L}_y + \hbar L_x = \hbar \hat{L}_+ \quad , \quad [\hat{L}_z, \hat{L}_-] = i\hbar \hat{L}_y - \hbar L_x = -\hbar \hat{L}_- \ . \qquad (325)$$

Further

$$[\hat{L}_+, \hat{L}_-] = [\hat{L}_x + i\hat{L}_y, \hat{L}_x - i\hat{L}_y] = 2\hbar \hat{L}_z \ . \qquad (326)$$

In addition, from

$$\hat{L}_+ \hat{L}_- = (\hat{L}_x + i\hat{L}_y)(\hat{L}_x - i\hat{L}_y) = \hat{L}_x^2 + \hat{L}_y^2 - i[\hat{L}_x, \hat{L}_y] = \hat{L}_x^2 + \hat{L}_y^2 + \hbar L_z \qquad (327)$$

we obtain

$$\hat{\boldsymbol{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = \hat{L}_+ \hat{L}_- - \hbar \hat{L}_z + \hat{L}_z^2 = \hat{L}_- \hat{L}_+ + \hbar \hat{L}_z + \hat{L}_z^2 \ . \qquad (328)$$

All this commutation relations will help us to put restrictions on the possible values of l and m. We start with m. From

$$\hat{L}_z \hat{L}_+ |l, m\rangle = (\hat{L}_+ \hat{L}_z + \hbar L_+) |l, m\rangle = \hbar(m+1) \hat{L}_+ |l, m\rangle \qquad (329)$$

and from

$$\hat{\boldsymbol{L}}^2 \hat{L}_+ |l,m\rangle = \hat{L}_+ \hat{\boldsymbol{L}}^2 |l,m\rangle = \hbar^2 l(l+1) \hat{L}_+ |l,m\rangle \tag{330}$$

follows that $\hat{L}_+ |l,m\rangle \propto |l,m+1\rangle$. Analogously,

$$\hat{L}_z \hat{L}_- |l,m\rangle = (\hat{L}_- \hat{L}_z - \hbar L_-) |l,m\rangle = \hbar(m-1) \hat{L}_+ |l,m\rangle \ , \tag{331}$$

$$\hat{\boldsymbol{L}}^2 \hat{L}_- |l,m\rangle = \hat{L}_- \hat{\boldsymbol{L}}^2 |l,m\rangle = \hbar^2 l(l+1) \hat{L}_- |l,m\rangle \tag{332}$$

and, therefore, $\hat{L}_+ |l,m\rangle \propto |l,m-1\rangle$. We observe that $\hat{L}_\pm$ act similar to the creation and annihilation operators of the harmonic oscillator.

Next we investigate the norm of the states $\hat{L}_\pm |l,m\rangle$:

$$\begin{aligned} \left\langle \hat{L}_+ \, l,m | \hat{L}_+ \, l,m \right\rangle &= \langle l,m| \, \hat{L}_- \hat{L}_+ \, |l,m\rangle = \langle l,m| \, \hat{\boldsymbol{L}}^2 - \hat{L}_z^2 - \hbar \hat{L}_z \, |l,m\rangle \\ &= \hbar^2 [l(l+1) - m(m+1)] \ . \end{aligned} \tag{333}$$

Analogously

$$\begin{aligned} \left\langle \hat{L}_- \, l,m | \hat{L}_- \, l,m \right\rangle &= \langle l,m| \, \hat{L}_+ \hat{L}_- \, |l,m\rangle = \langle l,m| \, \hat{\boldsymbol{L}}^2 - \hat{L}_z^2 + \hbar \hat{L}_z \, |l,m\rangle \\ &= \hbar^2 [l(l+1) - m(m-1)] \ . \end{aligned} \tag{334}$$

Since the norm must be positive we must demand that

$$l(l+1) \geq m(m+1) \quad \text{and} \quad l(l+1) \geq m(m-1) \ . \tag{335}$$

For $m > 0$ the first relation is more restrictive. For $m < 0$, the second relation can be written as $l(l+1) \geq -|m|(-|m|-1) = |m|(|m|+1)$ and is more restictive. Thus, both inequalities can be written as $|m| \leq l$. Since the operators $\hat{L}_\pm$ change m by ± 1, applying, e.g., $\hat{L}_+$. several times we would finally reach the values of m that violate the condition $|m| \leq l$. The only way to avoid this is to demand that the numbers l and m are such that upon applying $\hat{L}_+$ we at some stage reach $m = l$. Applying $\hat{L}_+$ once again we would get a state with zero norm, thus the state with $m = l+1$ would not emerge. We demand $m_{\max} = l$. Analogously, applying $\hat{L}_-$ several times, we arrive at the condition $m_{\min} = -l$. Since m changes by ± 1 this is possible only if

$$l = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots \tag{336}$$

This is an extremely important result, which we obtained purely algebraically, without specifying the wave functions $|l,m\rangle$. Finally, the normalization conditions (333,334) give

$$\hat{L}_+ |l,m\rangle = \hbar \sqrt{l(l+1) - m(m+1)} \, |l,m+1\rangle \ . \tag{337}$$

and

$$\hat{L}_- \, |l,m\rangle = \hbar\sqrt{l(l+1) - m(m-1)}\, |l,m-1\rangle \ . \tag{338}$$

From these equations we see again that upon reaching $m = \pm l$ the states with $m = \pm(l+1)$ are not created.

C. Angular momentum, wave functions

In the central potential problem the wave functions $|l,m\rangle$ should be represented by the wave functions that depend on θ and ϕ. We call those $Y_{l,m}(\theta,\phi)$. Using (316) we find

$$\begin{aligned}
\hat{L}_+ &= \hat{L}_x + i\hat{L}_y = \hbar e^{i\phi}\left(i\cot\theta\,\frac{\partial}{\partial\phi} + \frac{\partial}{\partial\theta}\right) \\
\hat{L}_- &= \hat{L}_x - i\hat{L}_y = \hbar e^{-i\phi}\left(i\cot\theta\,\frac{\partial}{\partial\phi} - \frac{\partial}{\partial\theta}\right) \\
\hat{L}_z &= -i\hbar\,\frac{\partial}{\partial\phi} \ .
\end{aligned} \tag{339}$$

We start with $\hat{L}_z$:

$$\hat{L}_z Y_{l,m}(\theta,\phi) = -i\hbar\,\frac{\partial}{\partial\phi} Y_{l,m}(\theta,\phi) = \hbar m\, Y_{l,m}(\theta,\phi) \ . \tag{340}$$

We immediately conclude that

$$Y_{l,m}(\theta,\phi) \propto e^{im\phi} \tag{341}$$

with $m = 0, \pm 1, \pm 2, \ldots$. Thus, only integer values of l can be realized, i.e., $l = 0, 1, 2, \ldots$. We use the following Ansatz

$$Y_{l,m}(\theta,\phi) = \frac{1}{\sqrt{2\pi}} \Lambda_{l,m}(\theta)\, e^{im\phi} \ . \tag{342}$$

The normalization coefficient $1/\sqrt{2\pi}$ is chosen so that the integration over ϕ in the norm calculation gives one.

Let us take $m = m_{\max} = l$. Then we must have $\hat{L}_+ \, |l,l\rangle = 0$. This gives

$$\hat{L}_+ Y_{l,l}(\theta,\phi) = \hbar e^{i\phi}\left(i\cot\theta\,\frac{\partial}{\partial\phi} + \frac{\partial}{\partial\theta}\right)\frac{1}{\sqrt{2\pi}}\,\Lambda_{l,l}(\theta)\, e^{il\phi} = 0 \ . \tag{343}$$

Calculating the derivative $\partial/\partial\phi$ we obtain

$$\left(-l\cot\theta + \frac{\partial}{\partial\theta}\right)\,\Lambda_{l,l}(\theta) = 0 \ . \tag{344}$$

This differential equation can be solved. The solution reads

$$\Lambda_{l,l}(\theta) = C \sin^l \theta \ , \tag{345}$$

where C is the normalization constant. It is found from the condition

$$\int\limits_0^\pi d\theta \sin\theta |\Lambda_{l,l}(\theta)|^2 = 1 \ . \tag{346}$$

This gives

$$C^2 \int\limits_0^\pi d\theta [\sin\theta]^{2l+1} = C^2 \frac{\sqrt{\pi}\Gamma[l+1]}{\Gamma[l+3/2]} = C^2 \frac{4^{l+1}(l+1)!}{(2l+2)!\sqrt{\pi}} \sqrt{\pi} l! = C^2 \frac{2 \cdot 4^l (l!)^2}{(2l+1)!} = 1 \ . \tag{347}$$

Calculating the normalization constant one obtains

$$Y_{l,l}(\theta,\phi) = \frac{(-1)^l}{2^l l!} \sqrt{\frac{(2l+1)!}{4\pi}} \sin^l \theta \, e^{il\phi} \ . \tag{348}$$

The factor $(-1)^l$ is a matter of convention. All the other functions $Y_{l,m}(\theta,\phi)$ with $m < l$ can be obtained by applying $\hat{L}_-$ in accordance with (338). For example

$$Y_{l,l-1}(\theta,\phi) = \frac{1}{\hbar\sqrt{2l}} \hbar e^{-i\phi} \left(i \cot\theta \frac{\partial}{\partial\phi} - \frac{\partial}{\partial\theta} \right) Y_{l,l}(\theta,\phi) \ . \tag{349}$$

The factor $\sqrt{2l}$ emerges from $\sqrt{l(l+1) - m(m-1)}$ and $m = l$. Next

$$Y_{l,l-2}(\theta,\phi) = \frac{1}{\hbar\sqrt{4l-2}} \hbar e^{-i\phi} \left(i \cot\theta \frac{\partial}{\partial\phi} - \frac{\partial}{\partial\theta} \right) Y_{l,l-1}(\theta,\phi) \ . \tag{350}$$

Here $\sqrt{4l-2} = \sqrt{l(l+1) - m(m-1)}$ for $m = l-1$. So one can construct all the functions $Y_{l,m}(\theta,\phi)$. These wave functions Y_{l_1,m_1} and Y_{l_2,m_2} are orthogonal unless $l_1 = l_2$ and $m_1 = m_2$. Indeed, if $l_1 \neq l_2$ or $m_1 \neq m_2$, these two are eigenvectors of a Hermitian operator with different eigenvalues (either $\hat{\boldsymbol{L}}^2$ or $\hat{L}_z$). Thus

$$\int\limits_0^\pi \sin\theta d\theta \int\limits_0^{2\pi} d\phi \ Y^*_{l_1,m_1}(\theta,\phi) \, Y_{l_2,m_2}(\theta,\phi) = \delta_{l_1,l_2} \delta_{m_1,m_2} \ . \tag{351}$$

The general form of $Y_{l,m}(\theta,\phi)$ is provided in Appendix E. See Schwabl for concrete examples and graphic representation of $Y_{l,m}(\theta,\phi)$.

A very important property of $Y_{l,m}$ is their behavior under the parity transformation. The transformation $\mathbf{r} \to -\mathbf{r}$ corresponds to $(\theta,\phi) \to (\pi - \theta, \phi + \pi)$. One can show that

$$\hat{P} Y_{l,m} = Y_{l,m}(\pi - \theta, \phi + \pi) = (-1)^l Y_{l,m}(\theta,\phi) \ . \tag{352}$$

D. Schrödinger equation for the central potential problem

We return back to the central potential problem with the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\hat{\boldsymbol{L}}^2}{2mr^2} + V(r) \ . \tag{353}$$

Since we now know the eigenfunctions of the operator $\hat{\boldsymbol{L}}^2$, we make the following Ansatz

$$\psi(\mathbf{r}) = R(r)Y_{l,m}(\theta,\phi) \ . \tag{354}$$

Then the stationary Schrödinger equation $\hat{H}\psi = E\psi$ reads

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r)\right] R(r) = ER(r) \ . \tag{355}$$

This is further simplified if we substitute

$$R(r) = \frac{u(r)}{r} \tag{356}$$

A simple calculation gives

$$\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right)\frac{u(r)}{r} = \frac{1}{r}\frac{\partial^2 u(r)}{\partial r^2} \ . \tag{357}$$

Thus we obtain

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r)\right] u(r) = Eu(r) \ . \tag{358}$$

This is a regular Schrödinger equation (only for $r \geq 0$) with the effective potential

$$V_{\text{eff}}(r) = V(r) + \frac{\hbar^2 l(l+1)}{2mr^2} \ . \tag{359}$$

The second part is the so-called centrifugal potential.

It is important to discuss the boundary condition at $r = 0$. Unless the potential $V(r)$ is very singular at $r = 0$, i.e., $V(\mathbf{r}) \propto \delta(\mathbf{r})$, the proper boundary condition is $u(0) = 0$. Indeed, if $u(0) \neq 0$, the wave function near $r = 0$ would contain (be dominated by) $u(0)/r$. The operator $\boldsymbol{\nabla}^2$ acting on $u(0)/r$ would produce $\propto u(0)\delta(\mathbf{r})$, which would not be compensated by anything in the Schrödinger equation. Another way of looking at it is to think that the potential is infinitely high at $r < 0$. As we have seen above, the proper boundary condition in this case is again $u(0) = 0$.

E. Hydrogen atom

The Hydrogen atom is a two-body problem: proton with mass m_p and electron with mass m_e attracting each other via the Coulomb potential. The Hamiltonian reads

$$\hat{H} = \frac{\hat{\mathbf{p}}_\mathbf{p}^2}{2m_p} + \frac{\hat{\mathbf{p}}_\mathbf{e}^2}{2m_e} + V(|\mathbf{r_e} - \mathbf{r_p}|) \ . \tag{360}$$

We transform to the center of mass frame:

$$\mathbf{R} = \frac{m_p \mathbf{r_p} + m_e \mathbf{r_e}}{m_p + m_e} \quad , \quad \mathbf{r} = \mathbf{r_e} - \mathbf{r_p} \ . \tag{361}$$

The standard calculation gives the Hamiltonian in the new frame:

$$\hat{H} = -\frac{\hbar^2}{2M}\boldsymbol{\nabla}_R^2 - \frac{\hbar^2}{2m}\boldsymbol{\nabla}_r^2 + V(r) \ . \tag{362}$$

Here $M \equiv m_p + m_e$ is the total mass and $m \equiv m_e m_p/(m_e + m_p)$ is the reduced mass. The Hamiltonian is a sum of a part describing the free motion of the center of mass and the relative motion with the attraction due to $V(r)$. We concentrate on the relative motion and consider the Hamiltonian

$$\hat{H}_r = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}_r^2 + V(r) \ . \tag{363}$$

In what follows we drop the index r. The potential is given by

$$V(r) = -\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r} \ . \tag{364}$$

For hydrogen atom $Z = 1$. We keep Z in order to be able to use the solution later for other atoms with Z protons in the atomic nucleus. The effective potential is

$$V_{\text{eff}}(r) = -\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r} + \frac{\hbar^2 l(l+1)}{2mr^2} \ . \tag{365}$$

As mentioned above we use the Ansatz

$$\psi(r,\theta,\phi) = \frac{u(r)}{r}\, Y_{l,m}(\theta,\phi) \ , \tag{366}$$

and the function $u(r)$ satisfies the Schrödinger equation (for $r \geq 0$, $u(0) = 0$)

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + V_{\text{eff}}(r)\right] u(r) = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + \frac{\hbar^2 l(l+1)}{2mr^2} - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r}\right] u(r) = E\, u(r) \ . \tag{367}$$

1. Bound states

We rewrite (367) as

$$\left[-\frac{\partial^2}{\partial r^2}+\frac{l(l+1)}{r^2}-\frac{Ze^2}{4\pi\epsilon_0}\frac{2m}{\hbar^2}\frac{1}{r}-\frac{2mE}{\hbar^2}\right]u(r)=0\ . \tag{368}$$

We introduce the Bohr radius

$$a_0=\frac{4\pi\epsilon_0\hbar^2}{me^2}\approx 0.53\times 10^{-10}\mathrm{m}\ , \tag{369}$$

and the Rydberg constant

$$R_y=\frac{\hbar^2}{2ma_0^2}\approx 13.6\mathrm{eV}\approx 2.18\times 10^{-18}\mathrm{J}\ . \tag{370}$$

which gives

$$\left[-\frac{\partial^2}{\partial r^2}+\frac{l(l+1)}{r^2}-\frac{2Z}{a_0}\frac{1}{r}-\frac{E}{a_0^2R_y}\right]u(r)=0\ . \tag{371}$$

We look for bound states with $E<0$. We introduce a new dimensionless variable

$$x\equiv\eta r\ , \tag{372}$$

where

$$\eta\equiv\sqrt{\frac{2m|E|}{\hbar^2}}=\sqrt{\frac{|E|}{R_y}}\frac{1}{a_0}\ , \tag{373}$$

and obtain

$$\left[\frac{\partial^2}{\partial x^2}-\frac{l(l+1)}{x^2}+\frac{x_0}{x}-1\right]u(x)=0\ , \tag{374}$$

where

$$x_0\equiv 2Z\sqrt{\frac{R_y}{|E|}}=\frac{2Z}{\eta a_0}\ . \tag{375}$$

For small x the dominant term is the centrifugal one and one has to solve the following differential equation $u''=l(l+1)u/x^2$. We try $u=x^{q+1}$ and obtain $q(q+1)=l(l+1)$. The possible solutions are $q=l$ and $q=-(l+1)$. The second solution is incompatible with the boundary condition $u(0)=0$. Thus we are left with $u(x)\propto x^{l+1}$ at small x. For large x the differential equation is approximately $u''=u$ and the decaying solution reads $u(x)\propto e^{-x}$. Motivated by these asymptotic solutions we make an Ansatz:

$$u(x)=x^{l+1}e^{-x}w(x)\ . \tag{376}$$

We substitute into (374) and obtain the differential equation for $w(x)$:

$$xw''(x) + 2(l+1-x)w'(x) + (x_0 - 2(l+1))w = 0 \ . \tag{377}$$

We try to solve this equation by using the following expansion

$$w(x) = \sum_{k=0}^{\infty} b_k x^k \ . \tag{378}$$

We now try to determine the coefficients b_k. We substitute this into the differential equation above and obtain

$$\sum_{k=1}^{\infty} b_k x^{k-1} \ [(k-1)k + 2(l+1)k] = \sum_{k=0}^{\infty} b_k x^k \ [2(l+1+k) - x_0] \ . \tag{379}$$

We shift k by one in the left hand side, i.e., we substitute $k = k' + 1$ and then drop the prime. This gives

$$\sum_{k=0}^{\infty} b_{k+1} x^k \ [k(k+1) + 2(l+1)(k+1)] = \sum_{k=0}^{\infty} b_k x^k \ [2(l+1+k) - x_0] \ . \tag{380}$$

This gives a recursion:

$$b_{k+1} = \frac{2(k+l+1) - x_0}{(k+1)(k+2(l+1))} \, b_k \ . \tag{381}$$

One can show that if this recursion does not stop, the function $w(x)$ would diverge at $x \to \infty$ so that even $u(x) = x^{l+1} e^{-x} w(x)$ would diverge. Indeed for $k \gg 2l+1$ we get $b_{k+1} \sim \frac{2}{k+1} \, b_k$. This, in turn, gives $w(x) \sim e^{2x}$.

Thus the normalizable solutions are obtained only if the recursion stops. This happens if for some $k = N$, where $N = 0, 1, 2, \ldots$, if the following relation holds

$$2(N + l + 1) = x_0 \ . \tag{382}$$

For this we need

$$\frac{x_0}{2} = Z \sqrt{\frac{R_y}{|E|}} = \frac{Z}{\eta a_0} = N + l + 1 \ . \tag{383}$$

We obtain

$$E = -\frac{Z^2 R_y}{(N+l+1)^2} \ , \tag{384}$$

and, equivalently

$$\eta = \frac{1}{a_0} \, \frac{Z}{N+l+1} \ . \tag{385}$$

We get an important result: for every $N = 0, 1, 2, 3, \ldots$ and every $l = 0, 1, 2, 3, \ldots$ we obtain a solution $w_{N,l}(x)$ and, thus, $u_{N,l}(x) = x^{l+1}e^{-x}w_{N,l}(x)$ whose energy is given by (384). The function $w_{N,l}(x)$ os a polynomial of grade N. The quantum numbers N and l are independent. The quantum number N is called the *radial quantum number*. However, there are multiple combinations of N and l leading to the same energy. One defines instead the new quantum number

$$n \equiv N + l + 1 \ , \tag{386}$$

called the *principal quantum number*, so that

$$E_n = -\frac{Z^2 R_y}{n^2} \ . \tag{387}$$

However n and l are no longer independent. We observe the important restriction $n \geq l+1$. Alternatively, one can first fix $n = 1, 2, 3, \ldots$ and then demand $l \leq n - 1$.

The ultimate expression for the eigenstates of the Hamiltonian can be cast in the following form:

$$|n, l, m\rangle = \psi_{n,l,m}(\mathbf{r}) = R_{n,l}(r)Y_{l,m}(\theta, \phi) \ . \tag{388}$$

For the radial part $R_{n,l}$ we have

$$R_{n,l}(r) = \frac{1}{r}\,(\eta_n r)^{l+1} e^{-\eta_n r} w_{N,l}(\eta_n r) \ , \tag{389}$$

where $\eta_n \equiv Z/(na_0)$. Since $N = n - l - 1$ and $w_{N,l}$ is the polynomial of grade N we observe that $R_{n,l}(r)$ as an exponential $e^{-\eta_n r}$ times a polynomial of grade $n - 1$. We also observe that for $l > 0$, the radial functions $R_{n,l}(r)$ vanish at $r = 0$. Further information about the functions $R_{n,l}(r)$ is provided in Appendix F.

The ground state is obtained at $n = 1$ with energy $E_1 = -Z^2 R_y$. It is not degenerate as only $l = 0, m = 0$ are possible. The first excited state is $n = 2$ with energy $E_2 = -Z^2 R_y/4$. Here $l = 0, m = 0$ and $l = 1, m = -1, 0, 1$ are possible. The degeneracy is, therefore, 4. For an arbitrary n the degeneracy is given by

$$g_n = \sum_{l=0}^{n-1}(2l + 1) = n(n - 1) + n = n^2 \ . \tag{390}$$

2. Scattering states

At $E > 0$ there is a continuum of states. Since $V_{\rm eff}(r \to \infty) \to 0$, the Schrödinger equation (367)

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + V_{\rm eff}(r)\right] u(r) = E\, u(r) \ . \tag{391}$$

becomes asymptotically (at $r \to \infty$) an equation for a free particle

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}\, u(r) = E\, u(r) \ . \tag{392}$$

This can be trivially solved as $u(r) = Ae^{-ikr} + Be^{ikr}$, where $\hbar k = \sqrt{2mE}$. The part $\propto e^{-ikr}$ is the incoming wave (we can thus choose, e.g., $A = 1$) and the part $\propto e^{ikr}$ is the reflected wave. Since the wave function cannot penetrate into the domain $r < 0$, it must be fully reflected, i.e., $|B| = |A| = 1$. To find the full solution and, in particular, the scattering phase $B = e^{i\delta}$ is an interesting and non-trivial problem. Yet, it is clear that for every $E = \frac{\hbar^2 k^2}{2m} > 0$ and every l there is a solution, which we call $u_{k,l}(r)$. Thus we have a continuum of scattering states

$$\psi_{k,l,m}(\mathbf{r}) = R_{k,l}(r) Y_{l,m}(\theta, \phi) \ , \tag{393}$$

where $R_{k,l}(r) \equiv u_{k,l}(r)/r$.

