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Göteborgs universitet
Fysiska institutionen
Prof. I.Lindgren/Doc. S.Salomonson

II. THE SCHRÖDINGER EQUATION

The time-dependent Schrödinger equation

Starting from de Broglie's relations

$$E = h\nu = \hbar\omega \qquad \text{(II.1)}$$

$$p = h/\lambda = \hbar k$$

we assume that we can represent a particle generally by the means of a wave packet or *wave function*

$$\Psi(x,t) = \int_{-\infty}^{\infty} dk\, e^{i(kx-\omega t)}\, a(k) \qquad \text{(II.2)}$$

If the particle is *free*, i.e., not affected by any external field, its momentum p is constant. The particle is then represented by a *single plane wave*

$$\Psi(x,t) = A\, e^{i(kx-\omega t)} \qquad \text{(II.3)}$$

where A is an arbitrary constant. For a free particle the energy is given by

$$E = \frac{p^2}{2m} \quad \text{or} \quad \hbar\omega = \frac{\hbar^2 k^2}{2m} \qquad \text{(II.4)}$$

with de Broglie's relations. This is a relation between k and ω, which must be satisfied by the wave function. For the wave function (II.3) we have

$$\frac{\partial}{\partial t}\Psi(x,t) = -i\omega\,\Psi(x,t)$$

$$\frac{\partial}{\partial x}\Psi(x,t) = ik\,\Psi(x,t)$$

$$\frac{\partial^2}{\partial x^2}\Psi(x,t) = -k^2\,\Psi(x,t)$$

This leads to the relation between the derivatives

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) \qquad \text{(II.5)}$$

This is the ***Schrödinger equation*** *(S.E.) for a free particle.* The general solution is given by the wave function (II.2).

For a particle moving in a potential field $V(x,t)$ we have instead of (II.4)

$$E = \frac{p^2}{2m} + V(x,t) \quad \text{or} \quad \hbar\omega = \frac{\hbar^2 k^2}{2m} + V(x,t) \qquad \text{(II.6)}$$

This leads us to write down the wave equation

$$\boxed{i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x,t)\right]\Psi(x,t)} \qquad \text{(II.7)}$$

which is ***the Schrödinger equation for a particle in a potential field V(x,t).***

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Separation of the variables

If the potential $V(x,t)$ is independent of time, we can solve the time dependent Schrödinger equation by separation of the variables. We then assume that the solution is of the form

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

Inserting into the S.E. (II.7) leads to

$$i\hbar\psi(x)\frac{dF(t)}{dt} = -\frac{\hbar^2}{2m}F(t)\frac{d^2\psi(x)}{dx^2} + V(x)\Psi(x)F(t)$$

Dividing by $\psi(x)F(t)$ gives

$$i\hbar\frac{1}{F(t)}\frac{dF(t)}{dt} = -\frac{1}{\Psi(x)}\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)$$

The left-hand side is here independent of x and the right-hand side independent of t. Hence, both sides must be equal to a constant (E), leading to two equations

$$i\hbar\frac{dF(t)}{dt} = EF(t) \qquad \text{(II.8a)}$$

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(x) = E\psi(x) \qquad \text{(II.8b)}$$

Both these equations are *eigenvalue equations*, and they have, in general, solutions only for specific values of the eigenvalue E. The last equation is ***the time-independent Schrödinger equation***. The first equation (II.8a) can be solved generally

$$F(t) = Ce^{-iEt/\hbar}$$

which means that the solution of the time-dependent S.E. corresponding to a solution $\psi_n(x)$ with the eigenvalue E_n of the time-independent S.E. is of the form

$$\Psi_n(x,t) = \psi_n(x)\,e^{-iE_nt/\hbar} \qquad \text{(II.9)}$$

Since the S.E. is linear, a linear *superposition* of solutions is also a solution. A general solution of the time-dependent S.E. (II.7) with a time-independent potential can the be written

$$\Psi(x,t) = \sum C_n\Psi_n(x,t) \qquad \text{(II.10)}$$

where C_n are constants. If the potential is time dependent, we can express the solution in a similar way with time-dependent constants $C_n(t)$.

Interpretation of the wave function

The wave function $\Psi(x,t)$ is interpreted as the *probability amplitude*, which means that the probability of finding the particle in the interval (x,x+dx) at the

time t is proportional to $|\Psi(x,t)|^2 dx$. If the function is *normalized*

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = 1 \qquad \text{(II.11)}$$

then $|\Psi(x,t)|^2 dx$ is equal to that probability.

In general, the probability distribution depends on time. If $\Psi(x,t)$ is of the form (II.9), then $|\Psi(x,t)|^2$ is time independent. Then the state is said to be *stationary*. This implies that *the solutions of the time-independent S.E. represent the stationary states.*

Expectation values

The expectation value of the coordinate x is obtained by integrating x over the coordinate space with $|\Psi|$ as the weight factor

$$\langle x \rangle = \int_{-\infty}^{\infty} |\Psi|^2 \, x \, dx = \int_{-\infty}^{\infty} \Psi^* x \Psi \, dx \qquad \text{(II.12)}$$

Similarly for any power of x or an arbitrary function of x

$$\langle x^n \rangle = \int_{-\infty}^{\infty} \Psi^* x^n \Psi \, dx \;\; ; \;\; \langle f(x) \rangle = \int_{-\infty}^{\infty} \Psi^* f(x) \Psi \, dx$$

In principle, these expectation values may depend on time. In a stationary state all expectation values are time independent.

In order to obtain an expression for the expectation value of the momentum, we consider the *fourier transform* of the wave function. For simplicity we consider the time-independent wave function.

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk \, e^{ikx} a(k)$$

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

We introduce

$$\phi(p) = \sqrt{\frac{2\pi}{h}} \, a(k) = \frac{1}{\sqrt{h}} \int_{-\infty}^{\infty} dx \, e^{-ikx} \psi(x)$$

which gives

$$\psi(x) = \frac{\sqrt{h}}{2\pi} \int_{-\infty}^{\infty} dk \, e^{ikx} \phi(p) = \frac{1}{\sqrt{h}} \int_{-\infty}^{\infty} dp \, e^{ikx} \phi(p)$$

Then $|\phi(p)|^2$ represents *the distribution in the momentum space,* i.e., $|\phi(p)|^2 dp$ represents the probability to find the particle in the momentum region $(p,p+dp)$. This can be shown as follows.

$$\int_{-\infty}^{\infty} dp \, |\phi(p)|^2 = \int_{-\infty}^{\infty} dp \, \phi^*(p) \frac{1}{\sqrt{h}} \int_{-\infty}^{\infty} dx \, e^{-ikx} \psi(x) = \int_{-\infty}^{\infty} dx \, \psi^*(x) \psi(x)$$

The expectation value of the momentum p can now be obtained

$$\langle p\rangle = \int_{-\infty}^{\infty} dp\,\phi^*(p)\,p\,\phi(p) = \int_{-\infty}^{\infty} dp \frac{1}{\sqrt{h}} \int_{-\infty}^{\infty} dx\, e^{ikx}\,\psi^*(x)\,p\,\phi(p)$$
$$= \int_{-\infty}^{\infty} dp \frac{1}{\sqrt{h}} \int_{-\infty}^{\infty} dx\,\psi^*(x)\left(-i\hbar\frac{\partial}{\partial x}\right) e^{ipx/\hbar}\,\phi(p) = \int_{-\infty}^{\infty} dx\,\psi^*(x)\left(-i\hbar\frac{\partial}{\partial x}\right)\psi(x)$$

Thus, it is found the operator $-i\hbar\dfrac{\partial}{\partial x}$ represents the (x component of the) momentum p also for a general wave function (not just a plane wave).

III. THE OPERATOR FORAMLISM

Basic definitions and assumptions

Quantum mechanics is based on the following basic assumptions:
1. *Each state of a physical system can be represented by a wave function.*
2. *Each (measurable) physical quantity is represented by a (hermitian) operator.*
3. *The eigenvalues of the operator are the possible results of an accurate measurement of the corresponding quantity.*

State	→	**Wave function**
(Measurable) quantity	→	**(Hermitian) operator**
Measurement	→	**Eigenvalue**

Two operators $\hat{A}$ and $\hat{B}$ are said to be equal if $\hat{A}\,\psi = \hat{B}\,\psi$ for all functions ψ in the space considered. (Hermitian operators are defined below.)