F. Complete set of commuting observables (CSCO)

We have characterized the eigenstates of the hydrogen atom Hamiltonian with three quantum numbers $|n, l, m\rangle$ for $E < 0$ and $|k, l, m\rangle$ for $E > 0$. These three correspond to three commuting operators $\hat{H}$, $\hat{\boldsymbol{L}}^2$, $\hat{L}_z$:

$$\hat{H}\,|n, l, m\rangle = E_n\,|n, l, m\rangle \quad , \quad E_n = -Z^2 R_y/n^2 \ , \tag{394}$$

or

$$\hat{H}\,|k, l, m\rangle = E_k\,|k, l, m\rangle \quad , \quad E_k = \frac{\hbar^2 k^2}{2m} \tag{395}$$

and

$$\hat{\boldsymbol{L}}^2\,|n, l, m\rangle = \hbar^2 l(l+1)\,|n, l, m\rangle \quad \text{or} \quad \hat{\boldsymbol{L}}^2\,|k, l, m\rangle = \hbar^2 l(l+1)\,|k, l, m\rangle \ , \tag{396}$$

and

$$\hat{L}_z\,|n, l, m\rangle = \hbar m\,|n, l, m\rangle \quad \text{or} \quad \hat{L}_z\,|k, l, m\rangle = \hbar m\,|k, l, m\rangle \ . \tag{397}$$

Specifying the three eigenvalues of $\hat{H}$, $\hat{\boldsymbol{L}}^2$ and $\hat{L}_z$, one identifies the unique eigenstate corresponding to these eigenvalues. There are no degeneracies left. The three operators $\hat{H}$, $\hat{\boldsymbol{L}}^2$ and $\hat{L}_z$ thus form the so-called *complete set of commuting observables* (CSCO).

Formal definition: a set of (independent) Hermitian operators $\hat{A}$, $\hat{B}$, $\hat{C}$, ... is called CSCO if all these operators pairwise commute and their mutual eigenbasis is not degenerate. That is, there exists a basis $|n\rangle$, such that $\hat{A}\,|n\rangle = a_n\,|n\rangle$, $\hat{B}\,|n\rangle = b_n\,|n\rangle$ etc. The sets of eigenvalues $(a_n, b_n, c_n, \ldots)$ are all different. There are no two states $|n_1\rangle$ and $|n_2\rangle$ such that $(a_{n_1}, b_{n_1}, c_{n_1}, \ldots) = (a_{n_2}, b_{n_2}, c_{n_2}, \ldots)$. It is convenient to denote the states using their eigenvalues, i.e. $|a, b, c, \ldots\rangle$.

What if we already have a complete set (CSCO) and find another operator $\hat{M}$ that commutes with all the operators of the set? Then $\hat{M}$ is not independent of $\hat{A}$, $\hat{B}$, $\hat{C}$, ... Indeed the eigenstate $|a, b, c, \ldots\rangle$ must be also an eigenstate of $\hat{M}$ with some eigenvalue m. Since the set $(a, b, c, \ldots)$ identifies the state uniquely, the eigenvalue m must be a single-valued function of $(a, b, c, \ldots)$, i.e,

$$\hat{M}\,|a, b, c, \ldots\rangle = m(a, b, c, \ldots)\,|a, b, c, \ldots\rangle \ . \tag{398}$$

Then, however, $\hat{M} = m(\hat{A}, \hat{B}, \hat{C}, \ldots)$.

What if we have a set of commuting observables, but there is still some degeneracy. Then, there must exist yet another hermitian operator, which commutes with the given set and is independent of it. This extra operator should lift (at least partially) the remaining degeneracy.

VII. SYMMETRIES, UNITARY OPERATORS, CONSERVATION LAWS

Unitary operators satisfy

$$\hat{U}^\dagger = \hat{U}^{-1} \ . \tag{399}$$

If we transform two states using $\hat{U}$, i.e., $|\psi'\rangle = \hat{U}\,|\psi\rangle$ and $|\phi'\rangle = \hat{U}\,|\phi\rangle$, we obtain

$$\langle\phi'|\psi'\rangle = \left\langle \hat{U}\phi | \hat{U}\psi \right\rangle = \left\langle \phi | \hat{U}^\dagger \hat{U}\psi \right\rangle = \langle\phi|\psi\rangle \ . \tag{400}$$

That is a unitary transformation conserves the scalar product.

A. Time evolution operator

A very important unitary operator is the time evolution operator:

$$\hat{U}(t) = \exp\left[-\frac{i}{\hbar}\, t\hat{H}\right] \tag{401}$$

This should be simply understood as

$$\hat{U}(t) = \sum_{n=0}^{\infty} \frac{1}{n!} \left(-\frac{i}{\hbar}\right)^n t^n \hat{H}^n \ . \tag{402}$$

Consider $|\psi(t)\rangle = \hat{U}(t)\,|\psi_0\rangle$. Then

$$i\hbar \frac{\partial}{\partial t}\,|\psi(t)\rangle = i\hbar \left[\frac{\partial}{\partial t}\,\hat{U}(t)\right] |\psi_0\rangle \tag{403}$$

Further

$$\begin{aligned}
\frac{\partial}{\partial t}\,\hat{U}(t) \ &= \ \sum_{n=1}^{\infty} \frac{1}{n!} \left(-\frac{i}{\hbar}\right)^n n\, t^{n-1} \hat{H}^n \\
&= \ \left(-\frac{i}{\hbar}\right) \hat{H} \sum_{n=1}^{\infty} \frac{1}{(n-1)!} \left(-\frac{i}{\hbar}\right)^{n-1} t^{n-1} \hat{H}^{n-1} \\
&= \ \left(-\frac{i}{\hbar}\right) \hat{H} \sum_{n=0}^{\infty} \frac{1}{n!} \left(-\frac{i}{\hbar}\right)^n t^n \hat{H}^n = \left(-\frac{i}{\hbar}\right) \hat{H}\, \hat{U}(t) \ .
\end{aligned} \tag{404}$$

Thus

$$i\hbar \frac{\partial}{\partial t}\,|\psi(t)\rangle = i\hbar \left[\frac{\partial}{\partial t}\,\hat{U}(t)\right] |\psi_0\rangle = \hat{H}\,\hat{U}(t)\ |\psi_0\rangle = \hat{H}\,|\psi(t)\rangle \ \ . \tag{405}$$

We have recovered the Schrödinger equation. Thus, indeed, $\hat{U}(t)$ is the time evolution operator.

B. Rotational symmetry

Consider now an infinitesimal rotation around the axis described by a unit length vector $\mathbf{n}$ by an angle $\delta\phi$. Such a rotation is described by

$$\mathbf{r} \to \mathbf{r}' = \mathbf{r} + \delta\mathbf{r} \ , \quad \text{where} \quad \delta\mathbf{r} = \delta\phi \cdot (\mathbf{n} \times \mathbf{r}) \ . \tag{406}$$

Consider now a "passive" transformation of the wave functions: $\psi(\mathbf{r}) \to \psi'(\mathbf{r})$, such that $\psi'(\mathbf{r}) = \psi(\mathbf{r}')$. It is passive because we rotate the coordinate system. (An equivalent

"active" transformation would satisfy $\psi'(\mathbf{r}') = \psi(\mathbf{r})$.) For an infinitesimal rotation the passive transformation reads

$$\psi'(\mathbf{r}) = \psi(\mathbf{r} + \delta\mathbf{r}) \ . \tag{407}$$

We now look for a unitary transformation $U_{\mathbf{n}}(\delta\phi)$ that transforms $\psi(\mathbf{r})$ into $\psi'(\mathbf{r})$, i.e. $\psi'(\mathbf{r}) = U_{\mathbf{n}}(\delta\phi)\psi(\mathbf{r})$. We obtain

$$\begin{aligned} U_{\mathbf{n}}(\delta\phi)\psi(\mathbf{r}) &= \psi(\mathbf{r} + \delta\mathbf{r}) \approx \psi(\mathbf{r}) + \delta\mathbf{r} \cdot \boldsymbol{\nabla}\psi(\mathbf{r}) = \psi(\mathbf{r}) + \delta\phi\,(\mathbf{n} \times \mathbf{r}) \cdot \boldsymbol{\nabla}\psi(\mathbf{r}) \\ &= \psi(\mathbf{r}) + \delta\phi\,\mathbf{n} \cdot (\mathbf{r} \times \boldsymbol{\nabla})\,\psi(\mathbf{r}) = [1 + \delta\phi\,\mathbf{n} \cdot (\mathbf{r} \times \boldsymbol{\nabla})]\,\psi(\mathbf{r}) \\ &= \left[1 + \frac{i}{\hbar}\,\delta\phi\,\mathbf{n} \cdot (\mathbf{r} \times \hat{\mathbf{p}})\right]\psi(\mathbf{r}) = \left[1 + \frac{i}{\hbar}\,\delta\phi\,\mathbf{n} \cdot \hat{\boldsymbol{L}}\right]\psi(\mathbf{r}) \ , \end{aligned} \tag{408}$$

and

$$U_{\mathbf{n}}(\delta\phi) \approx \left[1 + \frac{i}{\hbar}\,\delta\phi\,\mathbf{n} \cdot \hat{\boldsymbol{L}}\right] \ . \tag{409}$$

Next we calculate the unitary transformation corresponding to a rotation by an arbitrary angle ϕ. We have

$$U_{\mathbf{n}}(\phi + \delta\phi) = U_{\mathbf{n}}(\delta\phi)U_{\mathbf{n}}(\phi) = \left[1 + \frac{i}{\hbar}\,\delta\phi\,\mathbf{n} \cdot \hat{\boldsymbol{L}}\right]U_{\mathbf{n}}(\phi) \ . \tag{410}$$

This gives

$$U_{\mathbf{n}}(\phi + \delta\phi) - U_{\mathbf{n}}(\phi) = \frac{i}{\hbar}\,\delta\phi\,\mathbf{n} \cdot \hat{\boldsymbol{L}}\,U_{\mathbf{n}}(\phi) \ . \tag{411}$$

Further

$$\frac{U_{\mathbf{n}}(\phi + \delta\phi) - U_{\mathbf{n}}(\phi)}{\delta\phi} = \frac{i}{\hbar}\,\mathbf{n} \cdot \hat{\boldsymbol{L}}\,U_{\mathbf{n}}(\phi) \ . \tag{412}$$

In the limit $\delta\phi \to 0$ this gives

$$\partial_\phi U_{\mathbf{n}}(\phi) = \frac{i}{\hbar}\,\mathbf{n} \cdot \hat{\boldsymbol{L}}\,U_{\mathbf{n}}(\phi) \ . \tag{413}$$

Finally

$$U_{\mathbf{n}}(\phi) = \exp\left[\frac{i}{\hbar}\,\phi\,\mathbf{n} \cdot \hat{\boldsymbol{L}}\right] \ . \tag{414}$$

Assume an operator $\hat{A}$ transforms $\psi(\mathbf{r})$ to $\phi(\mathbf{r})$. Which operator would transform ψ' to ϕ'? We have $\phi = \hat{A}\psi$, then

$$\phi' = U\phi = U\hat{A}\psi = U\hat{A}U^{-1}U\psi = U\hat{A}U^{-1}\psi' \ . \tag{415}$$

Therefore

$$\hat{A}' = U\hat{A}U^{-1} \ . \tag{416}$$

Analogously, if ψ satisfies the Schrödinger equation $i\hbar\partial_t\psi = H\psi$, the transformed function would satisfy

$$i\hbar\partial_t\psi' = i\hbar\partial_t U\psi = Ui\hbar\partial_t\psi = U\hat{H}\psi = U\hat{H}U^{-1}\psi' \ . \tag{417}$$

Thus the Hamiltonian transforms as $\hat{H}' = U\hat{H}U^{-1} = U\hat{H}U^{\dagger}$.

What is the condition that the Hamiltonian in the new frame is the same as the Hamiltonian in the old frame, $\hat{H}' = \hat{H}$. We have

$$\exp\left[\frac{i}{\hbar}\,\phi\,\mathbf{n}\cdot\hat{\boldsymbol{L}}\right]\hat{H}\exp\left[-\frac{i}{\hbar}\,\phi\,\mathbf{n}\cdot\hat{\boldsymbol{L}}\right] = \hat{H} \ . \tag{418}$$

This is fulfilled if $[\mathbf{n}\cdot\hat{\boldsymbol{L}}, \hat{H}] = 0$. Should this symmetry be valid for arbitrary $\mathbf{n}$ the condition reads $[\hat{\boldsymbol{L}}, \hat{H}] = 0$. Thus, if the Hamiltonian is rotational symmetric, i.e, it does not change upon rotation of the coordinate frame, it commutes with the three components of $\hat{\boldsymbol{L}}$. If for example the Hamiltonian is only symmetric with respect to rotations around the $\hat{z}$-axis, it commutes with $\hat{L}_z$.

C. Conservation laws

Observables that commute with the Hamiltonian provide conserved quantities. Indeed, assume $[\hat{A}, \hat{H}] = 0$. Then for the expectation value of $\hat{A}$ in a state $|\psi\rangle$ we get

$$i\hbar\frac{d}{dt}\langle\psi|\,\hat{A}\,|\psi\rangle = \langle\psi|\,\hat{A}\hat{H}\,|\psi\rangle - \langle\psi|\,\hat{H}\hat{A}\,|\psi\rangle = \langle\psi|\,[\hat{A}, \hat{H}]\,|\psi\rangle = 0 \ . \tag{419}$$

Thus, as in the classical mechanics (Noether theorem), symmetries lead to conservation laws. In particular, for central potential, which is symmetric with respect to rotations around arbitrary axis $\mathbf{n}$, all three components $\hat{L}_x$, $\hat{L}_y$, $\hat{L}_z$ are conserved.

VIII. ELECTRON IN AN EXTERNAL ELECTRO-MAGNETIC FIELD. PART I: MAGNETIC MOMENT

In SI system we have the following relation between the electric and magnetic fields and the vector and scalar potentials

$$\mathbf{B} = \boldsymbol{\nabla}\times\mathbf{A} \ , \tag{420}$$

$$\mathbf{E} = -\frac{\partial\mathbf{A}}{\partial t} - \boldsymbol{\nabla}\varphi \ , \tag{421}$$

where the 4-vector potential is given by

$$A^{\mu} = \left(\frac{\varphi}{c}, \mathbf{A}\right) \ . \tag{422}$$

Here $\varphi(\mathbf{r}, t)$ is the scalar potential (sometimes called also U or V) and $\mathbf{A}(\mathbf{r}, t)$ is the vector potential. The Hamiltonian of a particle with charge q and mass m in an external electromagnetic field reads

$$\hat{H} = \frac{\left(\hat{\mathbf{p}} - q\mathbf{A}(\mathbf{r}, t)\right)^2}{2m} + q\varphi(\mathbf{r}, t) \ . \tag{423}$$

The fields $\mathbf{A}$ and ϕ are considered as given and classical (numbers, not operators)

This Hamiltonian follows from the Lagrangian

$$L = \frac{m\mathbf{v}^2}{2} - q\varphi + q\mathbf{v} \cdot \mathbf{A} \ . \tag{424}$$

This is the non-relativistic limit of

$$L = -mc^2\sqrt{1 - \frac{\mathbf{v}^2}{c^2}} - q\varphi + q\mathbf{v} \cdot \mathbf{A} \ . \tag{425}$$

We will concentrate on the case of a constant in space and time magnetic field. We choose the gauge such that

$$\mathbf{A}(\mathbf{r}) = \frac{1}{2}\,\mathbf{B} \times \mathbf{r} \ . \tag{426}$$

This vector potential satisfies the Coulomb gauge condition $\boldsymbol{\nabla} \cdot \mathbf{A} = 0$.

Let us analyze the kinetic energy

$$\begin{aligned} \hat{H}_{\rm kin} \ &= \ \frac{1}{2m}\,\left(-i\hbar\boldsymbol{\nabla} - q\mathbf{A}\right)^2 = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + \frac{i\hbar q}{2m}\,\mathbf{A} \cdot \boldsymbol{\nabla} + \frac{i\hbar q}{2m}\,\boldsymbol{\nabla} \cdot \mathbf{A} + \frac{q^2\mathbf{A}^2}{2m} \\ &= \ -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + \frac{i\hbar q}{m}\,\mathbf{A} \cdot \boldsymbol{\nabla} + \frac{q^2\mathbf{A}^2}{2m} = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + H_{\rm p} + H_{\rm d} \ . \end{aligned} \tag{427}$$

where we have used $\boldsymbol{\nabla} \cdot \mathbf{A} = 0$. Let us look closer at the so-called "paramagnetic" term

$$H_{\rm p} = \frac{i\hbar q}{m}\,\mathbf{A} \cdot \boldsymbol{\nabla} = \frac{i\hbar q}{2m}\,(\mathbf{B} \times \mathbf{r}) \cdot \boldsymbol{\nabla} = \frac{i\hbar q}{2m}\mathbf{B} \cdot (\mathbf{r} \times \boldsymbol{\nabla}) = -\frac{q}{2m}\mathbf{B} \cdot \hat{\mathbf{L}} \ . \tag{428}$$

One introduces here the magnetic moment of the particle

$$\hat{\boldsymbol{\mu}} = \frac{q}{2m}\hat{\boldsymbol{L}} \ , \tag{429}$$

so that the paramagnetic term reads

$$H_{\rm p} = -\hat{\boldsymbol{\mu}} \cdot \mathbf{B} \ . \tag{430}$$

For an electron $q = -|e|$ (e is sometimes considered positive or negative (e.g., in Schwabl $e < 0$), but the charge of an electron is definitely negative) and $m = m_e$. We multiply and divide by $\hbar$:

$$\hat{\boldsymbol{\mu}} = -\frac{\hbar|e|}{2m_e}\frac{\hat{\boldsymbol{L}}}{\hbar} \ . \tag{431}$$

The combination

$$\mu_B \equiv \frac{\hbar|e|}{2m_e} \sim 9.27 \times 10^{-24}\mathrm{J/T} \ . \tag{432}$$

is called the Bohr magneton. Thus we get

$$\hat{\boldsymbol{\mu}} = -\mu_B\frac{\hat{\boldsymbol{L}}}{\hbar} \ . \tag{433}$$

The minus sign here is due to the negative charge of the electron.

The last term of (427) is called "diamagnetic". It can be written as

$$H_{\mathrm{d}} = \frac{q^2\mathbf{A}^2}{2m} = \frac{q^2}{8m}\left(\mathbf{B}\times\mathbf{r}\right)^2 = \frac{q^2}{8m}\left(\mathbf{B}^2\mathbf{r}^2 - (\mathbf{B}\cdot\mathbf{r})^2\right) \ . \tag{434}$$

A. "Normal" Zeeman effect

Consider the hydrogen atom and assume $\mathbf{B} = B\mathbf{e}_z$. Then

$$H_{\mathrm{p}} = -\frac{q}{2m}B\hat{L}_z \ , \tag{435}$$

and

$$H_{\mathrm{d}} = \frac{q^2B^2}{8m}(x^2+y^2) \ . \tag{436}$$

To estimate the relevant importance of these two terms in the hydrogen atom we replace $\hat{L}_z$ by $\hbar$, whereas x^2+y^2 we replace by the Bohr radius squared a_0^2, where

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} \approx 0.53\times 10^{-10}\mathrm{m} \ . \tag{437}$$

Taking into account $|q| = |e|$ we get

$$\frac{H_d}{H_p} \sim \frac{|e|Ba_0^2}{4\hbar} \sim \frac{B}{10^6\mathrm{T}} \ . \tag{438}$$

That is H_{d} can become important at $B \sim 10^6$T.

Substituting $q = -|e|$ we get

$$H_p = \mu_B B\hat{L}_z/\hbar \ . \tag{439}$$

Consider now the hydrogen atom in a constant magnetic field. The total Hamiltonian is $H = H_0 + H_p$, where $H_0 = \frac{\mathbf{p}^2}{2m} - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$. We have $[H_p, H_0] = 0$ and the states $|n, l, m\rangle$ are eigenstates of both H_0 and H_p and, thus, of H. The eigenenergies are now given by

$$E_{n,l,m} = -\frac{R_y}{n^2} + \mu_B B m \ . \tag{440}$$

The shell of $2l + 1$ states with given n and l is now no longer degenerate but is split into a staircase of states with energy distance $\mu_B B$ between them.

IX. SPIN

A. Stern-Gerlach experiment

Otto Stern und Walther Gerlach (1922). The experiment was done with silver atoms, yet one could imagine it was done with hydrogen atoms. Assume the magnetic field is slowly $\mathbf{r}$-dependent, but changes very little on the scale of Bohr radius. Then, one can use the energy $-\boldsymbol{\mu} \cdot \mathbf{B}(\mathbf{r})$ and a potential energy of the atom in the magnetic field. The magnetic moment in that of the electron. The proton's mass m_p is ~ 1000 times larger than that of the electron. Thus the magnetic moment of the proton ($\sim \hbar|e|/2m_p$) should be negligible. In the experiment the magnetic field had a gradient in z-direction, so that a force was acting on the atom

$$\mathbf{F} = -\boldsymbol{\nabla}\left(-\boldsymbol{\mu} \cdot \mathbf{B}\right) = \boldsymbol{\nabla}\left(\boldsymbol{\mu} \cdot \mathbf{B}\right) \approx \mu_z \frac{\partial B_z}{\partial z}\, \mathbf{e_z} \ . \tag{441}$$

If the electron is in the ground state $n = 1$, $l = 0$, $m = 0$, the magnetic moment vanishes and there should be no force. Indeed, for the electron we expect

$$\hat{\boldsymbol{\mu}} = -\mu_B \frac{\hat{\boldsymbol{L}}}{\hbar} \ . \tag{442}$$

For $l = 0$ the expectation value of $\hat{\boldsymbol{\mu}}$ vanishes. Yet, in the experiment the atoms were deflected. On one half of them acted a positive force and on the other half a negative force.

B. Spin-1/2 operators

The experiment suggests that an electron has in addition to the orbital angular momentum $\hat{\boldsymbol{L}}$ an internal angular (and magnetic) momentum, which is called spin and is denoted

as $\hat{\mathbf{S}}$. The operators $\hat{S}_x$, $\hat{S}_y$ and $\hat{S}_z$ should satisfy the same commutation relations of the angular momentum, i.e.,

$$[\hat{S}_\alpha, \hat{S}_\beta] = i\hbar\epsilon_{\alpha\beta\gamma}\hat{S}_\gamma \ . \tag{443}$$

As we have seen for the operators $\hat{\boldsymbol{L}}$, this algebra allows for mutual eigenstates of $\hat{\boldsymbol{S}}^2$ and $\hat{S}_z$, with quantum numbers s and m_s so shat

$$\begin{aligned} \hat{\boldsymbol{S}}^2 \left|s, m_s\right\rangle &= \hbar^2 s(s+1) \left|s, m_s\right\rangle \ , \\ \hat{S}_z \left|s, m_s\right\rangle &= \hbar\, m_s \left|s, m_s\right\rangle \ . \end{aligned} \tag{444}$$

Here s can assume the values $0, 1/2, 1, 3/2, \ldots$ and $m_s = -s, -s+1, \ldots, s-1, s$. The experiment suggests that the internal magnetic moment has two possible values. Thus we are forced to choose $s = 1/2$. Thus electrons have spin-1/2. Then $m_s = \pm 1/2$. To shorten the notation we call the state $|s = 1/2, m_s = 1/2\rangle = |\uparrow_z\rangle$ and $|s = 1/2, m_s = -1/2\rangle = |\downarrow_z\rangle$.

This gives

$$\hat{S}_z \left|\uparrow_z\right\rangle = \frac{\hbar}{2} \left|\uparrow_z\right\rangle \quad , \quad \hat{\mathbf{S}}^2 \left|\uparrow_z\right\rangle = \frac{3\hbar^2}{4} \left|\uparrow_z\right\rangle \ , \tag{445}$$

$$\hat{S}_z \left|\downarrow_z\right\rangle = -\frac{\hbar}{2} \left|\downarrow_z\right\rangle \quad , \quad \hat{\mathbf{S}}^2 \left|\downarrow_z\right\rangle = \frac{3\hbar^2}{4} \left|\downarrow_z\right\rangle \ . \tag{446}$$

We can easily calculate how the operators $\hat{S}_x$ and $\hat{S}_y$ act on the states $|\uparrow_z\rangle$ and $|\downarrow_z\rangle$. We form $\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y$. From (337) we obtain

$$\begin{aligned} \hat{S}_+ \left|\downarrow_z\right\rangle &= \hat{S}_+ \left|s = 1/2, m_s = -1/2\right\rangle = \hbar\sqrt{s(s+1) - m_s(m_s+1)} \left|1/2, 1/2\right\rangle \\ &= \hbar \left|1/2, 1/2\right\rangle = \hbar \left|\uparrow_z\right\rangle \ . \end{aligned} \tag{447}$$

From (338) we get

$$\begin{aligned} \hat{S}_- \left|\uparrow_z\right\rangle &= \hat{S}_- \left|s = 1/2, m_s = 1/2\right\rangle = \hbar\sqrt{s(s+1) - m_s(m_s-1)} \left|1/2, -1/2\right\rangle \\ &= \hbar \left|1/2, -1/2\right\rangle = \hbar \left|\downarrow_z\right\rangle \ . \end{aligned} \tag{448}$$

In addition $\hat{S}_+ \left|\uparrow_z\right\rangle = 0$ and $\hat{S}_- \left|\downarrow_z\right\rangle = 0$.