Two operators $\hat{A}$ and $\hat{B}$ are said to commute if $\hat{A}\,\hat{B} = \hat{B}\,\hat{A}$.

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

$$\left[\hat{A}\,\hat{B}\right] = \hat{A}\,\hat{B} - \hat{B}\,\hat{A} \qquad \text{(III.1)}$$

We have found above the operators representing the position (x) and the momentum (p). Assuming that the same relations hold between operators as between the corresponding quantities (not always possible), we get the operator representing the kinetic energy

$$E_{kin} = p^2/2m \;\rightarrow\; \hat{E}_{kin} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \qquad \text{(III.2)}$$

Similarly, the operator representing the total energy in a potential field $V(x)$ becomes

$$H = p^2/2m + V(x) \quad \rightarrow \quad \hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \tag{III.3}$$

The function H is called the Hamilton function in classical mechanics, and the corresponding operator $\hat{H}$ is called the *Hamilton operator.*

Extension to three dimensions

The operator corresponding to the three-dimensional momentum $\mathbf{p}$ becomes

$$\mathbf{p} = (p_x, p_y, p_z) \quad \rightarrow \quad \hat{\mathbf{p}} = (\hat{p}_x, \hat{p}_y, \hat{p}_z) = -i\hbar\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}, \right) = -i\hbar\nabla \tag{III.4}$$

where ∇ is he gradient operator

$$\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}, \right) \tag{III.5}$$

Similarly, the Hamilton operator becomes

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \tag{III.6}$$

This leads to the *three-dimensional time-independent Schrödinger equation*

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right)\psi = E\psi \tag{III.7}$$

The Hamilton operator $\hat{H}$ (III.6) represents the total energy of the system, and the Schrödinger equation (III.7) is the corresponding eigenvalue equation. According to the basic assumptions above, these eigenvalues represent the possible energy values of the system that can be obtained in a measurement of the energy.

Hermitian operators

1. The *hermitian adjoint* $\hat{A}^\dagger$ of an operator $\hat{A}$ is defined by

$$\int_{-\infty}^{\infty} \psi_m^* \hat{A}\, \psi_n \, dv = \int_{-\infty}^{\infty} \left(\hat{A}^\dagger \psi_m\right)^* \psi_n \, dv \tag{III.8}$$

for all possible ψ_m and ψ_n.

The hermitian adjoint of the product of two operators $\hat{A}$ and $\hat{B}$ is the product of their hermitian adjoint operators in reverse order

$$\left(\hat{A}\hat{B}\right)^\dagger = \hat{B}^\dagger \hat{A}^\dagger \tag{III.9}$$

which follows from the definition of hermitian adjoint operators (III.8) by first moving $\hat{A}$ and then $\hat{B}$ to the left.

The operator $\hat{A}$ is said to be *hermitian* if $\hat{A}^\dagger = \hat{A}$.

From (III.9) it follows that the commutator between two hermitian operators is not hermitian. The hermitian adjoint of the commutator is found, using (III.9) to be

$$\left[\hat{A},\hat{B}\right]^{\dagger} = -\left[\hat{A},\hat{B}\right] \qquad \text{(III.10)}$$

and the commutator is therefor said to be antihermitian. It is then easy to show that $i\left[\hat{A},\hat{B}\right]$ is hermitian.

2. A hermitian operator has real eigenvalues and real expectation values.

Proof: The eigenvalue equation $\hat{A}\psi = a\psi$ leads to

$$\int_{-\infty}^{\infty} \psi^* \hat{A}\psi \, dv = a\int_{-\infty}^{\infty} \psi^* \psi \, dv$$

If $\hat{A}$ is hermitian, this is equal to

$$\int_{-\infty}^{\infty} \left(\hat{A}^{\dagger}\psi\right)^* \psi \, dv = a^* \int_{-\infty}^{\infty} \psi^* \psi \, dv$$

and hence $a^*=a$ and the eigenvalue a is real. The expectation value of a hermitian operator $\hat{A}$ is

$$\left\langle \hat{A} \right\rangle = \int \psi^* \hat{A}\, \psi \, dv = \int \left(\hat{A}\psi\right)^* \psi \, dv = \left(\int \psi^* \hat{A}\psi \, dv\right)^* = \left\langle \hat{A} \right\rangle^*$$

which means that it is real.

3. Eigenfunctions of a hermitian operator corresponding to *different* eigenvalues are orthogonal.

Proof: Assume $\hat{A}\psi_m = a_m\psi_m$ and $\hat{A}\psi_n = a_n\psi_n$ where $\hat{A}$ is hermitian and $a_m \neq a_n$. Then

$$\int \psi_m^* \hat{A}\, \psi_n \, dv = a_n \int \psi_m^* \psi_n \, dv = \int \left(\hat{A}^{\dagger}\psi_m\right)^* \psi_n \, dv = a_m \int \psi_m^* \psi_n \, dv$$

Since it is assumed that $a_m \neq a_n$, it follows that $\int \psi_m^* \psi_n \, dv = 0$, which means that the functions are orthogonal.

4. The eigenfunctions Ψ_n of a hermitian operator form a complete set, which implies that any function in the space considered can be expanded in terms of these functions

$$\hat{A}\psi_n = a_n\psi \quad \text{and} \quad \psi = \sum_n C_n \psi_n$$

5. A measurement of the quantity A in a state $\psi = \sum_n C_n \psi_n$, which is not an eigenstate of $\hat{A}$, will yield the result a_n with the probability $|C_n|^2$, provided that ψ is normalized

$$\sum_n |C_n|^2 = 1$$

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The uncertainty principle

The uncertainty ΔA of the quantity A is given by

$$\Delta A^2 = \left\langle \hat{A}^2 \right\rangle - \left\langle \hat{A} \right\rangle^2 = \left\langle \left(\hat{A} - \left\langle \hat{A} \right\rangle \right)^2 \right\rangle .$$

To prove the uncertainty relation between two quantities represented by the hermitian operators $\hat{A}$ and $\hat{B}$ we define two new operators $\hat{C}$ and $\hat{D}$ by subtracting the expectation values for a specific wave function ψ,

$$\hat{C} = \hat{A} - \left\langle \hat{A} \right\rangle$$

$$\hat{D} = \hat{B} - \left\langle \hat{B} \right\rangle .$$

Now consider

$$\mathrm{I}(\lambda) = \int dx \left(\hat{C}\psi + i\lambda \hat{D}\psi \right)^* \left(\hat{C}\psi + i\lambda \hat{D}\psi \right)$$

which has to be greater than or equal to zero for all values of λ since the integrand is an absolute value squared. Since $\hat{A}$ and $\hat{B}$ are hermitian operators also $\hat{C}$ and $\hat{D}$ will be hermitian. Thus we can expand

$$\begin{aligned} \mathrm{I}(\lambda) &= \int dx \left(\hat{C}\psi \right)^* \left(\hat{C}\psi \right) + \lambda^2 \int dx \left(\hat{D}\psi \right)^* \left(\hat{D}\psi \right) + \\ &\quad i\lambda \int dx \left\{ \left(\hat{C}\psi \right)^* \left(\hat{D}\psi \right) - \left(\hat{D}\psi \right)^* \left(\hat{C}\psi \right) \right\} = \\ &= \int dx \psi^* \left(\hat{C}^2 + \lambda^2 \hat{D}^2 + i\lambda \left[\hat{C}, \hat{D} \right] \right) \psi = \\ &= \Delta A^2 + \lambda^2 \Delta B^2 + \lambda \left\langle i \left[\hat{A}, \hat{B} \right] \right\rangle \geq 0 \end{aligned}$$

The minimum with respect to the λ is found by setting the derivative equal to zero

$$2\lambda_{\min} \Delta B^2 + + \left\langle i \left[\hat{A}, \hat{B} \right] \right\rangle = 0 .$$

With the expression for $\lambda_{\min}$ from this equation we get

$$\mathrm{I}(\lambda_{\min}) = \Delta A^2 + \frac{\left\langle i \left[\hat{A}, \hat{B} \right] \right\rangle^2}{4\Delta B^2} - \frac{\left\langle i \left[\hat{A}, \hat{B} \right] \right\rangle^2}{2\Delta B^2} \geq 0$$

which gives

$$\Delta A^2 \Delta B^2 \geq \frac{1}{4} \left\langle i \left[\hat{A}, \hat{B} \right] \right\rangle^2 .$$

This is the uncertainty relation. As shown in (III.10) $i\left[\hat{A}, \hat{B} \right]$ is hermitian and the expectation value is thus real.