These relations allow us to express $\hat{S}_x$, $\hat{S}_y$, and $\hat{S}_z$ in the matrix form. Assume the spin is in the state $|\psi\rangle = \alpha \left|\uparrow_z\right\rangle + \beta \left|\downarrow_z\right\rangle$. We can represent such a state as

$$|\psi\rangle = \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \ . \tag{449}$$

In particular

$$|\uparrow_z\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad , \quad |\downarrow_z\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \ . \tag{450}$$

Then

$$\hat{S}_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad , \quad \hat{S}_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad , \quad \hat{S}_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \ . \tag{451}$$

This further gives

$$\hat{S}_x = \frac{\hat{S}_+ + \hat{S}_-}{2} = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad , \quad \hat{S}_y = \frac{\hat{S}_+ - \hat{S}_-}{2i} = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \ . \tag{452}$$

We define 3 Pauli matrices

$$\sigma_x \equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad , \quad \sigma_y \equiv \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad , \quad \sigma_z \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \ . \tag{453}$$

and also

$$\sigma_+ \equiv \frac{\sigma_x + i\sigma_y}{2} = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad , \quad \sigma_- \equiv \frac{\sigma_x - i\sigma_y}{2} = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \ . \tag{454}$$

For the spin-1/2 operators we obtain

$$\hat{\boldsymbol{S}} = \frac{\hbar}{2} \boldsymbol{\sigma} \quad , \quad \hat{S}_+ = \hbar\sigma_+ \quad , \quad \hat{S}_- = \hbar\sigma_- \ . \tag{455}$$

As we have seen in the discussion of the orbital angular momentum $\hat{\boldsymbol{L}}$ one cannot find wave functions $\psi(\mathbf{r})$ that would correspond to $l = 1/2$. The solution is to postulate that the wave function of an electron is a 2-component spinor

$$|\psi\rangle = \begin{pmatrix} \psi_\uparrow(\mathbf{r}) \\ \psi_\downarrow(\mathbf{r}) \end{pmatrix} \ . \tag{456}$$

In the absence of the spin-orbit coupling (very important relativistic effect) the orbital $\mathbf{r}$-dependence and the spin-dependence are disentangled. So, an electron in the orbital state $\psi(\mathbf{r})$ and in the spin state $|\uparrow\rangle$ would be described by the wave function $|\psi, \uparrow_z\rangle = \psi(\mathbf{r}) \begin{pmatrix} 1 \\ 0 \end{pmatrix}$.

C. Magnetic moment of electron, Landé factor

Naively one would think that the spin part of the angular momentum would provide a corresponding contribution to the magnetic moment. That is we would have

$$\hat{\boldsymbol{\mu}}_{\text{orbital}} = -\mu_B \frac{\hat{\boldsymbol{L}}}{\hbar} \tag{457}$$

and a similar relation for $\hat{\boldsymbol{\mu}}_{\text{spin}}$. However, the experiment shows that the correct relation is

$$\hat{\boldsymbol{\mu}}_{\text{spin}} = -g\,\mu_B \frac{\hat{\boldsymbol{S}}}{\hbar}\ , \tag{458}$$

where $g = 2$ is the Landé factor. That is, for the spin the ratio between the magnetic momentum and the angular momentum (called gyromagnetic ratio) is twice larger than for the orbital angular motion. This invalidates a naive idea that the electron is a small charged ball spinning around. The Landé factor is very nicely explained in the relativistic quantum mechanics (Dirac equation).

The total magnetic moment of the electron is given by $\hat{\boldsymbol{\mu}} = \hat{\boldsymbol{\mu}}_{\text{orbital}} + \hat{\boldsymbol{\mu}}_{\text{spin}}$.

$$\hat{\boldsymbol{\mu}} = -\mu_B \frac{\hat{\boldsymbol{L}} + g\hat{\boldsymbol{S}}}{\hbar}\ . \tag{459}$$

D. Zeeman effect

To accommodate the spin and its magnetic moment we are forced to accept a new Hamiltonian of an electron in the external electromagnetic field

$$\hat{H} = \frac{\left(\hat{\mathbf{p}} - q\mathbf{A}(\mathbf{r},t)\right)^2}{2m} + q\varphi(\mathbf{r},t) - \hat{\boldsymbol{\mu}}_{\text{spin}} \cdot \mathbf{B}\ . \tag{460}$$

Here $q = -e$ (and $e > 0$), $m = m_e$. We thus obtain

$$\frac{\left(\hat{\mathbf{p}} + e\mathbf{A}(\mathbf{r},t)\right)^2}{2m} - e\varphi(\mathbf{r},t) + \frac{g\mu_B}{\hbar}\hat{\mathbf{S}} \cdot \mathbf{B}\ , \tag{461}$$

where $\mu_B = \frac{\hbar e}{2m}$. This Hamiltonian is called Pauli Hamiltonian. For the hydrogen atom in a constant magnetic field we obtain

$$H = H_0 + \frac{\mu_B}{\hbar}\left(\hat{\boldsymbol{L}} + g\,\hat{\boldsymbol{S}}\right) \cdot \mathbf{B}\ , \tag{462}$$

where the diamagnetic term is neglected. We now assume $\mathbf{B} = B\mathbf{e_z}$. Then

$$H = H_0 + \frac{\mu_B B}{\hbar}\left(\hat{L}_z + g\hat{S}_z\right)\ , \tag{463}$$

The state with quantum numbers $|n, l, m, m_s\rangle$ has then the energy

$$E_{n,l,m,m_s} = -\frac{R_y}{n^2} + \mu_B B(m + g m_s) \ . \tag{464}$$

Here $m = -l, -l+1, \ldots, l-1, l$ and $m_s = \pm 1/2$.

E. Stern-Gerlach experiment as strong, projective measurement

Stern-Gerlach experiment represents a paradigmatic example of a strong projective measurement. Theory of such measurements was developed by John von Neumann (Book: "Mathematical foundations of quantum mechanics".) The main idea: the measurement apparatus is also a quantum mechanical system. Let us consider spin-1/2 as a quantum system that is being measured. Before the measurement the spin is in the state $|\psi\rangle = \alpha\,|\uparrow_z\rangle + \beta\,|\downarrow_z\rangle$ (the normalization requires $|\alpha|^2 + |\beta|^2 = 1$). The measurement apparatus is in the state $|M_0\rangle$. The state of the total system is a direct product (a product state) $(\alpha\,|\uparrow_z\rangle + \beta\,|\downarrow_z\rangle) \otimes |M_0\rangle$. During the measurement the spin and the measurement apparatus are made to interact. The interaction Hamiltonian is proportional to the measured observable ($\hat{S}_z$ in our case) so that at the end the state of the whole system reads $\alpha\,|\uparrow_z\rangle \otimes |M_\uparrow\rangle + \beta\,|\downarrow_z\rangle \otimes |M_\downarrow\rangle$. The basis states $|\uparrow_z\rangle$ and $|\downarrow_z\rangle$ are eigenstates of the observable that is being measured, i.e., $\hat{S}_z$. Moreover, if the interaction was strong enough or the measurement was long enough the states $|M_\uparrow\rangle$ and $|M_\downarrow\rangle$ are (almost) orthogonal, $\langle M_\downarrow | M_\uparrow\rangle = 0$. In this case one says a strong projective measurement has happened. If one observed the measurement apparatus in state $|M_\uparrow\rangle$, it automatically means that the spin is in (is projected into) the state $|\uparrow_z\rangle$. This happens with probability $|\alpha|^2$. Analogously for the state $|\downarrow_z\rangle$. The states of the type $\alpha\,|\uparrow_z\rangle \otimes |M_\uparrow\rangle + \beta\,|\downarrow_z\rangle \otimes |M_\downarrow\rangle$ are called entangled states. An entangled state cannot be presented as a product state of the spin and the meter. It means it cannot be presented as $|\psi'\rangle \otimes |M'\rangle$.

The measurement problem is, actually, not solved. Indeed, we did not describe how the state of the measurement apparatus should be "observed". This would require another quantum measurement by yet another measurement apparatus. Von Neumann suggested a sequence of such measurements until the result is obvious.

In the Stern-Gerlach experiment the role of the measurement apparatus is played by the position $\mathbf{r}$ of the atom. The interaction Hamiltonian is $\frac{g\mu_B}{\hbar}\hat{\mathbf{S}} \cdot \mathbf{B}$. If the field $\mathbf{B}$ is along

the z-axis, the interaction Hamiltonian is proportional to $\hat{S}_z$. Thus, $\hat{S}_z$ is being measured. Before the measurement the state of the atom is $\psi(\mathbf{r})\begin{pmatrix}\alpha\\ \beta\end{pmatrix}$. After the measurement the state becomes $\begin{pmatrix}\alpha\psi_\uparrow(\mathbf{r})\\ \beta\psi_\downarrow(\mathbf{r})\end{pmatrix}$. The normalized wave functions $\psi_\uparrow$ and $\psi_\downarrow$ are localized around two very different points, and, thus, are almost orthogonal.

1. Repeated measurements

Assume the flux of atoms that were deflected up (state $|\uparrow_z\rangle$) is further let into a second Stern-Gerlach device that measures again $\hat{S}_z$. Clearly all the atoms (100%) will be deflected up in the second device.

Assume now the second Stern-Gerlach device measures $\hat{S}_x$. That is the magnetic field in the second device is along x-axis. The state of the atoms $|\uparrow_z\rangle$ at the entrance to the second device should now be expanded in the basis $|\uparrow_x\rangle$, $|\downarrow_x\rangle$. These two states are the eigenstates of $\hat{S}_x$ such that

$$\hat{S}_x\,|\uparrow_x\rangle = \frac{\hbar}{2}\,|\uparrow_x\rangle \quad , \quad \hat{S}_x\,|\downarrow_x\rangle = -\frac{\hbar}{2}\,|\uparrow_x\rangle \ . \tag{465}$$

These states are easy to find. These are the eigenstates of the Pauli matrix σ_x. We obtain

$$|\uparrow_x\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\ 1\end{pmatrix} = \frac{1}{\sqrt{2}}\left(|\uparrow_z\rangle + |\downarrow_z\rangle\right) \ . \tag{466}$$

Similarly

$$|\downarrow_x\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\ -1\end{pmatrix} = \frac{1}{\sqrt{2}}\left(|\uparrow_z\rangle - |\downarrow_z\rangle\right) \ . \tag{467}$$

From this we obtain

$$|\uparrow_z\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow_x\rangle + |\downarrow_x\rangle\right) \ . \tag{468}$$

The second measurement, thus, will split the atoms $50\% - 50\%$.

F. Spin rotation

In analogy to the unitary operator (414), describing the (passive) transformation of the wave function upon rotation of the system of coordinates, for the spin-1/2 wave function

the corresponding transformation reads

$$U_{\mathbf{n}}(\phi) = \exp\left[\frac{i}{\hbar}\,\phi\,\mathbf{n}\cdot\hat{\boldsymbol{S}}\right] = \exp\left[\frac{i}{2}\,\phi\,\mathbf{n}\cdot\hat{\boldsymbol{\sigma}}\right] \ . \tag{469}$$

Using the properties of the Pauli matrices we obtain

$$U_{\mathbf{n}}(\phi) = \cos(\phi/2) + i\mathbf{n}\cdot\boldsymbol{\sigma}\,\sin(\phi/2) \ . \tag{470}$$

Interestingly, a rotation by $\phi = 2\pi$ produces an original wave function multiplied by -1.

G. Interacting spins, triplet and singlet

Consider two spin-1/2 particles. We concentrate only on the spin degrees of freedom. Assume the Hamiltonian reads

$$\hat{H} = \frac{J}{\hbar^2}\,\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_2 \ . \tag{471}$$

Here J is the coupling constant of dimension energy. The Hilbert state is 4-dimensional and we can use the basis $|\uparrow\uparrow\rangle$, $|\downarrow\uparrow\rangle$, $|\uparrow\downarrow\rangle$, $|\downarrow\downarrow\rangle$. Not all of these are the eigenstates of the Hamiltonian. On the other hand one can observe that the total spin

$$\hat{\mathbf{S}} \equiv \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2 \ , \tag{472}$$

commutes with the Hamiltonian. Thus, it might be profitable to find the mutual eigenstates of $\hat{\mathbf{S}}^2$ and $\hat{S}_z$.

We first inspect $\hat{S}_z$:

$$\hat{S}_z\,|\uparrow\uparrow\rangle = \hbar\,|\uparrow\uparrow\rangle \ , \tag{473}$$

$$\hat{S}_z\,|\uparrow\downarrow\rangle = 0 \ , \tag{474}$$

$$\hat{S}_z\,|\downarrow\uparrow\rangle = 0 \ , \tag{475}$$

$$\hat{S}_z\,|\downarrow\downarrow\rangle = -\hbar\,|\downarrow\downarrow\rangle \ . \tag{476}$$

Further, using

$$\hat{\mathbf{S}}^2 = \hat{\mathbf{S}}_1^2 + \hat{\mathbf{S}}_2^2 + 2\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_2 = \frac{3}{2}\hbar^2 + 2\hat{S}_{1,z}\hat{S}_{2,z} + \hat{S}_{1,+}\hat{S}_{2,-} + \hat{S}_{1,-}\hat{S}_{2,+} \ , \tag{477}$$

we obtain

$$\hat{\mathbf{S}}^2\,|\uparrow\uparrow\rangle = \left(\frac{3}{2}\hbar^2 + 2\left(\frac{\hbar}{2}\right)^2\right)|\uparrow\uparrow\rangle = 2\hbar^2\,|\uparrow\uparrow\rangle \ . \tag{478}$$

$$\hat{\mathbf{S}}^2 \left|\downarrow\downarrow\right\rangle = \left(\frac{3}{2}\hbar^2 + 2\left(\frac{\hbar}{2}\right)^2\right)\left|\downarrow\downarrow\right\rangle = 2\hbar^2 \left|\downarrow\downarrow\right\rangle \ . \tag{479}$$

Thus, the state $|\uparrow\uparrow\rangle$ corresponds to $s = 1$ and $m_s = 1$. Accordingly, the state $|\downarrow\downarrow\rangle$ corresponds to $s = 1$ and $m_s = -1$. To obtain the state $s = 1, m_s = 0$ we should act with $\hat{S}_+ = \hat{S}_{1,+} + \hat{S}_{2,+}$ on the state $|\downarrow\downarrow\rangle = |s = 1, m_s = -1\rangle$. We obtain

$$\hat{S}_+ \left|\downarrow\downarrow\right\rangle = \hbar \left|\uparrow\downarrow\right\rangle + \hbar \left|\downarrow\uparrow\right\rangle = \hbar\sqrt{s(s+1) - m_s(m_s+1)}\,|s = 1, m_s = 0\rangle = \sqrt{2}\hbar\,|s = 1, m_s = 0\rangle \ . \tag{480}$$

Thus, we have obtained three states corresponding to $s = 1$, called *triplet* states

$$\begin{aligned} |s = 1, m_s = 1\rangle &= |\uparrow\uparrow\rangle \ , \\ |s = 1, m_s = 0\rangle &= \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right) \ , \\ |s = 1, m_s = -1\rangle &= |\downarrow\downarrow\rangle \ . \end{aligned} \tag{481}$$

The remaining state, called *singlet* is given by

$$|s = 0, m_s = 0\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right) \ . \tag{482}$$

It is easy to see that

$$\hat{\mathbf{S}}^2 \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right) = 0 \ , \tag{483}$$

and

$$\hat{S}_z \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right) = 0 \ . \tag{484}$$

Finally, to find the eigenenergies of $\hat{H}$ we use

$$\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 = \frac{1}{2}\left(\hat{\mathbf{S}}^2 - \hat{\mathbf{S}}_1^2 - \hat{\mathbf{S}}_2^2\right) = \frac{1}{2}\hat{\mathbf{S}}^2 - \frac{3}{4}\hbar^2 \ . \tag{485}$$

Therefore, the triplet states are degenerate and their energy is given by

$$E_T = \frac{1}{4}J \ , \tag{486}$$

whereas for the singlet state we get

$$E_S = -\frac{3}{4}J \ . \tag{487}$$

Assuming $J > 0$, the ground state is the singlet, and it is non-degenerate.

In an external magnetic field $\mathbf{B} = B\mathbf{e_z}$ the Hamiltonian is

$$\hat{H} = \frac{J}{\hbar^2}\,\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 + \frac{2\mu_B}{\hbar} B \hat{S}_z \ . \tag{488}$$

This splits the energies of the triplet states into $E_{T,+1} = \frac{1}{4}J + 2\mu_B B$ for $m_s = 1$, $E_{T,0} = \frac{1}{4}J$ for $m_s = 0$, and $E_{T,-1} = \frac{1}{4}J - 2\mu_B B$ for $m_s = -1$.

X. ELECTRON IN AN EXTERNAL ELECTRO-MAGNETIC FIELD. PART II

We come back to the quantum description of an electron in an external electro-magnetic field. Without taking into account the spin the Hamiltonian reads

$$\hat{H} = \frac{\left(\hat{\mathbf{p}} + e\mathbf{A}(\mathbf{r},t)\right)^2}{2m} - e\varphi(\mathbf{r},t) \ , \tag{489}$$

and the wave functions $\psi(\mathbf{r})$ have one component. Here we use $e > 0$ and the negative sign of the electron charge is taken into account explicitly.

With the spin the description is with the Pauli Hamiltonian:

$$\begin{aligned} \hat{H} &= \left[\frac{\left(\hat{\mathbf{p}} + e\mathbf{A}(\mathbf{r},t)\right)^2}{2m} - e\varphi(\mathbf{r},t)\right]\sigma_0 + \frac{g\mu_B}{\hbar}\hat{\mathbf{S}}\cdot\mathbf{B}(\mathbf{r},\mathbf{t}) \\ &= \left[\frac{\left(\hat{\mathbf{p}} + e\mathbf{A}(\mathbf{r},t)\right)^2}{2m} - e\varphi(\mathbf{r},t)\right]\sigma_0 + \mu_B\,\mathbf{B}(\mathbf{r},\mathbf{t})\cdot\boldsymbol{\sigma} \ , \end{aligned} \tag{490}$$

where $g = 2$ was used. The wave function is a 2-component spinor $\psi_\sigma(\mathbf{r}) = \begin{pmatrix} \psi_\uparrow(\mathbf{r}) \\ \psi_\downarrow(\mathbf{r}) \end{pmatrix}$. The Pauli matrices $\boldsymbol{\sigma}$ act in the spin space $\sigma = \uparrow / \downarrow$, whereas the other operators, e.g., the momentum $\hat{\mathbf{p}}$ act in the orbital space (dependence on $\mathbf{r}$).

An equivalent representation of the Pauli Hamiltonian reads

$$\hat{H} = \frac{\left[\boldsymbol{\sigma}\cdot\left(\hat{\mathbf{p}} + e\mathbf{A}\right)\right]\left[\boldsymbol{\sigma}\cdot\left(\hat{\mathbf{p}} + e\mathbf{A}\right)\right]}{2m} - e\varphi\,\sigma_0 \ . \tag{491}$$

This, in turn, is obtained from the Dirac equation (relativistic quantum mechanics).

A. Gauge invariance

It is well known that the physical fields

$$\mathbf{B} = \boldsymbol{\nabla}\times\mathbf{A} \ , \tag{492}$$

$$\mathbf{E} = -\frac{\partial\mathbf{A}}{\partial t} - \boldsymbol{\nabla}\varphi \ , \tag{493}$$

do not change under gauge transformations

$$\mathbf{A} \to \mathbf{A}' = \mathbf{A} + \boldsymbol{\nabla} f(\mathbf{r},t) \ , \tag{494}$$

$$\phi \to \phi' = \phi - \partial_t f(\mathbf{r}, t) \ . \tag{495}$$

These transformations alone would change the Hamiltonian and the corresponding Schrödinger equation. In order to retain the form of the Hamiltonian a simultaneous gauge transformation of the wave function is necessary

$$\psi(\mathbf{r}, t) \to \psi'(\mathbf{r}, t) = \exp\left[-\frac{ie}{\hbar} f(\mathbf{r}, t)\right] \psi(\mathbf{r}, t) \ . \tag{496}$$

Indeed, we have

$$\begin{aligned} (\hat{\mathbf{p}} + e\mathbf{A}')\,\psi' \ &= \ [-i\hbar\boldsymbol{\nabla} + e\mathbf{A} + e(\boldsymbol{\nabla} f)] \exp\left[-\frac{ie}{\hbar} f\right] \psi \\ &= \ \exp\left[-\frac{ie}{\hbar} f\right] (-i\hbar\boldsymbol{\nabla} + e\mathbf{A})\ \psi \ . \end{aligned} \tag{497}$$

Also

$$i\hbar\frac{\partial}{\partial t}\psi' = \exp\left[-\frac{ie}{\hbar} f\right] \left(i\hbar\frac{\partial}{\partial t} + e(\partial_t f)\right) \psi \ . \tag{498}$$

Substituting these two relations to the Schrödinger equation $i\hbar\partial_t\psi' = \hat{H}'\psi'$ we obtain $i\hbar\partial_t\psi = \hat{H}\psi$. Here $\hat{H}' = \hat{H}[\mathbf{A}', \phi']$. The gauge transformation does not involve spin, and, thus is valid also for Pauli Hamiltonian.

B. Aharonov-Bohm effect

Consider a situation in which an electron moves in the region, where $\mathbf{B} = \mathbf{0}$, but $\mathbf{A} \neq 0$. This is so because in other regions there is a finite magnetic field. Example - a coil (solenoid). Then (where $\mathbf{B} = \mathbf{0}$) we have $\boldsymbol{\nabla} \times \mathbf{A} = 0$. Thus, we can locally find a function $\chi(\mathbf{r})$ such that $\mathbf{A} = \boldsymbol{\nabla}\chi$. Performing a gauge transformation

$$\psi(\mathbf{r}, t) \to \psi'(\mathbf{r}, t) = \exp\left[\frac{ie}{\hbar} \chi(\mathbf{r})\right] \psi(\mathbf{r}, t) \ , \tag{499}$$

we obtain

$$\mathbf{A} \to \mathbf{A}' = \mathbf{A} - \boldsymbol{\nabla}\chi(\mathbf{r}) = 0 \ , \tag{500}$$

Thus ψ' is the solution of the Schrödinger equation with $\mathbf{A}' = 0$ and the original Schrödinger equation is solved by

$$\psi(\mathbf{r}, t) = \psi'(\mathbf{r}, t)\ \exp\left[-\frac{ie}{\hbar} \chi(\mathbf{r})\right] = \psi'(\mathbf{r}, t)\ \exp\left[-\frac{ie}{\hbar} \int\limits_{\mathbf{r_0}}^{\mathbf{r}} d\mathbf{s}\, \mathbf{A}(\mathbf{s})\right] \ . \tag{501}$$

The integration path over $\mathbf{s}$ must be completely in the region where $\mathbf{B} = 0$. An interesting situation emerges, if there are two path's P_1 and P_2 starting at $\mathbf{r_0}$ and ending at $\mathbf{r}$ such that a solenoid with magnetic field is inside the loop formed by P_1 and P_2. Then, the relative phase between the two path is given by

$$\Delta\theta = \theta_1 - \theta_2 = -\frac{e}{\hbar}\int\limits_{P_1} d\mathbf{s}\,\mathbf{A}(\mathbf{s}) + \frac{e}{\hbar}\int\limits_{P_2} d\mathbf{s}\,\mathbf{A}(\mathbf{s}) = \frac{e}{\hbar}\oint\limits_{P_2-P_1} d\mathbf{s}\,\mathbf{A}(\mathbf{s})\ . \tag{502}$$

We obtain $\Delta\theta = 2\pi\Phi/\Phi_0$. Here Φ is the magnetic flux through the loop $P_2 - P_1$ and $\Phi_0 \equiv 2\pi\hbar/e = h/e \approx 4.12 \times 10^{-15}$Wb is the flux quantum. The interference pattern is shifted by the magnetic flux in the solenoid even though the electrons never experience the magnetic field.

C. Landau levels

We consider free electrons in homogeneous time-independent magnetic field $\mathbf{B} = B\mathbf{e_z}$. The Hamiltonian reads

$$\hat{H} = \frac{\left(\hat{\mathbf{p}} + e\mathbf{A}(\mathbf{r})\right)^2}{2m}\,\sigma_0 + \mu_B\,B\,\sigma_z\ . \tag{503}$$

One can solve the problem separately for spin up electrons and for spin down electrons. Namely, substituting the wave function in the form $\psi_\uparrow(\mathbf{r})\begin{pmatrix}1\\0\end{pmatrix}$ we obtain the following Schrödinger equation

$$\frac{\left(\hat{\mathbf{p}} + e\mathbf{A}\right)^2}{2m}\,\psi_\uparrow + \mu_B\,B\,\psi_\uparrow = E\,\psi_\uparrow\ . \tag{504}$$

Accordingly, for spin down electrons we substitute $\psi_\downarrow(\mathbf{r})\begin{pmatrix}0\\1\end{pmatrix}$ and obtain

$$\frac{\left(\hat{\mathbf{p}} + e\mathbf{A}\right)^2}{2m}\,\psi_\downarrow - \mu_B\,B\,\psi_\downarrow = E\,\psi_\downarrow\ . \tag{505}$$

For both cases we can just solve the Schrödinger equation for "spinless" electrons

$$\frac{\left(\hat{\mathbf{p}} + e\mathbf{A}\right)^2}{2m}\,\psi = E\,\psi\ , \tag{506}$$

and, then, shift the energy by $\pm\mu_B\,B$ for spin up/down.

We choose the following gauge $\mathbf{A} = (-By, 0, 0)$. Then the Schrödinger equation reads

$$\frac{1}{2m}\left((\hat{p}_x - eBy)^2 + \hat{p}_y^2 + \hat{p}_z^2\right)\,\psi = E\psi\ . \tag{507}$$

The Hamiltonian is translationally invariant in x and z directions. That is $\hat{p}_x$ and $\hat{p}_z$ commute with the Hamiltonian and we can choose eigenvectors of $\hat{H}$ that are simultaneously the eigenvectors of $\hat{p}_x$ and $\hat{p}_z$. We make an ansatz

$$\psi(\mathbf{r}) = e^{ik_x x}\, e^{ik_z z}\, u(y)\ . \tag{508}$$

This gives the following

$$\frac{1}{2m}\left[(\hbar k_x - eBy)^2 + \hat{p}_y^2 + \hbar^2 k_z^2\right]\,u(y) = E\,u(y)\ . \tag{509}$$

Equivalently

$$\left[\frac{1}{2m}\hat{p}_y^2 + \frac{e^2B^2}{2m}\left(y - \frac{\hbar k_x}{eB}\right)^2\right]\,u(y) = \left(E - \frac{\hbar^2 k_z^2}{2m}\right)\,u(y)\ . \tag{510}$$

Introducing the frequency

$$\omega_L \equiv \frac{eB}{m} \tag{511}$$

and the coordinate

$$y_0 \equiv \frac{\hbar k_x}{eB}\ , \tag{512}$$

we obtain

$$\left[\frac{1}{2m}\hat{p}_y^2 + \frac{m\omega_L^2}{2}\left(y - y_0\right)^2\right]\,u(y) = \left(E - \frac{\hbar^2 k_z^2}{2m}\right)\,u(y)\ . \tag{513}$$

We obtain, thus, the Schrödinger equation for a linear oscillator. This gives the eigenenergies

$$E = \frac{\hbar^2 k_z^2}{2m} + \hbar\omega_L\left(n + \frac{1}{2}\right)\ . \tag{514}$$

The eigenstates are characterized by three quantum numbers k_x, k_z, n. They read

$$|k_x, k_z, n\rangle = e^{ik_x x}\, e^{ik_z z}\,\psi_n\left(y - \frac{\hbar k_x}{eB}\right)\ . \tag{515}$$

Here ψ_n are the eigenstates of a linear oscillator with mass m and frequency ω_L. The energy depends only on two quantum numbers k_z and n. Thus we have a degeneracy of infinite grade (k_x is continuous).

The eigenstates are localized in y-direction. The characteristic length, as we know from the discussion of harmonic oscillators (165), is given by

$$l_B = \sqrt{\frac{\hbar}{m\omega_L}} = \sqrt{\frac{\hbar}{eB}} \ . \tag{516}$$

This length is called the *magnetic length*.

The infinite degeneracy of the states with given n and k_z can be regularized by assuming the system has an area of size $A = L_x L_y$ in the $x-y$ plane. In the x-direction one introduces the periodic boundary conditions $\psi(x, y, z) = \psi(x + L_x, y, z)$. This "quantizes" the possible values of k_x, namely $k_x = \frac{2\pi}{L_x} n_x$, where n_x in an integer number. The distance between the neighboring values of k_x is $\Delta k_x = \frac{2\pi}{L_x}$. In addition, the wave number k_x provides the coordinate y_0 around which the state is localized in y-direction. We have $0 < y_0 < L_y$. Using $y_0 = \frac{\hbar k_x}{eB}$, we obtain $0 < k_x < \frac{eBL_y}{\hbar}$. Dividing this by the Δk_x we obtain the total number of allowed values of k_x, i.e.,

$$N = \frac{eBL_xL_y}{2\pi\hbar} = \frac{A}{2\pi l_B^2} \ . \tag{517}$$

XI. TIME-INDEPENDENT PERTURBATION THEORY

A. General idea

Assume we can find exactly the spectrum of $\hat{H}_0$. That is we can find the states $\left|n^{(0)}\right\rangle$ and the energies $E_n^{(0)}$, such that

$$\hat{H}_0 \left|n^{(0)}\right\rangle = E_n^{(0)} \left|n^{(0)}\right\rangle \ . \tag{518}$$

We want now to find the spectrum of

$$\hat{H} = \hat{H}_0 + \lambda \hat{V} \ , \tag{519}$$

where $\lambda \ll 1$. The part $\lambda\hat{V}$ is called the perturbation. The goal is to find the states $|n\rangle$ and the energies E_n such that

$$\hat{H} \left|n\right\rangle = E_n \left|n\right\rangle \ . \tag{520}$$

B. Non-degenerate, 1-st order

Assume the spectrum of $\hat{H}_0$ is non-degenerate and discrete. Then, if λ is sufficiently small, it is natural to expect that for each state $\left|n^{(0)}\right\rangle$ there will be a unique state $|n\rangle$, such

that the wave functions of these two states and their eigenenergies are close. The main idea is to expand both $|n\rangle$ and E_n in powers of λ so that in zeroth order (for $\lambda = 0$) one has $|n\rangle = \left|n^{(0)}\right\rangle$ and $E_n = E_n^{(0)}$. For non-zero λ we expand

$$|n\rangle = \left|n^{(0)}\right\rangle + \lambda \left|n^{(1)}\right\rangle + \lambda^2 \left|n^{(2)}\right\rangle + \dots \ , \tag{521}$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \ . \tag{522}$$

We multiply and obtain

$$\begin{aligned} &(\hat{H}_0 + \lambda \hat{V})(\left|n^{(0)}\right\rangle + \lambda \left|n^{(1)}\right\rangle + \lambda^2 \left|n^{(2)}\right\rangle + \dots) \\ &= (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots)(\left|n^{(0)}\right\rangle + \lambda \left|n^{(1)}\right\rangle + \lambda^2 \left|n^{(2)}\right\rangle + \dots) \ . \end{aligned} \tag{523}$$

We extract the terms of first order in λ:

$$\hat{H}_0 \left|n^{(1)}\right\rangle + \hat{V} \left|n^{(0)}\right\rangle = E_n^{(0)} \left|n^{(1)}\right\rangle + E_n^{(1)} \left|n^{(0)}\right\rangle \ . \tag{524}$$

To solve this both for $\left|n^{(1)}\right\rangle$ and $E_n^{(1)}$ we choose $\left|n^{(1)}\right\rangle$ to be orthogonal to $\left|n^{(0)}\right\rangle$. (In principle, if $\left|n^{(1)}\right\rangle$ is a solution, then also $\left|n^{(1)}\right\rangle - \alpha \left|n^{(0)}\right\rangle$ is a solution.) The state $|n\rangle = \left|n^{(0)}\right\rangle + \lambda \left|n^{(1)}\right\rangle + \dots$ is then definitely not normalized. Yet the deviation is of the second order in λ:

$$\langle n|n\rangle = \left\langle n^{(0)}|n^{(0)}\right\rangle + \lambda^2 \left\langle n^{(1)}|n^{(1)}\right\rangle + \dots = 1 + \lambda^2 \left\langle n^{(1)}|n^{(1)}\right\rangle + \dots \ . \tag{525}$$

We can then expand

$$\left|n^{(1)}\right\rangle = \sum_{m \neq n} \left|m^{(0)}\right\rangle \left\langle m^{(0)}|n^{(1)}\right\rangle \ . \tag{526}$$

The equation (524) now reads

$$\sum_{m \neq n} E_m^{(0)} \left|m^{(0)}\right\rangle \left\langle m^{(0)}|n^{(1)}\right\rangle + \hat{V} \left|n^{(0)}\right\rangle = E_n^{(0)} \sum_{m \neq n} \left|m^{(0)}\right\rangle \left\langle m^{(0)}|n^{(1)}\right\rangle + E_n^{(1)} \left|n^{(0)}\right\rangle \ . \tag{527}$$

Projecting (527) onto $\left|l^{(0)}\right\rangle$ with $l \neq n$ we obtain

$$\left\langle l^{(0)}\right| \hat{V} \left|n^{(0)}\right\rangle = (E_n^{(0)} - E_l^{(0)}) \left\langle l^{(0)}|n^{(1)}\right\rangle \ . \tag{528}$$

Thus

$$\left\langle l^{(0)}|n^{(1)}\right\rangle = \frac{\left\langle l^{(0)}\right| \hat{V} \left|n^{(0)}\right\rangle}{E_n^{(0)} - E_l^{(0)}} \ , \tag{529}$$

and (changing l back to m)

$$\left|n^{(1)}\right\rangle = \sum_{m\neq n} \left|m^{(0)}\right\rangle \left\langle m^{(0)}|n^{(1)}\right\rangle = \sum_{m\neq n} \left|m^{(0)}\right\rangle \frac{\left\langle m^{(0)}\right| \hat{V} \left|n^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}} \ . \tag{530}$$

Projecting (527) onto $\left|n^{(0)}\right\rangle$ we obtain

$$E_n^{(1)} = \left\langle n^{(0)}\right| \hat{V} \left|n^{(0)}\right\rangle \ . \tag{531}$$

The two last equations are the main result of the (non-degenerate) perturbation theory of the first order. Of course, now we can normalize the state $|n\rangle \approx \left|n^{(0)}\right\rangle + \lambda \left|n^{(1)}\right\rangle$ by multiplying it with $\left[\left\langle n^{(0)}|n^{(0)}\right\rangle + \lambda^2 \left\langle n^{(1)}|n^{(1)}\right\rangle\right]^{-1/2} = (1 + \lambda^2 \left\langle n^{(1)}|n^{(1)}\right\rangle)^{-1/2}$. Up to $O(\lambda^2$ this will only influence the amplitude of $\left|n^{(0)}\right\rangle$. That is the normalized state will look like $(1 - O(\lambda^2)) \left|n^{(0)}\right\rangle + \lambda \left|n^{(1)}\right\rangle$.

C. Non-degenerate, 2-st order

In the second order in λ we obtain from (523)

$$\hat{H}_0 \left|n^{(2)}\right\rangle + \hat{V} \left|n^{(1)}\right\rangle = E_n^{(2)} \left|n^{(0)}\right\rangle + E_n^{(1)} \left|n^{(1)}\right\rangle + E_n^{(0)} \left|n^{(2)}\right\rangle \ . \tag{532}$$

We choose again the correction to be orthogonal to the unperturbed wave-function $\left\langle n^{(2)}|n^{(0)}\right\rangle = 0$. Then, projecting on $\left|n^{(0)}\right\rangle$ we obtain

$$E_n^{(2)} = \left\langle n^{(0)}\right| \hat{V} \left|n^{(1)}\right\rangle = \left\langle n^{(0)}\right| \hat{V} \sum_{m\neq n} \left|m^{(0)}\right\rangle \left\langle m^{(0)}|n^{(1)}\right\rangle = \left\langle n^{(0)}\right| \hat{V} \sum_{m\neq n} \left|m^{(0)}\right\rangle \frac{\left\langle m^{(0)}\right| \hat{V} \left|n^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}} \ . \tag{533}$$

We get

$$E_n^{(2)} = \sum_{m\neq n} \frac{\left\langle n^{(0)}\right| \hat{V} \left|m^{(0)}\right\rangle \left\langle m^{(0)}\right| \hat{V} \left|n^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}} = \sum_{m\neq n} \frac{|\left\langle n^{(0)}\right| \hat{V} \left|m^{(0)}\right\rangle|^2}{E_n^{(0)} - E_m^{(0)}} \ . \tag{534}$$

An interesting result: the correction to the ground state energy is always negative.

D. Degenerate case

As we can observe from the non-degenerate perturbation theory the smallness of the corrections is guaranteed if

$$|\left\langle m^{(0)}\right| \lambda\hat{V} \left|n^{(0)}\right\rangle| \ll |E_n^{(0)} - E_m^{(0)}| \ . \tag{535}$$

If for the energy $E_n^{(0)}$ we have several degenerate eigenstates of $\hat{H}_0$: $\left|n_k^{(0)}\right\rangle$, where $k = 1, 2, \ldots N_n$ and N_n is the degree of degeneracy of the level n, the condition above cannot be satisfied if $\left\langle n_q^{(0)}\right| \hat{V} \left|n_k^{(0)}\right\rangle \neq 0$ for $k \neq q$. That is, if the perturbation $\hat{V}$ is not diagonal in the N_n-dimensional degenerate subspace of $E_{n,0}$. The solution of this problem is to diagonalize the operator $\hat{V}$ in the degenerate subspace. We want to find such superpositions of the N_n states:

$$\left|\tilde{n}_\alpha^{(0)}\right\rangle = \sum_{k=1}^{N_n} c_{k,\alpha} \left|n_k^{(0)}\right\rangle \ , \tag{536}$$

that

$$\left\langle \tilde{n}_\beta^{(0)}\right| \hat{V} \left|\tilde{n}_\alpha^{(0)}\right\rangle = \delta_{\beta,\alpha} v_\alpha \ . \tag{537}$$

Here $\alpha, \beta = 1, 2, \ldots, N_n$. The matrix $c_{k,\alpha}$ must be unitary. Substituting (536) into (537) we obtain (summation over repeated indexes)

$$c^*_{q,\beta} V_{q,k} c_{k,\alpha} = (c^\dagger)_{\beta,q} V_{q,k} c_{k,\alpha} = \delta_{\beta,\alpha} v_\alpha \ . \tag{538}$$

Here we have introduced $V_{q,k} \equiv \left\langle n_q^{(0)}\right| \hat{V} \left|n_k^{(0)}\right\rangle$. Multiplying with matrix $\hat{c}$ from the left we obtain

$$c_{p,\beta} (c^\dagger)_{\beta,q} V_{q,k} c_{k,\alpha} = c_{p,\beta} \delta_{\beta,\alpha} v_\alpha \ , \tag{539}$$

which gives

$$V_{p,k} c_{k,\alpha} = c_{p,\alpha} v_\alpha \ . \tag{540}$$

Thus, the columns of the matrix $c_{k,\alpha}$ are the eigenvectors of the matrix $V_{p,k}$ with the eigenvalues v_α. As usual, these eigenvalues are found by solving the "secular" equation (characteristic equation, characteristic polynom) $\det\left[V_{p,k} - v\delta_{p,k}\right] = 0$ for the unknown v.

To conclude, we found the new basis of states $\left|\tilde{n}_\alpha^{(0)}\right\rangle$, where $\alpha = 1, 2, \ldots, N_n$. All these states are eigenstates of $\hat{H}_0$ with the eigenvalue $E_n^{(0)}$:

$$\hat{H}_0 \left|\tilde{n}_\alpha^{(0)}\right\rangle = E_n^{(0)} \left|\tilde{n}_\alpha^{(0)}\right\rangle \ . \tag{541}$$

The perturbation $\lambda\hat{V}$ is diagonal in the new basis within this degenerate subspace (cf. Eq. (537)).

At this point we apply the non-degenerate version of the perturbation theory discussed earlier. The first order correction to the energies of the states $\left|\tilde{n}_\alpha^{(0)}\right\rangle$ reads

$$E_{n,\alpha}^{(1)} = \left\langle \tilde{n}_\alpha^{(0)}\right| \hat{V} \left|\tilde{n}_\alpha^{(0)}\right\rangle = v_\alpha \ . \tag{542}$$

The total energies (up to the first order) read

$$E_{n,\alpha} \approx E_n^{(0)} + \lambda \left\langle \tilde{n}_\alpha^{(0)} \right| \hat{V} \left| \tilde{n}_\alpha^{(0)} \right\rangle = E_n^{(0)} + \lambda v_\alpha \ . \tag{543}$$

If we have diagonalized the perturbation $\hat{V}$ in every degenerate subspace, we can apply now the non-degenerate perturbation theory. The first order corrections to the states $\left| \tilde{n}_\alpha^{(0)} \right\rangle$ will come only from the states, which do not belong to the degenerate subspace $E_n^{(0)}$.

E. Stark effect

We consider a hydrogen atom in a homogeneous electric field. We assume $\mathbf{E} = E\mathbf{e_z}$. The Hamiltonian reads

$$\hat{H} = \hat{H}_0 + \hat{V} \ , \tag{544}$$

where $\hat{H}_0$ is the hydrogen Hamiltonian discussed before and $\hat{V} = -e\phi(r)$ (here $e > 0$, the negative charge of the electron is taken into account explicitly). Since for static electric fields we can put $\mathbf{A} = 0$, we obtain $\mathbf{E} = -\boldsymbol{\nabla}\phi$. We can choose, therefore $\phi = -E \cdot z$. Thus the perturbation reads

$$\hat{V} = eE\hat{z} \ . \tag{545}$$

Since this perturbation does not involve the spin (commutes with $\hat{\boldsymbol{S}}$), the spin degeneracy of every level is not affected. Thus we can solve the problem as if the electron had no spin. We assume the electric field to be sufficiently weak and apply the perturbation theory. For this we need the matrix elements of the type

$$\langle n, l, m| \, \hat{z} \, |n', l', m'\rangle \ . \tag{546}$$

It would not be smart starting calculating these matrix elements for every choice of the quantum numbers n, l, m, n', l', m'. Instead, we first use the symmetries in order to decide which of these matrix elements do not vanish. This strategy produces the "selection rules". That is there are certain rules which immediately tell us which of the matrix elements are zero and which have a chance of being non-zero.

1) Since $\left[\hat{z}, \hat{L}_z\right] = 0$, we obtain

$$\begin{aligned} &\langle n, l, m| \left[\hat{z}, \hat{L}_z\right] |n', l', m'\rangle = \langle n, l, m| \, \hat{z}\hat{L}_z - \hat{L}_z\hat{z} \, |n', l', m'\rangle \\ &= \hbar(m' - m) \langle n, l, m| \, \hat{z} \, |n', l', m'\rangle = 0 \ . \end{aligned} \tag{547}$$

Thus, we observe that

$$\langle n,l,m|\,\hat{z}\,|n',l',m'\rangle = 0 \quad \text{if} \quad m' \neq m\ . \tag{548}$$

The first selection rule reads $m = m'$.

2) The second selection rule can be obtained using the parity operator $\hat{P}\psi(\mathbf{r}) = \psi(-\mathbf{r})$. As we have discussed around Eq. (352), we have $\hat{P}\,|n,l,m\rangle = (-1)^l\,|n,l,m\rangle$. On the other hand $\hat{P}\hat{z}\hat{P} = -\hat{z}$. Thus, we obtain

$$\langle n,l,m|\,\hat{P}\hat{z}\hat{P}\,|n',l',m'\rangle = -\,\langle n,l,m|\,\hat{z}\,|n',l',m'\rangle = (-1)^{l+l'}\,\langle n,l,m|\,\hat{P}\hat{z}\hat{P}\,|n',l',m'\rangle\ . \tag{549}$$

We conclude that the matrix element can be non-zero if $(-1)^{l+l'} = -1$, i.e., $l + l'$ is odd.

3) The third selection rule overrides completely the second one. (The second rule is a weaker subset of the third one.) The third rule reads $l' = l \pm 1$. We will not prove it here. The simplest way to prove is to use the knowledge about the "addition of angular momenta" (Wigner–Eckart theorem), which will be studied later.

1. Linear Stark effect

Consider the 4-fold degenerate subspace of states with $n = 2$. The states are $|2,0,0\rangle, |2,1,-1\rangle, |2,1,0\rangle, |2,1,1\rangle$. According to the selection rules the perturbation $\hat{V} = eE\hat{z}$ has only two matrix elements in this subspace, namely $\Delta \equiv \langle 2,0,0|\,\hat{V}\,|2,1,0\rangle = eE\,\langle 2,0,0|\,\hat{z}\,|2,1,0\rangle$ and its complex conjugate $\Delta^* = \langle 2,1,0|\,\hat{V}\,|2,0,0\rangle$. Since both wave functions $|2,0,0\rangle$ and $|2,1,0\rangle$ are real, we have $\Delta^* = \Delta$, i.e., the matrix element is real. Below we will estimate Δ.

We apply the degenerate perturbation theory. We have to diagonalize the 4×4 matrix of the matrix elements of the perturbation in the degenerate subspace. This matrix reads

$$V_{p,k} = \begin{pmatrix} 0 & 0 & \Delta & 0 \\ 0 & 0 & 0 & 0 \\ \Delta & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \tag{550}$$

This matrix is easy to diagonalize. The eigenstates are

$$\frac{1}{\sqrt{2}}\left(|2,0,0\rangle + |2,1,0\rangle\right) \quad \text{with eigenvalue} \quad v = \Delta\ , \tag{551}$$

$$\frac{1}{\sqrt{2}}\left(|2,0,0\rangle - |2,1,0\rangle\right) \quad \text{with eigenvalue} \quad v = -\Delta \ , \tag{552}$$

$$|2,1,-1\rangle \quad \text{with eigenvalue} \quad v = 0 \ , \tag{553}$$

$$|2,1,1\rangle \quad \text{with eigenvalue} \quad v = 0 \ . \tag{554}$$

As a result, the 4-fold degeneracy of the states with $n = 2$ and energy $E_2^{(0)} = -R_y/4$ is partially lifted. The two states retain their unperturbed energies. The two other states combine into symmetric and anti-symmetric combination with energies $-R_y/4 \pm \Delta$. Since $\Delta \propto E$, one observes the linear dependence of the splitting on the electric field. This explains the name "linear Stark effect".