The uncertainty principle implies that if two operators do not commute, the corresponding quantities cannot be measured simultaneously with unlimited

accuracy. If the operators commute, the quantities can be measured simultaneously. The quantities are then said to be *compatible.*

Example. The commutator of the operators $\hat{x}$ and $\hat{p}$ is

$$[\hat{x},\hat{p}] = -\mathrm{i}\hbar\left[\hat{x},\frac{\partial}{\partial x}\right]$$

The commutator is an *operator,* and in order to evaluate it we let it operate on an arbitrary function

$$\left[x,\frac{\partial}{\partial x}\right]\psi = \left(x\frac{\partial}{\partial x} - \frac{\partial}{\partial x}x\right)\psi = x\frac{\partial\psi}{\partial x} - \frac{\partial}{\partial x}(x\psi) = -\psi$$

(It should be noted that the operator $\partial/\partial x$ operates on everything appearing to the right.) Since ψ is an arbitrary function, we get the operator identity

$$[\hat{x},\hat{p}] = \mathrm{i}\hbar$$

The uncertainty principle then yields

$$\Delta x\,\Delta p \geq \hbar/2$$

In an eigenstate of an operator $\hat{A}$ with the eigenvalue a the measurement of the corresponding quantity yields with certainty the value a, which can be seen as follows.

$$\hat{A}\psi = a\psi \quad \text{and} \quad (\Delta A)^2 = \left\langle \tilde{A}^2 \right\rangle - \left\langle \tilde{A} \right\rangle^2$$

gives

$$\left\langle \tilde{A}^2 \right\rangle = \int \psi^* \tilde{A}^2 \psi\, dv = a^2 \int \psi^* \psi\, dv = a^2$$

and

$$\left\langle \tilde{A} \right\rangle = \int \psi^* \tilde{A} \psi\, dv = a \int \psi^* \psi\, dv = a$$

which leads to $(\Delta A) = 0$.

Constants of the motion

The physical quantity A is represented quantum-mecanically by the operator and the time derivative $\frac{dA}{dt}$ by the operator $\widehat{\frac{dA}{dt}}$. We then require that

$$\frac{d}{dt}\langle A\rangle = \left\langle \frac{dA}{dt} \right\rangle = \int \Psi(\mathbf{r},t)^* \widehat{\frac{dA}{dt}}\, \Psi(\mathbf{r},t)\, dv$$

where

$$\frac{d}{dt}\langle A\rangle = \frac{d}{dt}\int \Psi(\mathbf{r},t)^*\,\hat{A}\,\Psi(\mathbf{r},t)\,dv$$

With the time-dependent Schrödinger equation

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

this gives

$$\frac{d}{dt}\langle A\rangle = \int\frac{\partial\Psi(\mathbf{r},t)^*}{\partial t}\hat{A}\,\Psi(\mathbf{r},t)\,dv + \int\Psi(\mathbf{r},t)^*\,\hat{A}\,\frac{\partial\Psi(\mathbf{r},t)}{\partial t}\,dv + \int\Psi(\mathbf{r},t)^*\,\frac{\partial\hat{A}}{\partial t}\Psi(\mathbf{r},t)\,dv$$

$$= \frac{i}{\hbar}\left\{\int\left(\hat{H}\Psi(\mathbf{r},t)\right)^*\hat{A}\,\Psi(\mathbf{r},t)\,dv - \int\Psi(\mathbf{r},t)^*\,\hat{A}\hat{H}\,\Psi(\mathbf{r},t)\,dv\right\} + \int\Psi(\mathbf{r},t)^*\,\frac{\partial\hat{A}}{\partial t}\Psi(\mathbf{r},t)\,dv$$

$$= \frac{i}{\hbar}\int\Psi(\mathbf{r},t)^*\left[\hat{A},\hat{H}\right]\Psi(\mathbf{r},t)\,dv + \int\Psi(\mathbf{r},t)^*\,\frac{\partial\hat{A}}{\partial t}\Psi(\mathbf{r},t)\,dv$$