For the matrix element Δ, using $z = r\cos\theta$, we obtain

$$\Delta = eE \int_0^\infty r^2 dr R^*_{2,0}(r) r R_{2,1}(r) \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \, Y^*_{0,0}(\theta,\phi) \, \cos\theta \, Y_{1,0}(\theta,\phi) \ . \tag{555}$$

For the angular part we obtain

$$\begin{aligned}
&\int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \, Y^*_{0,0}(\theta,\phi) \, \cos\theta \, Y_{1,0}(\theta,\phi) \\
&= \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \, \frac{1}{\sqrt{4\pi}} \, \cos\theta \sqrt{\frac{3}{4\pi}} \cos\theta \\
&= \frac{\sqrt{3}}{2} \int_0^\pi \sin\theta d\theta \, \cos^2\theta = \frac{\sqrt{3}}{2} \int_{-1}^1 dx \, x^2 = \frac{1}{\sqrt{3}} \ .
\end{aligned} \tag{556}$$

For the radial part we obtain

$$\begin{aligned}
&\int_0^\infty r^2 dr R^*_{2,0}(r) r R_{2,1}(r) \\
&= \int_0^\infty r^2 dr \, 2 \left(\frac{1}{2a_0}\right)^{3/2} \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0} \, r \, \frac{2}{\sqrt{3}} \left(\frac{1}{2a_0}\right)^{3/2} \left(\frac{r}{2a_0}\right) e^{-r/2a_0} \\
&= \frac{4}{\sqrt{3}} \left(\frac{1}{2a_0}\right)^3 \int_0^\infty r^3 dr \, \left(1 - \frac{r}{2a_0}\right) \left(\frac{r}{2a_0}\right) \, e^{-r/a_0} \\
&= \frac{a_0}{4\sqrt{3}} \int_0^\infty x^3 dx (1 - x/2) x e^{-x} = \frac{a_0}{4\sqrt{3}} \left[\int_0^\infty dx \, x^4 e^{-x} - \frac{1}{2} \int_0^\infty dx \, x^5 e^{-x} \right] \\
&= -\frac{9a_0}{\sqrt{3}} \ .
\end{aligned} \tag{557}$$

Altogether we get

$$\Delta = -3a_0 eE \ . \tag{558}$$

2. Quadratic Stark effect

The ground state $|1,0,0\rangle$ is non-degenerate (remember we ignore the spin). Since $\langle 1,0,0|\,\hat{V}\,|1,0,0\rangle = 0$, the lowest order effect is the correction of the second order. Taking into account the selection rules, we obtain

$$E^{(2)}_{1,0,0} = e^2E^2 \sum_{n=2}^{\infty} \frac{|\,\langle 1,0,0|\,\hat{z}\,|n,1,0\rangle\,|^2}{E^{(0)}_{1,0,0} - E^{(0)}_{n,1,0}} \ . \tag{559}$$

The exact result of the summation is known:

$$E^{(2)}_{1,0,0} = -\frac{9}{4}\,(4\pi\epsilon_0)\,a_0^3E^2 \ . \tag{560}$$

F. Elements of the fine structure calculation: spin-orbit coupling

One of the corrections to the Hamiltonian of the hydrogen atom, which is obtained from the Dirac equation is the so-called spin-orbit coupling. As above we have the full Hamiltonian

$$\hat{H} = \hat{H}_0 + \lambda\hat{V} \ , \tag{561}$$

where $\hat{H}_0 = \frac{\hat{\boldsymbol{p}}^2}{2m} + U(r)$. Here $U(r) = -\frac{1}{4\pi\epsilon_0}\,\frac{Ze^2}{r}$.

The additional Hamiltonian (perturbation) reads

$$\lambda\hat{V} = \hat{H}_{\rm SO} = \frac{1}{2m^2c^2}\left[\frac{1}{r}\,\frac{d}{dr}U(r)\right]\,\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}} \ . \tag{562}$$

This Hamiltonian does not commute neither with $\hat{L}_z$ nor with $\hat{S}_z$. Thus, the quantum numbers m and m_s are no longer good quantum numbers. On the other hand $\hat{H}_{\rm SO}$ commutes with $\hat{\boldsymbol{L}}^2$ and with $\hat{\boldsymbol{S}}^2$. Therefore, we can further use l and $s = 1/2$.

We consider the degenerate subspace of the eigenstates of $\hat{H}_0$ for a given value of of the principal quantum number n. The degree of degeneracy including spin is $2n^2$. We apply the degenerate perturbation theory, which requires diagonalizing $\hat{H}_{\rm SO}$ in this subspace. That is, we have to diagonalize the following $2n^2 \times 2n^2$ matrix

$$\langle n,l,m,m_s|\,\hat{H}_{\rm SO}\,|n,l',m',m'_s\rangle \ . \tag{563}$$

Since $[\hat{H}_{\rm SO}, \hat{\boldsymbol{L}}^2]$ we immediately get the selection rule $l = l'$. Thus, we have to diagonalize for each value of l separately. For a given l the matrix to be diagonalized has dimensions $2(2l+1) \times 2(2l+1)$.

Recall that the orbital unperturbed states are given by $|n, l, m\rangle = R_{n,l}(r) Y_{l,m}(\theta, \varphi)$. For fixed n and l, the matrix elements of the perturbation read

$$\langle n, l, m, m_s | \, \hat{H}_{\rm SO} \, | n, l, m', m_s' \rangle = \frac{1}{2m^2c^2} \left\langle \left[\frac{1}{r} \frac{d}{dr} U(r) \right] \right\rangle_{n,l} \langle l, m, m_s | \, \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}} \, | l, m', m_s' \rangle \ . \quad (564)$$

Here

$$\left\langle \left[\frac{1}{r} \frac{d}{dr} U(r) \right] \right\rangle_{n,l} = \int_0^\infty r^2 dr \, R_{n,l}^*(r) \frac{1}{r} \left(\frac{dU(r)}{dr} \right) R_{n,l}(r) \ , \quad (565)$$

and

$$|l, m, m_s\rangle = |l, m\rangle \, |m_s\rangle = Y_{l,m}(\theta, \varphi) \, |m_s\rangle \ . \quad (566)$$

1. *Adding orbital momentum and spin 1/2*

We want now to diagonalize $\langle l, m, m_s | \, \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}} \, | l, m', m_s' \rangle$. We look for a basis in which the operator $\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}$ is diagonal. The situation is similar to the one of two spin-1/2 particles with the interaction proportional to $\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2$ (see Sec. IX G). The main idea is to consider the total angular momentum

$$\hat{\boldsymbol{J}} = \hat{\boldsymbol{L}} + \hat{\boldsymbol{S}} \ , \quad (567)$$

since $\hat{\boldsymbol{J}}$ commutes with $\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}$ (that is every component of $\hat{\boldsymbol{J}}$ commutes with $\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}$) and the three operators $\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}$, $\hat{\boldsymbol{J}}^2$ and $\hat{J}_z$ share the mutual basis of eigenstates. Thus, we look for the eigenstates of $\hat{\boldsymbol{J}}^2$ and $\hat{J}_z$ (with eigenvalues $\hbar^2 j(j+1)$ and $\hbar m_j$ respectively). Since $\hat{\boldsymbol{J}}$ commutes with $\hat{\boldsymbol{L}}^2$, states with different values of l will not be mixed. Thus the relevant basis of product states reads

$$|l, m\rangle \, |\uparrow\rangle = Y_{l,m}(\theta, \varphi) \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad |l, m\rangle \, |\downarrow\rangle = Y_{l,m}(\theta, \varphi) \begin{pmatrix} 0 \\ 1 \end{pmatrix} \ . \quad (568)$$

The total number of states in this basis is equal to $2(2l+1)$.

All the states (568) are eigenstates of $\hat{J}_z = \hat{L}_z + \hat{S}_z$. Indeed $\hat{J}_z \, |l, m\rangle \, |\uparrow\rangle = \hbar(m + 1/2) \, |l, m\rangle \, |\uparrow\rangle$ and $\hat{J}_z \, |l, m\rangle \, |\downarrow\rangle = \hbar(m - 1/2) \, |l, m\rangle \, |\downarrow\rangle$. Thus, we observe that $m_j = m \pm 1/2$. The maximal possible value of m_j equals $l + 1/2$. There is only one state with $m_j = l + 1/2$,

namely $|l,l\rangle|\uparrow\rangle$. Analogously, there is only one state with $m_j = -l-1/2$, namely $|l,-l\rangle|\downarrow\rangle$. For every one of the other possible values of m_j, namely for $m_j = -l+1/2, -l+3/2, \ldots, l-3/2, l-1/2$ there exist two states. These are $|l, m_j - 1/2\rangle|\uparrow\rangle$ and $|l, m_j + 1/2\rangle|\downarrow\rangle$.

One can, therefore, guess that only the states $|j, m_j\rangle$ will be present with $j = l + 1/2$ and $j = l - 1/2$ (for $l = 0$ only $j = 1/2$). The total number of such states is given by $2(l + 1/2) + 1 + 2(l - 1/2) + 1 = 2(2l + 1)$ (for $l = 0$ the total number of states is equal 2).

We start by constructing the states with $j = l + 1/2$. The state with the highest possible value of $m_j = l + 1/2$ is given by

$$|\psi\rangle = |l,l\rangle|\uparrow\rangle \ . \tag{569}$$

Indeed

$$\hat{J}_z|\psi\rangle = \hbar(l+1/2)|\psi\rangle \ . \tag{570}$$

Further, using

$$\hat{\boldsymbol{J}}^2 = \hat{\boldsymbol{L}}^2 + \hat{\boldsymbol{S}}^2 + 2\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}} = \hat{\boldsymbol{L}}^2 + \hat{\boldsymbol{S}}^2 + 2\hat{L}_z\hat{S}_z + \hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+ \ , \tag{571}$$

we obtain

$$\hat{\boldsymbol{J}}^2|\psi\rangle = \hbar^2\left(l(l+1) + \frac{3}{4} + 2l\,\frac{1}{2}\right)|\psi\rangle = \hbar^2\left(l+\frac{1}{2}\right)\left(l+\frac{3}{2}\right)|\psi\rangle \ . \tag{572}$$

We conclude that state $|\psi\rangle = |l,l\rangle|\uparrow\rangle$ corresponds to the state $|\psi\rangle = |j = l + 1/2, m_j = l + 1/2\rangle$. We will use the notation $|j, m_j\rangle_J$ for the new basis. Thus, we have obtained

$$|l+1/2, l+1/2\rangle_J = |l,l\rangle|\uparrow\rangle \ . \tag{573}$$

Next, we act with the operator $\hat{J}_- = \hat{L}_- + \hat{S}_-$.

$$\begin{aligned}
&\hat{J}_-|l+1/2, l+1/2\rangle_J = (\hat{L}_- + \hat{S}_-)|l,l\rangle|\uparrow\rangle \\
&= \hbar\sqrt{l(l+1) - l(l-1)}\,|l,l-1\rangle|\uparrow\rangle + \hbar|l,l\rangle|\downarrow\rangle \\
&= \hbar\sqrt{2l}\,|l,l-1\rangle|\uparrow\rangle + \hbar|l,l\rangle|\downarrow\rangle \ .
\end{aligned} \tag{574}$$

Normalizing this state we get

$$|l+1/2, l-1/2\rangle_J = \sqrt{\frac{2l}{2l+1}}\,|l,l-1\rangle|\uparrow\rangle + \sqrt{\frac{1}{2l+1}}\,|l,l\rangle|\downarrow\rangle \ . \tag{575}$$

Continuing this process one obtains

$$|l+1/2, m_j\rangle_J = \sqrt{\frac{l+m_j+1/2}{2l+1}}\,|l, m_j - 1/2\rangle|\uparrow\rangle + \sqrt{\frac{l-m_j+1/2}{2l+1}}\,|l, m_j+1/2\rangle|\downarrow\rangle \ . \tag{576}$$

The coefficients here are the so-called Clebsch-Gordan coefficients. We have thus constructed $2(l+1/2)+1$ states for $j=l+1/2$. We still need $2(l-1/2)+1$ states. For every m_j in (576) such that both states in (576) have non-zero coefficients, i.e., for $m_j = l-1/2, l-3/2, \ldots, -l+3/2, -l+1/2$, we can build the orthogonal to (576) state

$$|l-1/2, m_j\rangle_J = -\sqrt{\frac{l-m_j+1/2}{2l+1}}\,|l, m_j-1/2\rangle\,|\uparrow\rangle + \sqrt{\frac{l+m_j+1/2}{2l+1}}\,|l, m_j+1/2\rangle\,|\downarrow\rangle \ . \tag{577}$$

One can check that these states correspond to $j=l-1/2$. There are exactly $2(l-1/2)+1$ such states.

Since

$$\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}} = \frac{1}{2}\left(\hat{\boldsymbol{J}}^2 - \hat{\boldsymbol{L}}^2 - \hat{\boldsymbol{S}}^2\right) \ , \tag{578}$$

we get

$$\begin{aligned}\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}\,|l+1/2, m_j\rangle_J &= \frac{\hbar^2}{2}\left((l+1/2)(l+3/2) - l(l+1) - \frac{3}{4}\right)|l+1/2, m_j\rangle_J \\ &= \frac{\hbar^2 l}{2}\,|l+1/2, m_j\rangle_J \ .\end{aligned} \tag{579}$$

On the other hand

$$\begin{aligned}\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}\,|l-1/2, m_j\rangle_J &= \frac{\hbar^2}{2}\left((l-1/2)(l+1/2) - l(l+1) - \frac{3}{4}\right)|l-1/2, m_j\rangle_J \\ &= \frac{\hbar^2(-l-1)}{2}\,|l-1/2, m_j\rangle_J \ .\end{aligned} \tag{580}$$

Thus, we have diagonalized the operator $\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}$ in the subspace of given l. This subspace splits into $2(l+1/2)+1$ states with $j=l+1/2$ and the eigenvalue of $\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}$ equal to $\hbar^2 l/2$, and $2(l-1/2)+1$ states with $j=l-1/2$ and the eigenvalue of $\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}$ equal to $-\hbar^2(l+1)/2$.

2. Lifting degeneracy for $n=2$

For $n=2$ we have an 8-fold degeneracy. Namely, we have 2 states with $l=0$ ($2s$ states) and 6 states with $l=1$ ($2p$ states). For the new basis with given j one uses the following notation nl_j. For example, for the states $2s$ only one possibility exists and we obtain two $2s_{1/2}$ states. For $l=0$, $j=1/2$ the eigenvalue of $\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}$ is zero, thus no shift in energy.

Out of 6 states $2p$ we obtain four $2p_{3/2}$ states and two $2p_{1/2}$ states. The states $2p_{3/2}$ are shifted in energy by

$$\Delta E(2p_{3/2}) = \frac{1}{2m^2c^2}\left\langle\left[\frac{1}{r}\,\frac{d}{dr}U(r)\right]\right\rangle_{n=2,l=1} \times \frac{\hbar^2}{2} \ . \tag{581}$$

For the states $2p_{1/2}$ we obtain

$$\Delta E(2p_{1/2}) = \frac{1}{2m^2c^2}\left\langle\left[\frac{1}{r}\frac{d}{dr}U(r)\right]\right\rangle_{n=2,l=1} \times \frac{\hbar^2}{2}(-2) \ . \tag{582}$$

Important: *We considered only the spin-orbit (SO) coupling. There are other corrections contributing to the fine structure ($\propto \boldsymbol{p}^4$ correction to the kinetic energy and the Darwin term). These corrections, including the SO coupling, originate from the Dirac equation. As a result, the fine structure splittings are different from what we obtained. In particular, the energy shifts depend only on j and not on l. Therefore, the states $2s_{1/2}$ and $2p_{1/2}$ remain degenerate. Our calculation here was for training purposes only.*

XII. ADIABATIC APPROXIMATION (THEOREM), BERRY PHASE

Assume a Hamiltonian of a system changes slowly in time. How will the wave functions then evolve? It is convenient to think that the hamiltonian depends on a vector of parameters $\boldsymbol{R}$, i.e., we have the hamiltonian $\hat{H}(t) = \hat{H}(\boldsymbol{R}(t))$ and this vector of parameters depends in turn on time $\boldsymbol{R}(t)$. As an example consider a spin-1/2 in a magnetic field that depends (slowly) on time: $\hat{H}(t) = \mu_B \boldsymbol{B}(t)\cdot\boldsymbol{\sigma}$. In this case $\boldsymbol{R}(t) = \boldsymbol{B}(t)$.

Assume that for any t the parameters $\boldsymbol{R}(t)$ are such that the Hamiltonian $\hat{H}(\boldsymbol{R}(t))$ has a discrete non-degenerate spectrum $|n(t)\rangle = |n(\boldsymbol{R}(t))\rangle$ with eigenenergies $E_n(t) = E_n(\boldsymbol{R}(t))$. The energies E_n never cross. The states $|n(t)\rangle$ are called instantaneous eigenstates. For example, for spin-1/2 in a magnetic field this means that for any t the magnetic field is non-zero, i.e., $|\boldsymbol{B}(t)| > 0$.

The idea of the adiabatic approximation is that if at $t = 0$ the state of the system is one of the instantaneous eigenstates, $|\psi(t=0)\rangle = |n(t=0)\rangle$, and the Hamiltonian changes sufficiently slow (to be specified) the state will "follow" the Hamiltonian so that $|\psi(t)\rangle \approx |n(t)\rangle$.

To justify the adiabatic approximation we expand the wave function $|\psi(t)\rangle$ is the basis of instantaneous eigenstates

$$\psi(t) = \sum_m c_m(t)\,|m(\boldsymbol{R}(t))\rangle \ . \tag{583}$$

Initially $c_m(t=0) = \delta_{m,n}$. The Schrödinger equation gives

$$i\hbar\frac{d}{dt}|\psi\rangle = i\hbar\sum_m\left(\frac{dc_m(t)}{dt}|m(t)\rangle + c_m(t)\,|\dot{m}(t)\rangle\right) = \sum_m E_m(t)c_m(t)\,|m(t)\rangle \ . \tag{584}$$

Here

$$|\dot{m}(t)\rangle = \dot{\boldsymbol{R}}(t) \cdot \boldsymbol{\nabla}_{\boldsymbol{R}} |m(\boldsymbol{R})\rangle \ . \tag{585}$$

We project the Schrödinger equation on $\langle l(t)|$ and obtain

$$i\hbar \frac{dc_l}{dt} = E_l(t) c_l - i\hbar \sum_m \langle l(t)|\dot{m}(t)\rangle \, c_m \ . \tag{586}$$

We can consider this equation as a Schrödinger equation for the wave function $c_l(t)$, i.e., $i\hbar \frac{dc_l}{dt} = \tilde{H}_{l,m} c_m$, where the Hamiltonian matrix reads

$$\tilde{H}_{l,m} = \delta_{l,m} \Big[E_m(t) - i\hbar \langle m(t)|\dot{m}(t)\rangle \Big] - (1 - \delta_{l,m}) i\hbar \langle l(t)|\dot{m}(t)\rangle \ . \tag{587}$$

The matrix element $\langle l(t)|\dot{m}(t)\rangle$ is small if the "velocity" is the parameter space $\dot{\boldsymbol{R}}(t)$ is small. The idea of the adiabatic approximation is that one can neglect the off-diagonal terms in (587) if they are much smaller than the energy differences:

$$\hbar |\langle l(t)|\dot{m}(t)\rangle| \ll |E_m - E_l| \ . \tag{588}$$

Indeed, the off-diagonal terms contribute only in the second order whereas the diagonal one already in the first order.

Neglecting the off-diagonal elements (this is the adiabatic approximation) we obtain

$$\frac{dc_m(t)}{dt} = \left[-\frac{i}{\hbar} E_m(t) - \langle m(t)|\dot{m}(t)\rangle \right] c_m(t) \ . \tag{589}$$

This leads to

$$c_m(t) = c_m(0) e^{i\gamma_m(t)} \exp\left[-\frac{i}{\hbar} \int_0^t dt' \, E_m(t') \right] \ , \tag{590}$$

where

$$\gamma_m(t) = i \int_0^t dt' \ \langle m(t')|\dot{m}(t')\rangle \ . \tag{591}$$

Note that $\langle m(t)|\dot{m}(t)\rangle$ is purely imaginary. Indeed, from $\langle m(t)|m(t)\rangle = 1$ follows $\langle m(t)|\dot{m}(t)\rangle + \langle \dot{m}(t)|m(t)\rangle = 0$, and, therefore $\langle m(t)|\dot{m}(t)\rangle^* = \langle \dot{m}(t)|m(t)\rangle = -\langle m(t)|\dot{m}(t)\rangle$. Thus, in the adiabatic approximation $|c_m(t)|^2 = |c_m(0)|^2$. There are no transitions between the levels. If one starts in level $|n\rangle$ at $t = 0$, one always remains in $|n(t)\rangle$.

The amplitude of each state c_m gets in addition to the dynamical phase $\theta_m(t) = (1/\hbar) \int_0^t dt' E_m(t')$ an additional phase $\gamma_m(t)$.

An alternative justification is to definine

$$c_l(t) = a_l(t) \exp\left[-\frac{i}{\hbar}\int_0^t E_l(t')dt'\right] \ . \tag{592}$$

We obtain

$$\dot{a}_l = -\sum_m \langle l(t)|\dot{m}(t)\rangle \, a_m \exp\left[-\frac{i}{\hbar}\int_0^t (E_m(t') - E_l(t'))dt'\right] \tag{593}$$

The matrix element $\langle l(t)|\dot{m}(t)\rangle$ is small if the "velocity" in the parameter space $\dot{\boldsymbol{R}}(t)$ is small. In addition, since the energy splittings remain finite, the factors $\exp\left[-\frac{i}{\hbar}\int_0^t (E_m(t') - E_l(t'))dt'\right]$ oscillate quickly if $l \neq m$. The adiabatic approximation consists in neglecting the terms with $l \neq m$. It is a good approximation if

$$\hbar|\langle l(t)|\dot{m}(t)\rangle| \ll |E_m - E_l| \ . \tag{594}$$

This gives

$$\dot{a}_m = -\langle m(t)|\dot{m}(t)\rangle \, a_m \ . \tag{595}$$

Integrating one obtains

$$a_m(t) = \exp\left[-\int_0^t dt' \, \left\langle m(t')|\dot{m}(t')\right\rangle\right] a_m(0) = e^{i\gamma_m(t)} a_m(0) \ . \tag{596}$$

Finally,

$$c_m(t) = c_m(0) e^{i\gamma_m(t)} \exp\left[-\frac{i}{\hbar}\int_0^t dt' \, E_m(t')\right] \ . \tag{597}$$

The phase γ_m has a geometric nature. Indeed

$$\gamma_m(\tau) = i\int_0^\tau dt \ \langle m(t)|\dot{m}(t)\rangle = i\int_0^\tau dt \, \dot{\boldsymbol{R}}(t) \cdot \langle m| \boldsymbol{\nabla}_{\boldsymbol{R}} |m\rangle \ . \tag{598}$$

Recall that $|m\rangle = |m(\boldsymbol{R})\rangle$. The time can be excluded and we get

$$\gamma_m(\tau) = i\int_{\boldsymbol{R}(\mathbf{0})}^{\boldsymbol{R}(\boldsymbol{\tau})} d\boldsymbol{R} \cdot \langle m| \boldsymbol{\nabla}_{\boldsymbol{R}} |m\rangle \ . \tag{599}$$

The phase $\gamma_m(\tau)$ depends, therefore, only on the path in the parameter spate $\boldsymbol{R}(t)$ and not on how this path was followed in time (as long as it is slow).

The phase $\gamma_m(\tau)$ is not gauge invariant. Indeed, we could have defined the instantaneous eigenstates with different phases

$$|m'(\boldsymbol{R})\rangle = \exp\left[i\chi_m(\boldsymbol{R})\right] \, |m(\boldsymbol{R})\rangle \ . \tag{600}$$

This would lead to

$$\gamma'_m(\tau) = i\int_{\boldsymbol{R}(\mathbf{0})}^{\boldsymbol{R}(\boldsymbol{\tau})} d\boldsymbol{R} \cdot \langle m'| \boldsymbol{\nabla}_{\boldsymbol{R}} |m'\rangle = i\int_{\boldsymbol{R}(\mathbf{0})}^{\boldsymbol{R}(\boldsymbol{\tau})} d\boldsymbol{R} \cdot \Big[\langle m| \boldsymbol{\nabla}_{\boldsymbol{R}} |m\rangle + i\boldsymbol{\nabla}_{\boldsymbol{R}} \chi_m\Big] \tag{601}$$

However, for closed path, $\boldsymbol{R}(T) = \boldsymbol{R}(0)$, and $\gamma'_m(T) = \gamma_m(T)$.

A. Berry phase for spin 1/2

We consider

$$\hat{H}(t) = \mu_B \boldsymbol{B}(t) \cdot \boldsymbol{\sigma} \ . \tag{602}$$

We can always write $\boldsymbol{B}(t) = B(t)\boldsymbol{n}(t)$. Here B is the absolute value of the magnetic field and $\boldsymbol{n}(t)$ is the unity vector, which gives the direction of the magnetic field. We can use the spherical coordinates

$$\boldsymbol{n}(t) = (\sin\theta(t)\cos\varphi(t), \sin\theta(t)\sin\varphi(t), \cos\theta(t)) \ . \tag{603}$$

The eigenstates of the operator

$$\boldsymbol{n} \cdot \boldsymbol{\sigma} = \begin{pmatrix} \cos\theta & \sin\theta e^{-i\varphi} \\ \sin\theta e^{i\varphi} & -\cos\theta \end{pmatrix} \tag{604}$$

can be found

$$|\uparrow(\boldsymbol{n})\rangle = \begin{pmatrix} \cos\frac{\theta}{2} \\ e^{i\varphi}\sin\frac{\theta}{2} \end{pmatrix} \ , \tag{605}$$

$$|\downarrow(\boldsymbol{n})\rangle = \begin{pmatrix} -e^{-i\varphi}\sin\frac{\theta}{2} \\ \cos\frac{\theta}{2} \end{pmatrix} \ . \tag{606}$$

For the geometric (Berry) phase we need

$$\langle\uparrow(\boldsymbol{n})|\partial_t \uparrow(\boldsymbol{n})\rangle = i\dot{\varphi}\sin^2\frac{\theta}{2} = \frac{1}{2}\, i\dot{\varphi}(1-\cos\theta) \ . \tag{607}$$

$$\langle\downarrow(\boldsymbol{n})|\partial_t \downarrow(\boldsymbol{n})\rangle = -i\dot{\varphi}\sin^2\frac{\theta}{2} = -\frac{1}{2}\, i\dot{\varphi}(1-\cos\theta) \ . \tag{608}$$

This gives

$$\gamma_{\uparrow/\downarrow}(\tau) = \mp\frac{1}{2}\int_0^\tau dt\, \dot{\varphi}(t)(1-\cos\theta(t)) = \mp\frac{1}{2}\int_{\boldsymbol{n}(0)}^{\boldsymbol{n}(\tau)} d\varphi\,(1-\cos\theta) \ . \tag{609}$$

For a closed path we get $\boldsymbol{n}(T) = \boldsymbol{n}(0)$

$$\gamma_{\uparrow/\downarrow}(T) = \mp\frac{1}{2}\oint d\varphi\,(1-\cos\theta) \ . \tag{610}$$

The condition $\boldsymbol{n}(T) = \boldsymbol{n}(0)$ means $\theta(T) = \theta(0)$, $\varphi(T) = \varphi(0) + 2\pi N$, where N is an integer. The physical meaning has the difference of the two phases

$$\gamma_\uparrow(T) - \gamma_\downarrow(T) = -\oint d\varphi\,(1-\cos\theta) \ . \tag{611}$$

This is the solid angle encompassed by the trajectory $\boldsymbol{n}(t)$.

XIII. SCATTERING THEORY

We consider scattering of a particle with mass m on a scatterer described by the potential $V(\boldsymbol{r})$. The scatterer is located near the origin $\boldsymbol{r} = 0$ and the potential $V(\boldsymbol{r})$ vanished at $|\boldsymbol{r}| \to \infty$ sufficiently fast (faster than $1/r$). The Hamiltonian reads

$$\hat{H} = \frac{\boldsymbol{p}^2}{2m} + V(\boldsymbol{r}) \ . \tag{612}$$

Since at $|\boldsymbol{r}| \to \infty$ the potential vanished, asymptotically the solution should consist of free waves.

We look for a solution of the Schrödinger equation

$$\left[-\frac{\hbar^2}{2m} \boldsymbol{\nabla}^2 + V(\boldsymbol{r}) \right] \Psi(\boldsymbol{r}) = E \, \Psi(\boldsymbol{r}) \ . \tag{613}$$

Since asymptotically the solution is a plane wave with the wave number $\boldsymbol{k}$ we have

$$E = \frac{\hbar^2 k^2}{2m} \ . \tag{614}$$

A. Lippmann-Schwinger equation

The Schrödinger equation can be rewritten as follows

$$\left(\boldsymbol{\nabla}^2 + k^2 \right) \Psi(\boldsymbol{r}) = \frac{2m}{\hbar^2} V(\boldsymbol{r}) \Psi(\boldsymbol{r}) \ . \tag{615}$$

On the left side we have the Helmholtz operator and the equation has the structure of the inhomogeneous Helmholtz equation

$$\left(\boldsymbol{\nabla}^2 + k^2 \right) \Psi(\boldsymbol{r}) = g(\boldsymbol{r}) \ , \tag{616}$$

where $g(\boldsymbol{r}) = \frac{2m}{\hbar^2} V(\boldsymbol{r}) \, \Psi(\boldsymbol{r})$. The general solution of this equation is given by

$$\Psi(\boldsymbol{r}) = \Psi_0(\boldsymbol{r}) + \int d^3 r_1 \, G(\boldsymbol{r} - \boldsymbol{r_1}) \, g(\boldsymbol{r_1}) \ , \tag{617}$$

where $\Psi_0(\boldsymbol{r})$ is a solution of the homogeneous equation and $G(\boldsymbol{r})$ is the Green function satisfying

$$\left(\boldsymbol{\nabla}^2 + k^2 \right) G(\boldsymbol{r}) = \delta^{(3)}(\boldsymbol{r}) \ . \tag{618}$$

The Green function is not unique. Indeed, one can add to $G(\boldsymbol{r})$ a solution of the homogeneous equation. There are two particular solutions that are very important

$$G_{\pm}(\boldsymbol{r}) = -\frac{1}{4\pi} \, \frac{e^{\pm ikr}}{r} \ , \tag{619}$$

where G_+ is the retarded Green function and G_- is the advanced one. We choose G_+ (retarded Green function) since it satisfies the needed boundary conditions as will be shown below. Namely, it describes scattered waves propagating away from the scatterer. We, thus, obtain

$$\Psi(\boldsymbol{r}) = \Psi_0(\boldsymbol{r}) + \int d^3r_1 \, G_+(\boldsymbol{r} - \boldsymbol{r_1}) \, \frac{2m}{\hbar^2} \, V(\boldsymbol{r_1}) \, \Psi(\boldsymbol{r_1}) \ . \tag{620}$$

This is one of the versions of the Lippmann-Schwinger equation.

The more abstract form is obtained from

$$(E - H_0) \, |\Psi\rangle = V \, |\Psi\rangle \ . \tag{621}$$

On the left side we can add an arbitrary eigenstate $|\Psi_0\rangle$ satisfying $(E - H) \, |\Psi_0\rangle = 0$. Then we get

$$(E - H_0)(|\Psi\rangle - |\Psi_0\rangle) = V \, |\Psi\rangle \ . \tag{622}$$

Inverting formally we obtain

$$|\Psi\rangle = |\Psi_0\rangle + \frac{V}{E - H_0} \, |\Psi\rangle \ . \tag{623}$$

The matrix $E - H_0$ cannot actually be inverted. We have to regularize. For example replacing $E \to E + i\epsilon$, where ϵ is infinitesimal and positive, produces

$$|\Psi\rangle = |\Psi_0\rangle + \frac{V}{E - H_0 + i\epsilon} \, |\Psi\rangle \ . \tag{624}$$

It can be shown that

$$\frac{1}{E - H_0 + i\epsilon} = \frac{2m}{\hbar^2} \, G_+ \ . \tag{625}$$

Further

$$\Psi(\boldsymbol{r}) = \Psi_0(\boldsymbol{r}) - \frac{m}{2\pi\hbar^2} \int d^3r_1 \, \frac{e^{ik|\boldsymbol{r} - \boldsymbol{r_1}|}}{|\boldsymbol{r} - \boldsymbol{r_1}|} \, V(\boldsymbol{r_1}) \, \Psi(\boldsymbol{r_1}) \ . \tag{626}$$

The potential $V(\boldsymbol{r_1})$ decays fast for $|\boldsymbol{r_1}| \to \infty$. We want to investigate the solution at $|\boldsymbol{r}| \gg |\boldsymbol{r_1}|$, where the scattering potential is already negligible. For $|\boldsymbol{r}| \gg |\boldsymbol{r_1}|$ we have

$$\begin{aligned} k|\boldsymbol{r} - \boldsymbol{r_1}| &= k\sqrt{\boldsymbol{r}^2 - 2\boldsymbol{r} \cdot \boldsymbol{r_1} + \boldsymbol{r_1}^2} = kr\sqrt{1 - \frac{2}{r^2} \, \boldsymbol{r} \cdot \boldsymbol{r_1} + \frac{r_1^2}{r^2}} \\ &= kr \left(1 - \frac{1}{r^2} \, \boldsymbol{r} \cdot \boldsymbol{r_1} + \dots\right) = kr - k \, \frac{\boldsymbol{r}}{r} \cdot \boldsymbol{r_1} = kr - k \, \boldsymbol{n} \cdot \boldsymbol{r_1} + \dots \ , \end{aligned} \tag{627}$$

where

$$\boldsymbol{n}(\theta, \varphi) = \frac{\boldsymbol{r}}{r} \ . \tag{628}$$

In the denominator of (626) we approximate

$$\frac{1}{|\boldsymbol{r} - \boldsymbol{r_1}|} = \frac{1}{r} + O\left(\frac{1}{r^2}\right) \ . \tag{629}$$

Thus we obtain

$$\Psi(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} + \frac{e^{ikr}}{r} \, f_{\boldsymbol{k}}(\boldsymbol{n}) + O\left(\frac{1}{r^2}\right) \ , \tag{630}$$

where

$$f_{\boldsymbol{k}}(\boldsymbol{n}) = -\frac{m}{2\pi\hbar^2}\int d^3r_1\, e^{-ik\,\boldsymbol{n}\cdot\boldsymbol{r_1}}\, V(\boldsymbol{r_1})\,\Psi(\boldsymbol{r_1}) \tag{631}$$

is the scattering amplitude. For the solution of the homogenous equation we took $\Psi_0(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$. Frequently, one introduces the wave vector in the direction of scattering $\boldsymbol{k'} \equiv \boldsymbol{n}k$ (remember $\boldsymbol{k}$ is the wave vector of the incoming plane wave). The alternative notation is $f_{\boldsymbol{k}}(\boldsymbol{n}) = f_{\boldsymbol{k},\boldsymbol{k'}}$.

B. Differential cross section

We calculate the current density. We take r to be very large, so that the asymptotic expression (630) holds:

$$\Psi(\boldsymbol{r}) = \Psi_{in} + \Psi_{sc} = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} + \frac{e^{ikr}}{r}\, f_{\boldsymbol{k}}(\boldsymbol{n})\ , \tag{632}$$

where $\Psi_{in} = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$ and $\Psi_{sc} = \frac{e^{ikr}}{r}\, f_{\boldsymbol{k}}(\boldsymbol{n})$.

The current density is given by

$$\mathbf{j} = \frac{\hbar}{2mi}(\Psi^*\,[\boldsymbol{\nabla}\Psi] - [\boldsymbol{\nabla}\Psi^*]\,\Psi)\ . \tag{633}$$

For the density of the incoming current we obtain

$$\boldsymbol{j}_{in} = \frac{\hbar}{2mi}(\Psi^*_{in}\,[\boldsymbol{\nabla}\Psi_{in}] - [\boldsymbol{\nabla}\Psi^*_{in}]\,\Psi_{in}) = \frac{\hbar\boldsymbol{k}}{m}\ . \tag{634}$$

For the scattering part we get

$$\boldsymbol{j}_{sc} = \frac{\hbar}{2mi}(\Psi^*_{sc}\,[\boldsymbol{\nabla}\Psi_{sc}] - [\boldsymbol{\nabla}\Psi^*_{sc}]\,\Psi_{sc})\ . \tag{635}$$

We are mostly interested in the projection of the current onto the unit vector $\boldsymbol{n}$, i.e the current in the radial direction. We use the following expression for $\boldsymbol{\nabla}$ in the spherical coordinates:

$$\boldsymbol{\nabla} = \mathbf{e}_r\,\frac{\partial}{\partial r} + \frac{1}{r}\,\mathbf{e}_\theta\,\frac{\partial}{\partial\theta} + \frac{1}{r\sin\theta}\,\mathbf{e}_\phi\,\frac{\partial}{\partial\phi}\ . \tag{636}$$

Using $\boldsymbol{n} = \boldsymbol{e}_r$ and $\boldsymbol{n}\cdot\boldsymbol{\nabla} = \frac{\partial}{\partial r} = \partial_r$ we obtain

$$\boldsymbol{n}\cdot\boldsymbol{j}_{sc} = \frac{\hbar}{2mi}(\Psi^*_{sc}\,[\partial_r\Psi_{sc}] - [\partial_r\Psi^*_{sc}]\,\Psi_{sc})\ . \tag{637}$$

This gives

$$\boldsymbol{n}\cdot\boldsymbol{j}_{sc} = \frac{\hbar k}{mr^2}|f_{\boldsymbol{k}}(\boldsymbol{n})|^2\ . \tag{638}$$

The differential cross section is defined as

$$d\sigma = \frac{Current\ of\ scattered\ particles\ into\ solid\ angle\ d\Omega\ in\ direction\ \boldsymbol{n}}{Current\ density\ of\ incoming\ particles} \ . \tag{639}$$

This gives

$$d\sigma = \frac{\boldsymbol{n}\cdot\boldsymbol{j}_{sc}\, r^2 d\Omega}{|\boldsymbol{j}_{in}|} = |f_{\boldsymbol{k}}(\boldsymbol{n})|^2\, d\Omega \ . \tag{640}$$

The total cross section is then given by

$$\sigma = \int d\sigma = \int d\Omega\, |f_{\boldsymbol{k}}(\boldsymbol{n})|^2 \ . \tag{641}$$

C. Optical theorem

For simplicity we consider the incoming wave propagating along the z-axis, $\boldsymbol{k} \parallel \boldsymbol{e}_z$. Then, the scattering direction $\boldsymbol{n} = \boldsymbol{e}_z$ ($\theta = 0$ is spherical coordinates) corresponds to forward-scattering. We calculate the current flowing through the surface of a sphere of radius r. We take r to be very large, so that the asymptotic expression (630) holds.

As calculated above

$$\boldsymbol{j}_{in} = \frac{\hbar}{2mi}(\Psi^*_{in}\,[\boldsymbol{\nabla}\Psi_{in}] - [\boldsymbol{\nabla}\Psi^*_{in}]\,\Psi_{in}) = \frac{\hbar\boldsymbol{k}}{m} \ . \tag{642}$$

Since this current is homogeneous, we obtain

$$I_{in} = \oint_r r^2\, d\Omega\, \boldsymbol{n}\cdot\boldsymbol{j}_{in} = 0 \ . \tag{643}$$

For the scattering part we get (see previous subsection)

$$\boldsymbol{n}\cdot\boldsymbol{j}_{sc} = \frac{\hbar}{2mi}(\Psi^*_{sc}\,[\partial_r\Psi_{sc}] - [\partial_r\Psi^*_{sc}]\,\Psi_{sc}) \ . \tag{644}$$

This gives

$$\boldsymbol{n}\cdot\boldsymbol{j}_{sc} = \frac{\hbar k}{mr^2}|f_{\boldsymbol{k}}(\boldsymbol{n})|^2 \ . \tag{645}$$

Finally

$$I_{sc} = \oint_S r^2\, d\Omega\, \boldsymbol{n}\cdot\boldsymbol{j}_{sc} = \frac{\hbar k}{m}\oint_S d\Omega\, |f_{\boldsymbol{k}}(\boldsymbol{n})|^2 = \frac{\hbar k}{m}\,\sigma \ . \tag{646}$$

We got a results that seemingly contradicts the conservation of current, since the current through a closed surface does not vanish. In reality we just have to take into account the interference (mixed) contribution. This reads

$$\boldsymbol{j}_{inter} = \frac{\hbar}{2mi}(\Psi^*_{in}\,[\boldsymbol{\nabla}\Psi_{sc}] - [\boldsymbol{\nabla}\Psi^*_{in}]\,\Psi_{sc} + \Psi^*_{sc}\,[\boldsymbol{\nabla}\Psi_{in}] - [\boldsymbol{\nabla}\Psi^*_{sc}]\,\Psi_{in}) \ . \tag{647}$$

Using again $\boldsymbol{n}\cdot\boldsymbol{\nabla}=\frac{\partial}{\partial r}=\partial_r$ and $\Psi_{in}=e^{ikr\cos\theta}$ we obtain

$$\partial_r\,\Psi_{in}=\partial_r e^{ikr\cos\theta}=ik\cos\theta e^{ikr\cos\theta}\ . \tag{648}$$

We use also

$$\partial_r\,\frac{e^{ikr}}{r}=\frac{e^{ikr}}{r}\left(ik-\frac{1}{r}\right)\ . \tag{649}$$

We obtain

$$\boldsymbol{n}\cdot\boldsymbol{j}_{inter}=\frac{\hbar}{2mi}\left[\frac{e^{ikr(1-\cos\theta)}}{r}\left(ik(1+\cos\theta)-\frac{1}{r}\right)f_{\boldsymbol{k}}(\boldsymbol{n})-c.c.\right]\ . \tag{650}$$

We have to calculate

$$I_{inter}=\oint_S r^2\,d\Omega\,\boldsymbol{n}\cdot\boldsymbol{j}_{inter}=r^2\int\limits_0^{\pi}\sin\theta d\theta\int_0^{2\pi}d\varphi\,\boldsymbol{n}\cdot\boldsymbol{j}_{inter}\ . \tag{651}$$

Introducing $x\equiv 1-\cos\theta$ we get

$$I_{inter}=\frac{\hbar r^2}{2mi}\int_0^{2\pi}d\varphi\int\limits_0^{2}dx\,\left[\frac{e^{ikrx}}{r}\left(ik(2-x)-\frac{1}{r}\right)f_{\boldsymbol{k}}(\boldsymbol{n})-c.c.\right]\ . \tag{652}$$

We expect that for $r\to\infty$ the integral is dominated by contributions near $\theta=0$, i.e, $x=0$. Assuming $f_{\boldsymbol{k}}(\boldsymbol{n}(\boldsymbol{\theta},\boldsymbol{\varphi}))$ is a smooth function for $\theta\approx 0$ we can approximate $f_{\boldsymbol{k}}(\boldsymbol{n}(\boldsymbol{\theta},\boldsymbol{\varphi}))\approx f_{\boldsymbol{k}}(\theta=0)$. We integrate in the interval $x\in[0,\epsilon]$, where $\epsilon\ll 1$ and obtain

$$\begin{aligned}
I^{\epsilon}_{inter}\ &\approx\ \frac{\hbar r^2}{2mi}2\pi\int\limits_0^{\epsilon}dx\,\left[\frac{e^{ikrx}}{r}\left(ik(2-x)-\frac{1}{r}\right)f_{\boldsymbol{k}}(\theta=0)-c.c.\right]\\
&\approx\ \frac{\hbar r^2}{2mi}2\pi\int\limits_0^{\epsilon}dx\,\left[\frac{e^{ikrx}}{r}\left(2ik-\frac{1}{r}\right)f_{\boldsymbol{k}}(\theta=0)-c.c.\right]\\
&\approx\ \frac{\hbar r^2}{2mi}2\pi\,\left[\frac{e^{ikr\epsilon}-1}{ikr^2}\left(2ik-\frac{1}{r}\right)f_{\boldsymbol{k}}(\theta=0)-c.c.\right]\ .
\end{aligned} \tag{653}$$

Taking the limit $r\to\infty$ we observe that the exponent $e^{ikr\epsilon}$ will always average out to zero. This will happen, e.g., if we consider a wave packet and integrate over k (sufficient to integrate even over a small interval of width Δk). Thus, the integral is independent of ϵ and is given by

$$I^{\epsilon}_{inter}\approx-\frac{4\pi\hbar}{m}\,\frac{[f_{\boldsymbol{k}}(\theta=0)-f^*_{\boldsymbol{k}}(\theta=0)]}{2i}=-\frac{4\pi\hbar}{m}\,\mathrm{Im}\,[f_{\boldsymbol{k}}(\theta=0)]\ . \tag{654}$$

Demanding $I_{in} + I_{sc} + I_{inter} = 0$ we obtain the optical theorem, which states that

$$\sigma = \frac{4\pi}{k} \operatorname{Im} \left[f_{\boldsymbol{k}}(\theta = 0) \right] \ . \tag{655}$$

Since the interference contribution is important only for $\theta = 0$, our results above, which did not take into account the interference contribution are still correct for $\theta \neq 0$.

D. Spherically symmetric scatterer

If the scattering potential is spherically symmetric, i.e., $V(\boldsymbol{r}) = V(r)$ we can use the formalism developed for the problem of central potential (VI E 2). There we have seen that the wave functions with $E > 0$ (scattering states) can be written as

$$\psi_{k,l,m}(\mathbf{r}) = R_{k,l}(r) Y_{l,m}(\theta, \phi) \ , \tag{656}$$

where $R_{k,l}(r) \equiv u_{k,l}(r)/r$. The functions $u_{k,l}(r)$ satisfy the following equation

$$\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r) \right] u_{k,l}(r) = E\, u_{k,l}(r) = \frac{\hbar^2 k^2}{2m} u_{k,l}(r) \ . \tag{657}$$

The effective potential reads

$$V_{\text{eff}}(r) = \frac{\hbar^2 l(l+1)}{2mr^2} + V(r) \ . \tag{658}$$

1. Asymptotic solution

Since $V_{\text{eff}}(r \to \infty) \to 0$, the Schrödinger equation (657)

$$\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} + V_{\text{eff}}(r) \right] u_{k,l}(r) = E\, u_{k,l}(r) \ . \tag{659}$$

becomes asymptotically (at $r \to \infty$) an equation for a free particle

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} u_{k,l}(r) = E\, u_{k,l}(r) \ . \tag{660}$$

This can be trivially solved as $u_{k,l}(r) = Ce^{-ikr} + De^{ikr}$, where $\hbar k = \sqrt{2mE}$. The part $\propto e^{-ikr}$ is the incoming wave and the part $\propto e^{ikr}$ is the reflected wave. Since the wave function cannot penetrate into the domain $r < 0$, it must be fully reflected, i.e., $|D| = |C|$. We can choose $|C| = |D| = 1$.

It is convenient to encode the relative phase between C and D in the scattering phase shift $\delta_l(k)$, such that for $r \to \infty$

$$u_{k,l}(r) = 2 \sin\left(kr - \frac{l\pi}{2} + \delta_l(k)\right) \ . \tag{661}$$

The phase shift $\delta_l(k)$ depends both on l and on k and might be difficult to calculate. Yet, assuming we know $\delta_l(k)$, we can express the scattering amplitudes and the cross section via these phase shifts. The parametrization (661) is chosen so that for $V(r) = 0$ all the scattering phases vanish, $\delta_l(k) = 0$. Indeed, for $V(r) = 0$ the solutions of the Schrödinger equation (657) (with the proper boundary conditions at $r = 0$, i.e., $u_{k,l}(r \to 0) = 0$) are given by $u_{k,l}(r) = r\, R_{k,l}(r) \sim r\, j_l(kr)$, where $j_l(x)$ are the *spherical Bessel* functions:

$$j_l(x) = (-x)^l \left(\frac{1}{x}\frac{d}{dx}\right)^l \frac{\sin x}{x} \ . \tag{662}$$

Their asymptotic behavior is given by $j_l(x) \approx (1/x)\sin(x - l\pi/2)$ for $x \to \infty$.

The other possible solutions of the Schrödinger equation (657) with $V(r) = 0$ are given by $u_{k,l}(r) = r\, R_{k,l}(r) \sim r\, n_l(kr)$, where $n_l(x)$ are the *spherical Neumann* functions:

$$n_l(x) = -(-x)^l \left(\frac{1}{x}\frac{d}{dx}\right)^l \frac{\cos x}{x} \ . \tag{663}$$

These solutions *do not* satisfy the boundary condition at $r \to 0$, but are still important for solving problems where $V(r) \neq 0$, e.g., near $r = 0$. The asymptotic behavior of the *spherical Neumann* functions is given by $n_l(x) \approx -(1/x)\cos(x - l\pi/2)$ for $x \to \infty$.

The solution of the Schrödinger equation (657) with $V(r) = 0$, which corresponds to the asymptotic form (661) reads

$$R_{k,l}(r) = u_{k,l}(r)/r \propto 2\left[j_l(kr)\cos\delta_l - n_l(kr)\sin\delta_l\right] \ . \tag{664}$$

We will use this solution below.

2. Relation between scattering amplitudes and scattering phases

To establish the relation between scattering amplitudes and scattering phases we expand the scattering state in the basis of $\psi_{k,l,m}(\mathbf{r})$. Since the incoming wave is directed along z-axis and the scattering potential is symmetric, the scattering state should be independent of φ.