We then find that the time derivative of the quantity A is represented by the operator

$$\widehat{\frac{dA}{dt}} = \frac{\partial\hat{A}}{\partial t} - \frac{i}{\hbar}\left[\hat{A},\hat{H}\right]$$

The first term on the right-hand side is non-zero only if the operator $\hat{A}$ depends explicitly on time. If this is not the case and if $\hat{A}$ commutes with $\hat{H}$, then the operator representing the time derivative vanishes. This implies that $\frac{d}{dt}\langle A\rangle$ vanishes for all states, satisfying the time-dependent Schrödinger equation - not only for stationary states (for which all expectation values are time independent) - and A is then said to be a constant of the motion.

A physical quantity is a constant of the motion, if the corresponding operator does not depend explicitly on time and commutes with the hamiltonian of the system.

The virial theorem

For *stationary states* all expectation values are time independent. Thus

$$\frac{d}{dt}\langle\mathbf{r}\cdot\mathbf{p}\rangle = -\frac{i}{\hbar}\int\Psi(\mathbf{r},t)^*\left[\mathbf{r}\cdot\hat{\mathbf{p}},\hat{H}\right]\Psi(\mathbf{r},t)\,dv = 0$$

if $\Psi(\mathbf{r},t)$ represents a stationary state. (Since the operator $\mathbf{r}\cdot\hat{\mathbf{p}}$ is time independent, there is no addidtional term.) The hamiltonian for an electron in a potential field $V(\boldsymbol{r})$ is

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + V(\mathbf{r}) \quad \text{with} \quad \hat{\mathbf{p}} = -i\hbar\nabla$$

The relations

$$\left[\mathbf{r}\cdot\hat{\mathbf{p}},\hat{\mathbf{p}}^2\right]=\hat{\mathbf{p}}\cdot\left[\mathbf{r}\cdot\hat{\mathbf{p}},\hat{\mathbf{p}}\right]+\left[\mathbf{r}\cdot\hat{\mathbf{p}},\hat{\mathbf{p}}\right]\cdot\hat{\mathbf{p}}$$

$$\left[\mathbf{r}\cdot\hat{\mathbf{p}},\hat{\mathbf{p}}\right]=-\hbar^2\left[\mathbf{r}\cdot\nabla,\nabla\right]=\hbar^2\nabla=i\hbar\hat{\mathbf{p}}$$

give

$$\left[\mathbf{r}\cdot\hat{\mathbf{p}},\hat{\mathbf{p}}^2\right]=2i\hbar\hat{\mathbf{p}}^2$$

and together with

$$\left[\mathbf{r}\cdot\hat{\mathbf{p}},V(\mathbf{r})\right]=-i\hbar\left(\mathbf{r}\cdot\nabla\right)V(\mathbf{r})=-i\hbar\,\mathbf{r}\cdot grad\,V(\mathbf{r})$$

we then get

$$\left[\mathbf{r}\cdot\hat{\mathbf{p}},\hat{H}\right]=i\hbar\left\{2\frac{\hat{\mathbf{p}}^2}{2m}-\mathbf{r}\cdot grad\,V(\mathbf{r})\right\}$$

Thus,

$$\frac{d}{dt}\langle\mathbf{r}\cdot\mathbf{p}\rangle=\int\Psi(\mathbf{r},t)^*\left\{2\frac{\hat{\mathbf{p}}^2}{2m}-\mathbf{r}\cdot grad\,V(\mathbf{r})\right\}\Psi(\mathbf{r},t)\,dv=\left\langle 2\frac{\mathbf{p}^2}{2m}-\mathbf{r}\cdot grad\,V(\mathbf{r})\right\rangle$$