In particular, the scattering amplitudes depend only on θ. Thus, only the states with $m = 0$ should be used. Finally, we recall that $Y_{l,0} \propto P_l(\cos\theta)$. So, we use the Legendre polynomials

$$P_l(\mu) = \frac{1}{2^l l!} \frac{d^l}{d\mu^l}(\mu^2 - 1)^l \tag{665}$$

instead of $Y_{l,0}$. The expansion reads

$$\Psi(\boldsymbol{r}) = \sum_l A_l P_l(\cos\theta) R_{k,l}(r) \ , \tag{666}$$

where A_l are yet unknown coefficients. We should choose the coefficients A_l so that asymptotically, for $r \to \infty$

$$\Psi(\boldsymbol{r}) = e^{ikz} + \frac{e^{ikr}}{r} f_k(\theta) = \sum_{l=0}^{\infty} A_l P_l(\cos\theta) \frac{2\sin\left(kr - \frac{l\pi}{2} + \delta_l\right)}{r} \ . \tag{667}$$

We use the well-known expansion of the plane wave

$$e^{ikz} = e^{ikr\cos\theta} = \sum_{l=0}^{\infty} i^l (2l+1) j_l(kr) P_l(\cos\theta) \ , \tag{668}$$

where $j_l(x)$ are the spherical Bessel functions. For $r \to \infty$ the asymptotic expansion reads

$$e^{ikz} \approx \frac{1}{2ikr} \sum_{l=0}^{\infty} (2l+1) P_l(\cos\theta) \left[e^{ikr} + (-1)^{l+1} e^{-ikr}\right] \ . \tag{669}$$

We have used the asymptotic form of the spherical Bessel function $j_l(x) \approx (1/x)\sin(x - l\pi/2)$ for $x \to \infty$.

Comparing the r.h.s. and the l.h.s. of Eq. (667) we obtain

$$A_l = \frac{2l+1}{2k} (i)^l e^{i\delta_l} \ , \tag{670}$$

and

$$f_k(\theta) = \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1) P_l(\cos\theta) \left[e^{2i\delta_l} - 1\right] \ . \tag{671}$$

Thus, the total scattering amplitude splits into contributions of different "l-channels". One talks about scattering in s-channel ($l = 0$), p-channel ($l = 1$) etc.

From this result we can calculate the total cross section. We can either use

$$\sigma = \int d\Omega \, |f_{\boldsymbol{k}}(\boldsymbol{n})|^2 = 2\pi \int_0^{\pi} \sin\theta d\theta |f_k(\theta)|^2 \ , \tag{672}$$

and, in addition, $\int_0^\pi \sin\theta d\theta P_l(\cos\theta)P_{l'}(\cos\theta) = \frac{2}{2l+1}\delta_{l,l'}$. Alternatively we can use the optical theorem

$$\sigma = \frac{4\pi}{k}\,\mathrm{Im}\left[f_{\boldsymbol{k}}(\theta=0)\right] \ . \tag{673}$$

Both ways lead to

$$\sigma = \sum_{l=0}^{\infty}\sigma_l = \frac{4\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\sin^2\delta_l \ . \tag{674}$$

3. Example: hard sphere

Assume $V(r) = \infty$ for $r \leq a$ and $V(t) = 0$ for $r > a$. The boundary condition is $R_{k,l}(r=a) = 0$. Thus, using (664) for $r > a$ we immediately find the scattering phases

$$\tan\delta_l = \frac{j_l(ka)}{n_l(ka)} \ . \tag{675}$$

For $l = 0$ we immediately obtain $\tan\delta_0 = -\tan(ka)$. An interesting limit is that of scattering at low energy, i.e., $ka \ll 1$. Using the asymptotic properties of $j_l(x)$ and $n_l(x)$ for $x \to 0$ one can show that

$$\tan\delta_l \propto (ka)^{2l+1} \ll 1 \ . \tag{676}$$

This means that scattering in higher l-channels is strongly suppressed. Using (674) we obtain

$$\sigma \approx \sigma_0 = 4\pi a^2 \ . \tag{677}$$

We get a result that is $4\times$ the classical cross section.

E. Born series

If the scattering potential is weak or the energy of the incoming particles is high one can use the Born series. We start again from the Lippmann-Schwinger equation

$$\Psi(\boldsymbol{r}) = \Psi_0(\boldsymbol{r}) + \int d^3r_1\, G_+(\boldsymbol{r}-\boldsymbol{r_1})\,\frac{2m}{\hbar^2}\,V(\boldsymbol{r_1})\,\Psi(\boldsymbol{r_1}) \ . \tag{678}$$

Let us write this symbolically as

$$\Psi = \Psi_0 + \tilde{G}_+ V\Psi \ , \tag{679}$$

where $\tilde{G}_+ = \frac{2m}{\hbar^2} G_+$. Assuming V is weak, we can iterate. The 0-th iteration is $\Psi = \Psi_0$ (no scattering). The next iteration reads

$$\Psi = \Psi_0 + \tilde{G}_+ V \Psi_0 \ . \tag{680}$$

This is the 1-st Born approximation. The next iteration (2-nd Born approximation) reads

$$\Psi = \Psi_0 + \tilde{G}_+ V(\Psi_0 + \tilde{G}_+ V \Psi_0) = \Psi_0 + \tilde{G}_+ V \Psi_0 + \tilde{G}_+ V \tilde{G}_+ V \Psi_0 \ . \tag{681}$$

This iteration can be continued and produce the Born series.

Let us write explicitly the result of the 1-st Born approximation:

$$\Psi(r) = \Psi_0(\boldsymbol{r}) + \int d^3 r_1 \, G_+(\boldsymbol{r} - \boldsymbol{r_1}) \, \frac{2m}{\hbar^2} \, V(\boldsymbol{r_1}) \, \Psi_0(\boldsymbol{r_1}) \ . \tag{682}$$

Taking

$$G_+(\boldsymbol{r}) = -\frac{1}{4\pi} \, \frac{e^{ikr}}{r} \ , \tag{683}$$

and

$$\Psi_0 = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \ , \tag{684}$$

we get

$$\Psi^{(1)}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} - \frac{m}{2\pi\hbar^2} \int d^3 r_1 \, \frac{e^{ik|\boldsymbol{r}-\boldsymbol{r_1}|}}{|\boldsymbol{r}-\boldsymbol{r_1}|} \, V(\boldsymbol{r_1}) \, e^{i\boldsymbol{k}\cdot\boldsymbol{r}_1} \ . \tag{685}$$

For the scattering amplitude this gives

$$f^{(1)}_{\boldsymbol{k}}(\boldsymbol{n}) = -\frac{m}{2\pi\hbar^2} \int d^3 r_1 \, e^{i\boldsymbol{k}\cdot\boldsymbol{r}_1} \, e^{-ik\,\boldsymbol{n}\cdot\boldsymbol{r_1}} \, V(\boldsymbol{r_1}) \ . \tag{686}$$

Introducing $\boldsymbol{k'} \equiv k\boldsymbol{n}$ we obtain

$$f^{(1)}_{\boldsymbol{k},\boldsymbol{k'}} = -\frac{m}{2\pi\hbar^2} \int d^3 r_1 \, e^{i(\boldsymbol{k}-\boldsymbol{k'})\cdot\boldsymbol{r}_1} \, V(\boldsymbol{r_1}) = -\frac{m}{2\pi\hbar^2} \tilde{V}(\boldsymbol{k'} - \boldsymbol{k}) \ . \tag{687}$$

Here $\tilde{V}(\boldsymbol{k})$ is the Fourier image of $V(\boldsymbol{r})$.

1. Example: Yukawa potential

As an example we consider the Yukawa potential

$$V(r) = \frac{A}{r} \, e^{-\lambda r} \ . \tag{688}$$

The Fourier image reads

$$\tilde{V}(\boldsymbol{k}) = \int d^3r\, V(\boldsymbol{r})\, e^{-i\boldsymbol{kr}} \ . \tag{689}$$

For spherically symmetric potentials we get

$$\begin{aligned} \tilde{V}(\boldsymbol{k}) \ &= \ \int d^3r\, V(r)\, e^{-i\boldsymbol{kr}} = \int\limits_0^\infty r^2 dr\, V(r)\, 2\pi \int\limits_0^\pi \sin\theta d\theta\, e^{-ikr\cos\theta} \\ &= \int\limits_0^\infty r^2 dr\, V(r)\, 2\pi \int\limits_{-1}^1 dx\, e^{-ikrx} = \int\limits_0^\infty r^2 dr\, V(r)\, \frac{4\pi}{kr}\, \sin(kr) \ . \end{aligned} \tag{690}$$

For the Yukawa potential this gives

$$\tilde{V}(\boldsymbol{k}) = A \int\limits_0^\infty r^2 dr\, \frac{e^{-\lambda r}}{r}\, \frac{2\pi}{ikr} \left(e^{ikr} - e^{-ikr}\right) = \frac{2\pi A}{ik} \left(\frac{1}{\lambda - ik} - \frac{1}{\lambda + ik}\right) = \frac{4\pi A}{\lambda^2 + k^2} \ . \tag{691}$$

For the scattering amplitude we need

$$(\boldsymbol{k'} - \boldsymbol{k})^2 = 2k^2(1 - \cos\theta) = \left(2k \sin^2 \frac{\theta}{2}\right)^2 \ . \tag{692}$$

Thus

$$f^{(1)}_{\boldsymbol{k},\boldsymbol{k'}} = -\frac{m}{2\pi\hbar^2}\, \frac{4\pi A}{\lambda^2 + \left(2k \sin^2 \frac{\theta}{2}\right)^2} \ . \tag{693}$$

The differential cross section reads

$$\frac{d\sigma}{d\Omega} = |f^{(1)}_{\boldsymbol{k},\boldsymbol{k'}}|^2 = \frac{m^2}{(2\pi\hbar^2)^2}\, \frac{(4\pi A)^2}{\left(\lambda^2 + \left(2k \sin^2 \frac{\theta}{2}\right)^2\right)^2} = \frac{A^2}{\left(4E_k^2 \sin^2 \frac{\theta}{2} + \frac{\hbar^2\lambda^2}{2m}\right)^2} \ . \tag{694}$$

Here $E_k = \hbar^2 k^2/2m$. Interestingly, for $\lambda \to 0$ we obtain the Rutherford formula, even though our theory was not supposed to work for the Coulomb potential.

XIV. QUASI-CLASSICAL APPROXIMATION, WENTZEL-KRAMERS-BRILLOUIN (WKB) METHOD

This is a very important approximation, which resembles the approximation which leads from the wave optics to the geometric optics. The main idea is that the phase of the wave function oscillates fast, e.g., because the energy is much higher than the ground state energy. We restrict ourselves to 1D. The 1-D Schrödinger equation reads

$$-\hbar^2\, \frac{\partial^2 \psi(x)}{\partial x^2} = 2m(E - V(x))\psi(x) \ . \tag{695}$$

Ansatz:

$$\psi(x) = e^{iS(x)/\hbar} \ . \tag{696}$$

We obtain

$$\frac{\partial \psi(x)}{\partial x} = \frac{i}{\hbar}\frac{\partial S}{\partial x}\,\psi(x) \ . \tag{697}$$

$$\frac{\partial^2 \psi(x)}{\partial x^2} = \frac{i}{\hbar}\frac{\partial^2 S}{\partial x^2}\,\psi(x) + \left(\frac{i}{\hbar}\frac{\partial S}{\partial x}\right)^2 \psi(x) \ . \tag{698}$$

Substituting into the Schrödinger equation we obtain

$$\left(\frac{\partial S}{\partial x}\right)^2 - i\hbar\frac{\partial^2 S}{\partial x^2} = 2m(E - V(x)) \ . \tag{699}$$

The main idea now is that the second term in the l.h.s. is much smaller than the first term. That is the phase changes fast, but the rate of its change (the second derivative) is slow. Since the second term in the l.h.s. is the only one containing $\hbar$, one can formally present this an as expansion in powers of $\hbar$ (since $\hbar$ is dimension-full, one should be careful):

$$S = S_0 + \frac{\hbar}{i}\,S_1 + \left(\frac{\hbar}{i}\right)^2 S_2 + \dots \ . \tag{700}$$

Zeroth order:

$$\left(\frac{\partial S_0}{\partial x}\right)^2 = 2m(E - V(x)) \ . \tag{701}$$

First order

$$2\frac{\partial S_0}{\partial x}\,\frac{\partial S_1}{\partial x} = -\frac{\partial^2 S_0}{\partial x^2} \ . \tag{702}$$

The zeroth order equation is solved (assuming $E > V(x)$) by

$$\frac{\partial S_0}{\partial x} = \pm|p(x)| \ , \tag{703}$$

where

$$|p(x)| \equiv \sqrt{2m(E - V(x))} \tag{704}$$

is the absolute value of the classical momentum. This gives

$$S_0(x) = \pm\int_a^x |p(x')|\,dx' \ . \tag{705}$$

The lower integration limit is for now arbitrary, but the whole interval $[a, x]$ should be in the allowed domain, i.e., $E > V(x)$.

The WKB expansion is justified if

$$\left| i\hbar \frac{\partial^2 S_0}{\partial x^2} \right| \ll \left| \frac{\partial S_0}{\partial x} \right|^2 \quad \rightarrow \quad \left| \hbar \frac{dp}{dx} \right| \ll |p^2| \ . \tag{706}$$

In terms of the de Broglie wave length $\lambda(x) = \frac{2\pi\hbar}{|p|}$ this means

$$\left| \frac{d\lambda(x)}{dx} \right| \ll 2\pi \ . \tag{707}$$

This condition means that de Broglie wave length does not change much on its own scale.

For $S_1(x)$ we get

$$\frac{\partial S_1}{\partial x} = -\frac{1}{2} \frac{\frac{\partial^2 S_0}{\partial x^2}}{\frac{\partial S_0}{\partial x}} = -\frac{1}{2} \frac{\partial}{\partial x} \log \left[\frac{\partial S_0}{\partial x} \right] = -\frac{1}{2} \frac{\partial}{\partial x} \log |p(x)| \ . \tag{708}$$

We further obtain

$$S_1(x) = -\frac{1}{2} \log |p(x)| + const. \ . \tag{709}$$

Thus

$$e^{\frac{i}{\hbar}\left(\frac{\hbar}{i}\right)S_1} = e^{S_1} = \frac{C}{\sqrt{|p|}} \ . \tag{710}$$

For the wave function we obtain

$$\psi(x) = \frac{C_1}{\sqrt{|p(x)|}} \, e^{\frac{i}{\hbar}\int_a^x |p(x')|dx'} + \frac{C_2}{\sqrt{|p(x)|}} \, e^{-\frac{i}{\hbar}\int_a^x |p(x')|dx'} \ . \tag{711}$$

The quasi-classical expansion (700) works formally also for $E < V(x)$, i.e., in the classically forbidden region. There we obtain

$$\frac{\partial S_0}{\partial x} = \pm i\sqrt{2m(V(x) - E)} = \pm i|p(x)| \ , \tag{712}$$

where now $|p(x)| = \sqrt{2m(V(x) - E)}$. We obtain again

$$S_1(x) = -\frac{1}{2} \log |p(x)| + const. \ . \tag{713}$$

and the most general solution reads

$$\psi(x) = \frac{D_1}{\sqrt{|p(x)|}} \, e^{\frac{1}{\hbar}\int_a^x |p(x')|dx'} + \frac{D_2}{\sqrt{|p(x)|}} \, e^{-\frac{1}{\hbar}\int_a^x |p(x')|dx'} \ . \tag{714}$$

Now, the whole interval $[a, x]$ should be in the forbidden region.

Consider now a turning point $x = a$, where $V(a) = E$. Assume that right of this point there is a forbidden region and left of this point there is an allowed region. That is

$$\begin{aligned} V(x) > E \quad \text{for} \quad x > a \ , \\ V(x) < E \quad \text{for} \quad x < a \ . \end{aligned} \tag{715}$$

If the forbidden region extends from a to $+\infty$, only the decaying solution is allowed for $x > a$:

$$\psi(x) = \frac{D}{\sqrt{|p(x)|}} \, e^{-\frac{1}{\hbar}\int_a^x |p(x')|dx'} \ . \tag{716}$$

To find the corresponding solution in the allowed region $x < a$ one can either solve the problem exactly near $x = a$ or use another trick of going around the point $x = 0$ in the complex plain of x (Landau & Lifschitz). The result reads $C_1 = De^{i\pi/4}$ and $C_2 = De^{-i\pi/4}$. Thus, the wave function for $x < 0$ reads

$$\begin{aligned} \psi(x) &= \frac{De^{i\pi/4}}{\sqrt{|p(x)|}} \, e^{\frac{i}{\hbar}\int_a^x |p(x')|dx'} + \frac{De^{-i\pi/4}}{\sqrt{|p(x)|}} \, e^{-\frac{i}{\hbar}\int_a^x |p(x')|dx'} \\ &= \frac{2D}{\sqrt{|p(x)|}} \cos\left(\frac{1}{\hbar}\int_a^x |p(x')|dx' + \frac{\pi}{4}\right) \ . \end{aligned} \tag{717}$$

Similarly, if the turning point is such that

$$\begin{aligned} V(x) > E \quad \text{for} \quad x < b \ , \\ V(x) < E \quad \text{for} \quad x > b \ , \end{aligned} \tag{718}$$

and the forbidden region extends to $x = -\infty$ we obtain for $x < b$

$$\psi(x) = \frac{G}{\sqrt{|p(x)|}} \, e^{\frac{1}{\hbar}\int_b^x |p(x')|dx'} \ . \tag{719}$$

For $x > b$ we get

$$\begin{aligned} \psi(x) &= \frac{Ge^{-i\pi/4}}{\sqrt{|p(x)|}} \, e^{\frac{i}{\hbar}\int_b^x |p(x')|dx'} + \frac{Ge^{i\pi/4}}{\sqrt{|p(x)|}} \, e^{-\frac{i}{\hbar}\int_b^x |p(x')|dx'} \\ &= \frac{2G}{\sqrt{|p(x)|}} \cos\left(\frac{1}{\hbar}\int_b^x |p(x')|dx' - \frac{\pi}{4}\right) \ . \end{aligned} \tag{720}$$

Assume now the allowed region is between b and $a > b$ and the forbidden regions are from $-\infty$ to b and from a to ∞. Then, comparing the two solutions in the middle interval

$[b,a]$ we obtain

$$De^{i\pi/4} = Ge^{-i\pi/4}e^{\frac{i}{\hbar}\int_b^a |p(x')|dx'} \ , \tag{721}$$

$$De^{-i\pi/4} = Ge^{i\pi/4}e^{-\frac{i}{\hbar}\int_b^a |p(x')|dx'} \ . \tag{722}$$

This gives the Bohr-Sommerfeld quantization condition

$$\frac{1}{\hbar}\oint |p(x)|dx = 2\pi\left(n+\frac{1}{2}\right) \ . \tag{723}$$

1. Boundary condition

Consider the point $x=a$, where the forbidden region is to the right of a. Near $x=a$ we can expand

$$V(x) = V(a) - F_a(x-a) = E - F_a(x-a) \ , \tag{724}$$

where $F_a = -\partial V/\partial x|_a$ is the force. In our case $F_a < 0$.

One way is just to solve exactly the Schrödinger equation near $x=a$:

$$-\hbar^2\frac{\partial^2\psi(x)}{\partial x^2} = [2mF_a](x-a)\psi(x) \ . \tag{725}$$

The solution is known and is given by the so-called Airy function.

An alternative way it to try to go around the point $x=a$ in the complex plane. The idea is always to keep far enough from $x=a$ so that the quasi-classical solutions hold. For $x>a$ we have $|p(x)| = \sqrt{2m|F_a|(x-a)}$ and

$$\int_a^x |p(x')|dx' = (2/3)\sqrt{2m|F_a|}(x-a)^{3/2} \ . \tag{726}$$

For the wave function at $x>0$ (far enough from the turning point) we obtain

$$\psi(x) = \frac{D}{(2m|F_a|)^{1/4}}\frac{1}{(x-a)^{1/4}}e^{-(2/3)\sqrt{2m|F_a|}(x-a)^{3/2}} \ . \tag{727}$$

Introduce $z = x-a = \rho e^{i\varphi}$ and consider z in the complex plane around $z=0$. The positive direction $x>a$ corresponds to $\varphi = 0$. We get

$$\psi(x) = \frac{D}{(2m|F_a|)^{1/4}}\frac{1}{z^{1/4}}e^{-Az^{3/2}} = \frac{1}{\rho^{1/4}e^{i\varphi/4}}\exp\left[-A\rho^{3/2}e^{i3\varphi/2}\right] \ . \tag{728}$$

Here $A = (2/3)\sqrt{2m|F_a|}$.

If we go around in the upper half plane, i.e., we follow the path $\varphi = 0 \to \varphi = \pi$ the wave functions at $x < a$ becomes

$$\frac{D}{(2m|F_a|)^{1/4}} \frac{e^{-i\pi/4}}{\rho^{1/4}} \exp\left[-A\, i\rho^{3/2}\right] \ . \tag{729}$$

This corresponds to the term C_2 of (711). Thus we obtain $C_2 = De^{-i\pi/4}$.

If we go around in the lower half plane, i.e., we follow the path $\varphi = 0 \to \varphi = -\pi$ the wave functions at $x < a$ becomes

$$\frac{D}{(2m|F_a|)^{1/4}} \frac{e^{i\pi/4}}{\rho^{1/4}} \exp\left[A\, i\rho^{3/2}\right] \ . \tag{730}$$

This corresponds to the term C_1 of (711). Thus we obtain $C_1 = De^{i\pi/4}$.

Why do we "loose" one of the components in each of the ways? This is explained by the so called Stokes phenomenon.