This vanishes, if $\Psi(\mathbf{r},t)$ represents a stationary state, in which case

$$2\left\langle\frac{\mathbf{p}^2}{2m}\right\rangle=\langle\mathbf{r}\cdot grad\,V(\mathbf{r})\rangle$$

Introducing the kinetic energy $T=\dfrac{\mathbf{p}^2}{2m}$ and the corresponding operator $\hat{T}=\dfrac{\hat{\mathbf{p}}^2}{2m}$, we can write this relation

$$2\langle T\rangle=\langle\mathbf{r}\cdot grad\,V(\mathbf{r})\rangle$$

which is ***the virial theorem.***

For a spherically symmetric potential that is proportional to a power of r, $V(\mathbf{r})=Kr^n$, we have $\langle\mathbf{r}\cdot grad\,V(\mathbf{r})\rangle=n\langle V\rangle$. Particularly for the harmonic oscillator with n=2 we have equal expectation values for the kinetic and the potential energy. For the hydrogen atom with n=-1 get $2\langle T\rangle=-\langle V\rangle$.

The harmonic oscillator

We consider a particle in a one-dimensional potential of the form

$$V(x)=\tfrac{1}{2}kx^2=\tfrac{1}{2}m\omega^2x^2\qquad\omega=\sqrt{k/m}\tag{A.1}$$

which gives the hamiltonian

$$\hat{H}=\frac{\hat{p}^2}{2m}+\tfrac{1}{2}m\omega^2x^2\tag{A.2}$$

We now make the substitution

$$Q=\sqrt{\frac{m\omega}{\hbar}}\,x;\quad\hat{P}=\sqrt{\frac{1}{m\hbar\omega}}\,\hat{\mathrm{p}}=\text{-i}\sqrt{\frac{\hbar}{m\omega}}\,\frac{\mathrm{d}}{\mathrm{dx}}=\text{-i}\,\frac{\mathrm{d}}{\mathrm{dQ}}\tag{A.3}$$

which gives

$$\hat{H} = \tfrac{1}{2}\hbar\omega\left(\hat{P}^2 + Q^2\right) \tag{A.4}$$

From the commutation relation $[\hat{p},x] = -i\hbar$ it follows that

$$\left[\hat{P},Q\right] = -i \tag{A.5}$$

The Schrödinger equation $H\psi = E\psi$ now becomes

$$\tfrac{1}{2}\hbar\omega\left(-\frac{d^2}{dQ^2} + Q^2 - \varepsilon\right)\psi(Q) = 0 \tag{A.6}$$

where $E = \tfrac{1}{2}\hbar\omega\,\varepsilon$ is the energy eigenvalue.

We then introduce the new operators

$$\hat{a} = \tfrac{1}{\sqrt{2}}\left(Q + i\hat{P}\right) = \tfrac{1}{\sqrt{2}}\left(Q + \frac{d}{dQ}\right); \quad \hat{a}^\dagger = \tfrac{1}{\sqrt{2}}\left(Q - i\hat{P}\right) = \tfrac{1}{\sqrt{2}}\left(Q - \frac{d}{dQ}\right) \tag{A.7}$$

which satisfy the commutation rule

$$\left[\hat{a},\hat{a}^\dagger\right] = \hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a} = 1 \tag{A.8}$$

With these operators the hamiltonian (A.4) can be expressed

$$\hat{H} = \tfrac{1}{2}\hbar\omega\left(\hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a}\right) \tag{A.9}$$

Using the commutation rule (A.8), this becomes

$$\hat{H} = \hbar\omega\left(\hat{a}^\dagger\hat{a} + \tfrac{1}{2}\right) = \hbar\omega\left(\hat{N} + \tfrac{1}{2}\right) \tag{A.10}$$

where

$$\hat{N} = \hat{a}^\dagger\hat{a} \tag{A.11}$$

will be called *the number operator.*

We shall now find the eigenvalues and eigenfunctions of the hamiltonian (A.10) and start by the eigenvalue equation of the number operator (A.11)

$$\hat{N}\varphi_n = \hat{a}^\dagger\hat{a}\,\varphi_n = \varepsilon_n\varphi_n \tag{A.12}$$