2. Stokes phenomenon

Consider the differential equation

$$\frac{d^2u(z)}{dz^2} = zu(z) \ . \tag{731}$$

One of its solutions is the Airy function $Ai(x)$:

$$Ai(z) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp\left[i\left(zt + \frac{t^3}{3}\right)\right] dt \ . \tag{732}$$

Airy function is an entire function, i.e., it is analytical (holomorphic) in the whole complex plane. Asymptotically, for $|z| \to \infty$, one can use the WKB method and get the two solutions

$$u_\pm = \frac{1}{z^{1/4}} \exp\left[\pm\frac{2}{3}z^{3/2}\right] \ . \tag{733}$$

These functions are not single valued. Once the argument of z makes a 2π rotation the functions $u_\pm(z)$ are modified. Therefore, a simple asymptotic formula $Ai(z) = C_+u_+(z) + C_-u_-(z)$ cannot be correct for all z such that $|z| \to \infty$. The coefficients $C_\pm$ should change (possibly jump) as the argument of z changes. The actual asymptotic expressions for $Ai(x)$ for real x are

$$Ai(x) \approx \frac{1}{2\sqrt{\pi}} \frac{e^{-2/3x^{3/2}}}{x^{1/4}} \quad \text{for} \quad x \to +\infty \ , \tag{734}$$

$$Ai(x) \approx \frac{1}{\sqrt{\pi}} \frac{\sin\left(\frac{2}{3}(-x)^{3/2} + \frac{\pi}{4}\right)}{(-x)^{1/4}} \quad \text{for} \quad x \to -\infty \ . \tag{735}$$

Appendix A: $\boldsymbol{\nabla}$ and $\boldsymbol{\nabla}^2$ in spherical coordinates

The spherical coordinates are defined via

$$\begin{aligned} x &= r\sin\theta\cos\phi \ , \\ y &= r\sin\theta\sin\phi \ , \\ z &= r\cos\theta \ . \end{aligned} \tag{A1}$$

Evidently $r \in [0, +\infty]$, $\theta \in [0, \pi]$, and $\phi \in [0, 2\pi]$. The inverse relations read

$$\begin{aligned} r &= \sqrt{x^2 + y^2 + z^2}, \\ \cos\theta &= \frac{z}{r} \ , \\ \tan\phi &= \frac{y}{x} \ . \end{aligned} \tag{A2}$$

The last relation does not define ϕ unambiguously. If $x > 0$ and $y > 0$ the angle ϕ should be taken from the quadrant $\phi \in [0, \pi/2]$ etc.. We calculate, first, the components of $\boldsymbol{\nabla} = (\partial/\partial x, \partial/\partial y, \partial/\partial z)$:

1) x**-component**:

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x}\frac{\partial}{\partial \phi} \ . \tag{A3}$$

We get

$$\frac{\partial r}{\partial x} = \frac{x}{r} = \sin\theta\cos\phi \ . \tag{A4}$$

From

$$\frac{\partial \cos\theta}{\partial x} = -\sin\theta\frac{\partial \theta}{\partial x} = -\frac{z}{r^2}\frac{\partial r}{\partial x} = -\frac{xz}{r^3} = -\frac{\cos\phi\sin\theta\cos\theta}{r} \tag{A5}$$

we obtain

$$\frac{\partial \theta}{\partial x} = \frac{\cos\phi\cos\theta}{r} \ . \tag{A6}$$

From

$$\frac{\partial \tan\phi}{\partial x} = \frac{1}{\cos^2\phi}\frac{\partial \phi}{\partial x} = -\frac{y}{x^2} = -\frac{\sin\phi}{r\sin\theta\cos\phi^2} \tag{A7}$$

we obtain

$$\frac{\partial \phi}{\partial x} = -\frac{\sin\phi}{r\sin\theta} \ . \tag{A8}$$

We collect

$$\frac{\partial}{\partial x} = \sin\theta\cos\phi\,\frac{\partial}{\partial r} + \frac{\cos\theta\cos\phi}{r}\,\frac{\partial}{\partial \theta} - \frac{\sin\phi}{r\sin\theta}\,\frac{\partial}{\partial \phi} \ . \tag{A9}$$

2) y-**component**:

$$\frac{\partial}{\partial y} = \frac{\partial r}{\partial y}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial y}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial y}\frac{\partial}{\partial \phi} \ . \tag{A10}$$

We get

$$\frac{\partial r}{\partial y} = \frac{y}{r} = \sin\theta \sin\phi \ . \tag{A11}$$

From

$$\frac{\partial \cos\theta}{\partial y} = -\sin\theta \frac{\partial \theta}{\partial y} = -\frac{z}{r^2}\frac{\partial r}{\partial y} = -\frac{yz}{r^3} = -\frac{\sin\phi \sin\theta \cos\theta}{r} \tag{A12}$$

we obtain

$$\frac{\partial \theta}{\partial y} = \frac{\sin\phi \cos\theta}{r} \ . \tag{A13}$$

From

$$\frac{\partial \tan\phi}{\partial y} = \frac{1}{\cos^2\phi}\frac{\partial \phi}{\partial y} = \frac{1}{x} = \frac{1}{r\sin\theta\cos\phi} \tag{A14}$$

we obtain

$$\frac{\partial \phi}{\partial y} = \frac{\cos\phi}{r\sin\theta} \ . \tag{A15}$$

We collect

$$\frac{\partial}{\partial y} = \sin\theta\sin\phi\,\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\,\frac{\partial}{\partial \theta} + \frac{\cos\phi}{r\sin\theta}\,\frac{\partial}{\partial \phi} \ . \tag{A16}$$

3) z-**component:**

$$\frac{\partial}{\partial z} = \frac{\partial r}{\partial z}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial z}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial z}\frac{\partial}{\partial \phi} \ . \tag{A17}$$

We get

$$\frac{\partial r}{\partial z} = \frac{z}{r} = \cos\theta \ . \tag{A18}$$

From

$$\frac{\partial \cos\theta}{\partial z} = -\sin\theta\frac{\partial \theta}{\partial z} = -\frac{z}{r^2}\frac{\partial r}{\partial z} + \frac{1}{r} = -\frac{z^2}{r^3} + \frac{1}{r} = \frac{\sin^2\theta}{r} \tag{A19}$$

we obtain

$$\frac{\partial \theta}{\partial z} = -\frac{\sin\theta}{r} \ . \tag{A20}$$

From

$$\frac{\partial \tan\phi}{\partial z} = \frac{1}{\cos^2\phi}\frac{\partial \phi}{\partial z} = 0 \tag{A21}$$

we obtain

$$\frac{\partial \phi}{\partial z} = 0 \ . \tag{A22}$$

We collect

$$\frac{\partial}{\partial z} = \cos\theta\,\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\,\frac{\partial}{\partial \theta} \ . \tag{A23}$$

4) We calculate

$$\begin{aligned}\boldsymbol{\nabla}^2 &= \left(\sin\theta\cos\phi\,\frac{\partial}{\partial r}+\frac{\cos\theta\cos\phi}{r}\,\frac{\partial}{\partial\theta}-\frac{\sin\phi}{r\sin\theta}\,\frac{\partial}{\partial\phi}\right)^2\\ &+\left(\sin\theta\sin\phi\,\frac{\partial}{\partial r}+\frac{\cos\theta\sin\phi}{r}\,\frac{\partial}{\partial\theta}+\frac{\cos\phi}{r\sin\theta}\,\frac{\partial}{\partial\phi}\right)^2\\ &+\left(\cos\theta\,\frac{\partial}{\partial r}-\frac{\sin\theta}{r}\,\frac{\partial}{\partial\theta}\right)^2 .\end{aligned} \tag{A24}$$

It is easy to collect terms that contain two derivatives, i.e., the derivatives do not act on the coefficients. Among these only diagonal terms survive. These are

$$\frac{\partial^2}{\partial r^2}+\frac{1}{r^2}\,\frac{\partial^2}{\partial\theta^2}+\frac{1}{r^2\sin^2\theta}\,\frac{\partial^2}{\partial\phi^2} . \tag{A25}$$

Next we examine the terms in which one of the derivatives acts on the coefficients and only one remains. Among the diagonal terms no such combinations survive. From the mixed terms of the type $\partial_\theta\ldots\partial_r$ we get the contribution

$$\frac{1}{r}\,\frac{\partial}{\partial r} . \tag{A26}$$

Another such contribution comes from the mixed terms of the type $\partial_\phi\ldots\partial_r$. Finally, the mixed terms of the type $\partial_\phi\ldots\partial_\theta$ produce

$$\frac{1}{r^2}\,\frac{\cos\theta}{\sin\theta}\,\frac{\partial}{\partial\theta} . \tag{A27}$$

Adding all terms we get

$$\begin{aligned}\boldsymbol{\nabla}^2 &= \frac{\partial^2}{\partial r^2}+\frac{2}{r}\,\frac{\partial}{\partial r}+\frac{1}{r^2}\,\frac{\partial^2}{\partial\theta^2}+\frac{1}{r^2}\,\frac{\cos\theta}{\sin\theta}\,\frac{\partial}{\partial\theta}+\frac{1}{r^2\sin^2\theta}\,\frac{\partial^2}{\partial\phi^2}\\ &= \frac{\partial^2}{\partial r^2}+\frac{2}{r}\,\frac{\partial}{\partial r}+\frac{1}{r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\,\sin\theta\,\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\,\frac{\partial^2}{\partial\phi^2}\right) .\end{aligned} \tag{A28}$$

Appendix B: Components of the angular momentum in spherical coordinates, operator $\hat{\boldsymbol{L}}^2$

We start with $\hat{L}_z$:

$$\begin{aligned}\hat{L}_z &= \hat{x}\hat{p}_y-\hat{y}\hat{p}_x=-i\hbar\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)\\ &= -\,i\hbar\left[r\sin\theta\cos\phi\left(\sin\theta\sin\phi\,\frac{\partial}{\partial r}+\frac{\cos\theta\sin\phi}{r}\,\frac{\partial}{\partial\theta}+\frac{\cos\phi}{r\sin\theta}\,\frac{\partial}{\partial\phi}\right)\right.\\ &\quad\left.-\,r\sin\theta\sin\phi\left(\sin\theta\cos\phi\,\frac{\partial}{\partial r}+\frac{\cos\theta\cos\phi}{r}\,\frac{\partial}{\partial\theta}-\frac{\sin\phi}{r\sin\theta}\,\frac{\partial}{\partial\phi}\right)\right]\\ &= -\,i\hbar\,\frac{\partial}{\partial\phi} .\end{aligned} \tag{B1}$$

Next is $\hat{L}_x$:

$$\begin{aligned}\hat{L}_x &= \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\\ &= -i\hbar\left[r\sin\theta\sin\phi\left(\cos\theta\,\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\,\frac{\partial}{\partial\theta}\right)\right.\\ &\quad \left. - r\cos\theta\left(\sin\theta\sin\phi\,\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\,\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\,\frac{\partial}{\partial\phi}\right)\right]\\ &= i\hbar\left[\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right]\,. \end{aligned} \tag{B2}$$

Finally is $\hat{L}_y$:

$$\begin{aligned}\hat{L}_y &= \hat{z}\hat{p}_x - \hat{x}\hat{p}_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\\ &= -i\hbar\left[r\cos\theta\left(\sin\theta\cos\phi\,\frac{\partial}{\partial r} + \frac{\cos\theta\cos\phi}{r}\,\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\,\frac{\partial}{\partial\phi}\right)\right.\\ &\quad \left. - r\sin\theta\cos\phi\left(\cos\theta\,\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\,\frac{\partial}{\partial\theta}\right)\right]\\ &= i\hbar\left[-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right]\,. \end{aligned} \tag{B3}$$

For the operator $\hat{\boldsymbol{L}}^2$ we, thus, obtain

$$\hat{\boldsymbol{L}}^2 = -\hbar^2\left[\left(\frac{\partial}{\partial\phi}\right)^2 + \left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)^2 + \left(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)^2\right]\,. \tag{B4}$$

We, first, collect the terms with two derivatives, i.e., those where the derivatives do not act on the coefficients. These are

$$-\hbar^2\left[\frac{\partial^2}{\partial\phi^2} + \cot^2\theta\frac{\partial^2}{\partial\phi^2} + \frac{\partial^2}{\partial\theta^2}\right] = -\hbar^2\left[\frac{1}{\sin^2\theta}\,\frac{\partial^2}{\partial\phi^2} + \frac{\partial^2}{\partial\theta^2}\right]\,. \tag{B5}$$

In the combinations $\partial\phi\ldots\partial\theta$ there are contributions where $\partial\phi$ acts on the coefficients. These give

$$-\hbar^2\left[\cot\theta\,\frac{\partial}{\partial\theta}\right]\,. \tag{B6}$$

Altogether we get

$$\hat{\boldsymbol{L}}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\,\frac{\partial}{\partial\theta}\,\sin\theta\,\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\,\frac{\partial^2}{\partial\phi^2}\right]\,. \tag{B7}$$

We can now see that

$$\begin{aligned}\boldsymbol{\nabla}^2 &= \frac{\partial^2}{\partial r^2} + \frac{2}{r}\,\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\,\sin\theta\,\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\,\frac{\partial^2}{\partial\phi^2}\right)\\ &= \frac{\partial^2}{\partial r^2} + \frac{2}{r}\,\frac{\partial}{\partial r} - \frac{\hat{\boldsymbol{L}}^2}{\hbar^2 r^2}\,. \end{aligned} \tag{B8}$$

Appendix C: Local basis in spherical coordinates, $\boldsymbol{\nabla}$ in local basis and $\boldsymbol{\nabla}^2$

It is a bit more elegant to use the local basis. This can be defined using again the relations

$$\begin{aligned} x &= r\sin\theta\cos\phi \ , \\ y &= r\sin\theta\sin\phi \ , \\ z &= r\cos\theta \ . \end{aligned} \tag{C1}$$

An infinitesimal differential of $\mathbf{r} = (x, y, z)$ can be written as

$$d\mathbf{r} = \frac{\partial \mathbf{r}}{\partial r}dr + \frac{\partial \mathbf{r}}{\partial \theta}d\theta + \frac{\partial \mathbf{r}}{\partial \phi}d\phi \ . \tag{C2}$$

We obtain

$$\frac{\partial \mathbf{r}}{\partial r} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta) \ . \tag{C3}$$

This vector is normalized, thus we call it

$$\mathbf{e}_r = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta) \ . \tag{C4}$$

Next

$$\frac{\partial \mathbf{r}}{\partial \theta} = r(\cos\theta\cos\phi, \cos\theta\sin\phi, -\sin\theta) \ . \tag{C5}$$

Since $|\frac{\partial \mathbf{r}}{\partial \theta}| = r$ we normalize it and introduce

$$\mathbf{e}_\theta = (\cos\theta\cos\phi, \cos\theta\sin\phi, -\sin\theta) \ . \tag{C6}$$

Finally,

$$\frac{\partial \mathbf{r}}{\partial \phi} = r(-\sin\theta\sin\phi, \sin\theta\cos\phi, 0) \ . \tag{C7}$$

For the norm we obtain $|\frac{\partial \mathbf{r}}{\partial \phi}| = r\sin\theta$. We normalize and introduce a unit length vector

$$\mathbf{e}_\phi = (-\sin\phi, \cos\phi, 0) \ . \tag{C8}$$

For the differential we obtain

$$d\mathbf{r} = \mathbf{e}_r dr + r\mathbf{e}_\theta d\theta + r\sin\theta\mathbf{e}_\phi d\phi \ . \tag{C9}$$

The basis $\mathbf{e}_r, \mathbf{e}_\theta, \mathbf{e}_\phi$ is orthonormal. We rewrite the expressions for $\mathbf{e}_r, \mathbf{e}_\theta, \mathbf{e}_\phi$ as

$$\begin{aligned} \mathbf{e}_r &= \sin\theta\cos\phi\,\mathbf{e}_x + \sin\theta\sin\phi\,\mathbf{e}_y + \cos\theta\,\mathbf{e}_z \ , \\ \mathbf{e}_\theta &= \cos\theta\cos\phi\,\mathbf{e}_x + \cos\theta\sin\phi\,\mathbf{e}_y - \sin\theta\,\mathbf{e}_z \ , \\ \mathbf{e}_\phi &= -\sin\phi\,\mathbf{e}_x + \cos\phi\,\mathbf{e}_y \ . \end{aligned} \tag{C10}$$

In the matrix form this looks like

$$\begin{pmatrix} \mathbf{e}_r \\ \mathbf{e}_\theta \\ \mathbf{e}_\phi \end{pmatrix} = \begin{pmatrix} \sin\theta\cos\phi & \sin\theta\sin\phi & \cos\theta \\ \cos\theta\cos\phi & \cos\theta\sin\phi & -\sin\theta \\ -\sin\phi & \cos\phi & 0 \end{pmatrix} \begin{pmatrix} \mathbf{e}_x \\ \mathbf{e}_y \\ \mathbf{e}_z \end{pmatrix} . \tag{C11}$$

We invert this relation. The matrix above is orthogonal, thus to invert it we just have to transpose:

$$\begin{pmatrix} \mathbf{e}_x \\ \mathbf{e}_y \\ \mathbf{e}_z \end{pmatrix} = \begin{pmatrix} \sin\theta\cos\phi & \cos\theta\cos\phi & -\sin\phi \\ \sin\theta\sin\phi & \cos\theta\sin\phi & \cos\phi \\ \cos\theta & -\sin\theta & 0 \end{pmatrix} \begin{pmatrix} \mathbf{e}_r \\ \mathbf{e}_\theta \\ \mathbf{e}_\phi \end{pmatrix} . \tag{C12}$$

We are now in a position to calculate the operator $\boldsymbol{\nabla}$ in spherical coordinates. We use

$$\boldsymbol{\nabla} = \mathbf{e}_x \frac{\partial}{\partial x} + \mathbf{e}_y \frac{\partial}{\partial y} + \mathbf{e}_z \frac{\partial}{\partial z} \tag{C13}$$

and substitute (C12) as well as the relations (A9,A16,A23) obtained above and provided below for clarity

$$\frac{\partial}{\partial x} = \sin\theta\cos\phi \frac{\partial}{\partial r} + \frac{\cos\theta\cos\phi}{r} \frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta} \frac{\partial}{\partial\phi} . \tag{C14}$$

$$\frac{\partial}{\partial y} = \sin\theta\sin\phi \frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r} \frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta} \frac{\partial}{\partial\phi} . \tag{C15}$$

$$\frac{\partial}{\partial z} = \cos\theta \frac{\partial}{\partial r} - \frac{\sin\theta}{r} \frac{\partial}{\partial\theta} . \tag{C16}$$

Collecting the terms we obtain

$$\boldsymbol{\nabla} = \mathbf{e}_r \frac{\partial}{\partial r} + \frac{1}{r} \mathbf{e}_\theta \frac{\partial}{\partial\theta} + \frac{1}{r\sin\theta} \mathbf{e}_\phi \frac{\partial}{\partial\phi} . \tag{C17}$$

We now attempt to calculate $\boldsymbol{\nabla}^2$:

$$\boldsymbol{\nabla}^2 = \left(\mathbf{e}_r \frac{\partial}{\partial r} + \frac{1}{r} \mathbf{e}_\theta \frac{\partial}{\partial\theta} + \frac{1}{r\sin\theta} \mathbf{e}_\phi \frac{\partial}{\partial\phi} \right) \left(\mathbf{e}_r \frac{\partial}{\partial r} + \frac{1}{r} \mathbf{e}_\theta \frac{\partial}{\partial\theta} + \frac{1}{r\sin\theta} \mathbf{e}_\phi \frac{\partial}{\partial\phi} \right) . \tag{C18}$$

The problem is that the operators in the left brackets acts also on the coefficients and the unit vectors $\mathbf{e}_r(\theta,\phi)$, $\mathbf{e}_\theta(\theta,\phi)$, $\mathbf{e}_\phi(\theta,\phi)$ in the right bracket. First we collect the terms with second derivatives, i.e., those where the derivatives in the left bracket do not act on the coefficients or the unit vectors in the right bracket. These are

$$\frac{\partial^2}{\partial r^2} + \frac{1}{r^2} \frac{\partial^2}{\partial\theta^2} + \frac{1}{r^2\sin^2\theta} \frac{\partial^2}{\partial\phi^2} . \tag{C19}$$

To get the terms with one derivative we use (C11) and obtain

$$\frac{\partial \mathbf{e}_r}{\partial \theta} = \mathbf{e}_\theta \quad , \quad \frac{\partial \mathbf{e}_\theta}{\partial \theta} = -\mathbf{e}_r \quad , \quad \frac{\partial \mathbf{e}_\phi}{\partial \theta} = 0 \ . \tag{C20}$$

$$\frac{\partial \mathbf{e}_r}{\partial \phi} = \sin\theta\, \mathbf{e}_\phi \quad , \quad \frac{\partial \mathbf{e}_\theta}{\partial \phi} = \cos\theta\, \mathbf{e}_\phi \quad , \quad \frac{\partial \mathbf{e}_\phi}{\partial \phi} = -\sin\theta\, \mathbf{e}_r - \cos\theta\, \mathbf{e}_\theta \ . \tag{C21}$$

From the combination $\partial\theta \ldots \partial r$ we get

$$\frac{1}{r}\frac{\partial}{\partial r} \ . \tag{C22}$$

The same we obtain from $\partial\phi \ldots \partial r$. Finally, from $\partial\phi \ldots \partial\theta$ we get

$$\frac{1}{r^2}\frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial \theta} \ . \tag{C23}$$

Collecting we obtain again

$$\boldsymbol{\nabla}^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) \ . \tag{C24}$$

Appendix D: Mutual basis of eigenstates of two commuting Hermitian operators

Consider two Hermitian operators $\hat{A}$ and $\hat{B}$, such that $[A, B] = 0$. Consider an eigenstate $|\psi_n\rangle$ of $\hat{A}$, so that $\hat{A}\,|\psi_n\rangle = a_n\,|\psi_n\rangle$. If ψ_n is not degenerate, then from

$$\hat{A}\hat{B}\,|\psi_n\rangle = \hat{B}\hat{A}\,|\psi_n\rangle = a_n\hat{B}\,|\psi_n\rangle \tag{D1}$$

it follows that $\hat{B}\,|\psi_n\rangle$ is an eigenvector of $\hat{A}$ with eigenvalue a_n. Since there is only one such eigenvector, we have $\hat{B}\,|\psi_n\rangle \propto |\psi_n\rangle$. Thus, $|\psi_n\rangle$ is also an eigenvector of $\hat{B}$.

Assume now that there are several eigenstates of $\hat{A}$ with the same eigenvalue a_n. We will call these states $|\psi_{n,m}\rangle$. The index $m \in [1, 2, \ldots M]$, where M is the degree of degeneracy. We have $\hat{A}\,|\psi_{n,m}\rangle = a_n\,|\psi_{n,m}\rangle$ for all m. From

$$\hat{A}\hat{B}\,|\psi_{n,m}\rangle = \hat{B}\hat{A}\,|\psi_{n,m}\rangle = a_n\hat{B}\,|\psi_{n,m}\rangle \tag{D2}$$

we conclude that $\hat{B}\,|\psi_{n,m}\rangle$ belongs to the subspace spanned by the degenerate eigenvectors $|\psi_{n,m}\rangle$. That is

$$\hat{B}\,|\psi_{n,m}\rangle = \sum_k C_{mk}\,|\psi_{n,k}\rangle \quad \text{with} \quad C_{mk} = \langle\psi_{n,k}|\,\hat{B}\,|\psi_{n,m}\rangle = C^*_{km} \ . \tag{D3}$$

Matrix C_{mk} represents the operator $\hat{B}$ in the M-dimentional subspace $|\psi_{n,m}\rangle$. It is Hermitian and can be diagonalized, i.e. it has M eigenvectors in this subspace. These are, thus, mutual eigenvectors of $\hat{A}$ and $\hat{B}$.

Appendix E: General formulas for $Y_{l,m}$

The spherical functions $Y_{l,m}$ are, in general, given by

$$Y_{l,m}(\theta,\phi) = (-1)^{\frac{m+|m|}{2}} \sqrt{\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}\, P_l^{|m|}(\cos\theta)\, e^{im\phi} \ . \tag{E1}$$

Here

$$P_l^m(\mu) \equiv (1-\mu^2)^{m/2}\, \frac{d^m P_l(\mu)}{d\mu^m} \tag{E2}$$

are the associated Legendre polynomials (for $m \geq 0$) and

$$P_l(\mu) = \frac{1}{2^l l!}\frac{d^l}{d\mu^l}(\mu^2-1)^l \tag{E3}$$

are the Legendre polynomials.

Here are several examples

$$Y_{0,0} = \frac{1}{\sqrt{4\pi}} \quad , \quad Y_{1,0} = \sqrt{\frac{3}{4\pi}}\cos\theta \quad , \quad Y_{1,1} = -\sqrt{\frac{3}{8\pi}}\cos\theta\, e^{i\phi} \ . \tag{E4}$$

$$Y_{2,0} = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1) \quad , \quad Y_{2,1} = -\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\, e^{i\phi} \quad , \quad Y_{2,2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{2i\phi} \ . \tag{E5}$$

For $m < 0$ one can use

$$Y_{l,-m} = (-1)^m Y_{l,m}^* \ . \tag{E6}$$

Appendix F: Radial functions $R_{n,l}(r)$

The radial functions are expressed using the associated Laguerre polynomials. See Schwabl. Here are several examples for low values of n:

$$R_{1,0}(r) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0} \ . \tag{F1}$$

$$R_{2,0}(r) = 2\left(\frac{Z}{2a_0}\right)^{3/2}\left(1-\frac{Zr}{2a_0}\right) e^{-Zr/2a_0} \ . \tag{F2}$$

$$R_{2,1}(r) = \frac{2}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2}\left(\frac{Zr}{2a_0}\right) e^{-Zr/2a_0} \ . \tag{F3}$$

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[1] One can choose the numbers from any field F. Then the vector space is said to be a vector space over the field F.

[2] The full mathematical definition of a vector space includes also 1) the existence of a zero vector $\mathbf{0}$ such that for any $\mathbf{v}$ one has $\mathbf{v} + \mathbf{0} = \mathbf{v}$; 2) the existence of an additive inverse $(-\mathbf{v})$ for each $\mathbf{v}$, such that $(-\mathbf{v}) + \mathbf{v} = \mathbf{0}$; 3) associativity: $(\mathbf{v} + \mathbf{u}) + \mathbf{w} = \mathbf{v} + (\mathbf{u} + \mathbf{w})$; 4) distributivity $c(\mathbf{v} + \mathbf{u}) = c\mathbf{v} + c\mathbf{u}$ etc.

[3] Strictly speaking, for unbounded operators in infinite-dimensional Hilbert spaces, one should take care of the domains in which $\hat{A}$ and $\hat{A}^\dagger$ are defined. We will not address this problem here.

[4] Strictly, our consideration here is valid for bounded operators.