Obviously, these eigenfunctions are also eigenfunctions of the hamiltonian (A.10) with the eigenvalue

$$E = \hbar\omega\left(\varepsilon_n + \tfrac{1}{2}\right) \tag{A.13}$$

Using the commutation rule (A.12), we then have

$$\hat{N}\hat{a}\varphi_n = \hat{a}^\dagger\hat{a}\hat{a}\varphi_n = \left(\hat{a}\hat{a}^\dagger - 1\right)\hat{a}\varphi_n = \hat{a}\left(\hat{a}^\dagger\hat{a} - 1\right)\varphi_n = \left(\varepsilon_n - 1\right)\hat{a}\varphi_n \tag{A.14a}$$

$$\hat{N}\hat{a}^\dagger\varphi_n = \hat{a}^\dagger\hat{a}\hat{a}^\dagger\varphi_n = \hat{a}^\dagger\left(\hat{a}^\dagger\hat{a} + 1\right)\varphi_n = \left(\varepsilon_n + 1\right)\hat{a}^\dagger\varphi_n \tag{A.14b}$$

This shows that the functions $\hat{a}\varphi_n$ and $\hat{a}^\dagger\varphi_n$ are new eigenfunctions of $\hat{N}$ with the eigenvalues $(\varepsilon_n - 1)$ and $(\varepsilon_n + 1)$, respectively. The new eigenfunctions are not normalized, which can be seen by evaluating the norm

$$\int\left(\hat{a}\varphi_n\right)^*\hat{a}\varphi_n\,dv = \int\varphi_n^*\hat{a}^\dagger\hat{a}\varphi_n\,dv = \varepsilon_n \tag{A.15a}$$

$$\int\left(\hat{a}^\dagger\varphi_n\right)^*\hat{a}^\dagger\varphi_n\,dv = \int\varphi_n^*\hat{a}\hat{a}^\dagger\varphi_n\,dv = \varepsilon_n + 1 \tag{A.15b}$$

It follows from the relations (A.14) that knowing one eigenfunction of $\hat{N}$ or $\hat{H}$, it is possible to generate a sequence of eigenfunctions with successively lower

and higher eigenvalues. However, there must exist a *lowest* eigenvalue of $\hat{H}$, corresponding to the ground state of the system. This means that *the down-going sequence must terminate* at some point. This will happen if and only if one of the wave functions vanishes, which is the case if ε_n *is zero for some value of n*. This means that the possible eigenvalues of the number operator (A.11,12) is

$$\varepsilon_n = 0, 1, 2, 3, \ldots \tag{A.16}$$

This gives the eigenvalues (A.13) of the hamiltonian (A.10)

$$E = \hbar\omega\left(n + \tfrac{1}{2}\right) \quad \text{n=0,1,2,3.....} \tag{A.17}$$

The normalized eigenfunctions of $\hat{N}$ or $\hat{H}$ are given by the recursion formula

$$\varphi_{n+1} = \tfrac{1}{\sqrt{n+1}}\hat{a}^\dagger\varphi_n \tag{A.18}$$

or

$$\varphi_n = \tfrac{1}{\sqrt{n!}}\left(\hat{a}^\dagger\right)^n\varphi_0 \tag{A.19}$$

It is easy to show that the function $\psi(Q) = e^{-Q^2/2}$ is a solution of the Schrödinger equation (A.6) corresponding to ε=1 or $E = \tfrac{1}{2}\hbar\omega$. Hence, this function is (apart from normalization) identical to the function φ_0,

$$\varphi_0 = e^{-Q^2/2} \tag{A.20a}$$

The following eigenfunctions are obtained by successively applying (A.18)

$$\varphi_1 = \hat{a}^\dagger\varphi_0 = \tfrac{1}{\sqrt{2}}\left(Q - \frac{d}{dQ}\right)e^{-Q^2/2} = \sqrt{2}\,Q\,e^{-Q^2/2} \tag{A.20b}$$

$$\varphi_2 = \tfrac{1}{\sqrt{2}}\hat{a}^\dagger\varphi_1 = \left(Q - \frac{d}{dQ}\right)Qe^{-Q^2/2} = \left(2Q^2 - 1\right)e^{-Q^2/2} \tag{A.20c}$$

etc.