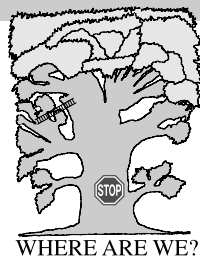


Chapter 2

THE SCHRÖDINGER EQUATION



Where are we?

The postulates constitute the foundation of quantum mechanics (the base of the TREE trunk). One of their consequences is the Schrödinger equation for stationary states. Thus we begin our itinerary on the TREE. The second part of this chapter is devoted to the time-dependent Schrödinger equation, which, from the pragmatic point of view, is outside the main theme of this book (this is why it is a side branch on the left side of the TREE).

An example

A friend asked us to predict what the UV spectrum of anthracene¹ looks like. One can predict any UV spectrum if one knows the electronic stationary states of the molecule. The *only* way to obtain such states and their energies is to solve the time-independent Schrödinger equation. Thus, one has to solve the equation for the Hamiltonian for anthracene, then find the ground (the lowest) and the excited stationary states. The energy differences of these states will tell us where (in the energy scale), to expect light absorption, and finally then the wave functions will enable us to compute the intensity of this absorption.

What is it all about

Symmetry of the Hamiltonian and its consequences (S♦)

p. 57

- The non-relativistic Hamiltonian and conservation laws
- Invariance with respect to translation
- Invariance with respect to rotation
- Invariance with respect to permutations of identical particles (fermions and bosons)
- Invariance of the total charge
- Fundamental and less fundamental invariances
- Invariance with respect to inversion – parity
- Invariance with respect to charge conjugation
- Invariance with respect to the symmetry of the nuclear framework
- Conservation of total spin
- Indices of spectroscopic states

¹Three condensed benzene rings.

Schrödinger equation for stationary states (▲)**p. 70**

- Wave functions of class Q
- Boundary conditions
- An analogy
- Mathematical and physical solutions

The time-dependent Schrödinger equation (Δ)**p. 76**

- Evolution in time
- Normalization is preserved
- The mean value of the Hamiltonian is preserved
- Linearity

Evolution after switching a perturbation (§)**p. 79**

- The two-state model
- First-order perturbation theory
- Time-independent perturbation and the Fermi golden rule
- The most important case: periodic perturbation.

The *time-independent* Schrödinger equation is the one place where stationary states can be produced as solutions of the equation. The *time-dependent* Schrödinger equation plays a role as the equation of motion, describing the evolution of a given wave function as time passes. As always for an equation of motion, one has to provide an initial state (starting point), i.e. the wave function for $t = 0$. Both the stationary states, and the evolution of the non-stationary states, depend on the energy operator (Hamiltonian). If one finds some symmetry of the Hamiltonian, this will influence the symmetry of the wave functions. At the end of this chapter we will be interested in the evolution of a wave function after applying a perturbation.

Why is this important?

The wave function is a central notion in quantum mechanics, and is obtained as a solution of the Schrödinger equation. Hence this chapter is necessary for understanding quantum chemistry.

What is needed?

- Postulates of quantum mechanics, Chapter 1 (necessary).
- Matrix algebra, Appendix A, p. 889 (advised).
- Centre-of-mass separation, Appendix I, p. 971 (necessary).
- Translation vs momentum and rotation vs angular momentum, Appendix F, p. 955 (necessary).
- Dirac notation, p. 19 (necessary).
- Two-state model, Appendix D, p. 948 (necessary).
- Dirac delta, Appendix E, p. 951 (necessary).

Classical works

A paper by the mathematician Emmy Noether “*Invariante Variationsprobleme*” published in *Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen*, 1918, pp. 235–257 was the first to follow the conservation laws of certain physical quantities with the symmetry of theoretical descriptions of the system. ★ Four papers by Erwin Schrödinger, which turned out

to cause an “earth-quake” in science: *Annalen der Physik*, 79 (1926) 361, *ibid.* 79 (1926) 489, *ibid.* 80 (1926) 437, *ibid.* 81 (1926) 109, all under the title “*Quantisierung als Eigenwertproblem*” presented quantum mechanics as an eigenvalue problem (known from the developed differential equation theory), instead of an abstract Heisenberg algebra. Schrödinger proved the equivalence of both theories, gave the solution for the hydrogen atom, and introduced the variational principle. ★ The time-dependent perturbation theory described in this chapter was developed by Paul Adrien Maurice Dirac in 1926. Twenty years later, Enrico Fermi, lecturing at the University of Chicago coined the term “The Golden Rule” for these results. From then on, they are known as the Fermi Golden Rule.

2.1 SYMMETRY OF THE HAMILTONIAN AND ITS CONSEQUENCES

2.1.1 THE NON-RELATIVISTIC HAMILTONIAN AND CONSERVATION LAWS

From classical mechanics it follows that for an isolated system (and assuming the forces to be central and obeying the action-reaction principle), its *energy*, *momentum* and *angular momentum* are conserved.

Imagine a well isolated space ship observed in an inertial coordinate system. Its *energy is preserved*, its centre of mass moves along a straight line with constant velocity (*the total, or centre-of-mass, momentum vector is preserved*), it rotates about an axis with an angular velocity (*total angular momentum preserved*²). The same is true for a molecule or atom, but the conservation laws have to be formulated in the language of quantum mechanics.

Where did the conservation laws come from? Emmy Noether proved that they are related to the symmetry operations, with respect to which the equation of motion is invariant.³

Emmy Noether (1882–1935), German mathematician, informally professor, formally only the assistant of David Hilbert at the University of Göttingen (in the first quarter of the twentieth century women were not allowed to be professors in Germany). Her outstanding achievements in mathematics meant nothing to the Nazis, because Noether was Jewish (people should reminded of such problems) and in 1933 Noether



has been forced to emigrate to the USA (Institute for Advanced Study in Princeton).

²I.e. its *length and direction*. Think of a skater performing a spin: extending the arms sideways slows down her rotation, while stretching them along the axis of rotation results in faster rotation. *But all the time the total angular momentum vector is the same*. If the space ship captain wanted to stop the rotation of the ship which is making the crew sick, he could either throw something (e.g., gas from a steering jet) away from the ship, or spin a well oriented body, fast, inside the ship. But even the captain is unable to change the *total angular momentum*.

³In case of a one-parameter family of operations $\hat{S}_\alpha \hat{S}_\beta = \hat{S}_{\alpha+\beta}$, e.g., translation (α, β stand for the translation vectors), rotation (α, β are rotational angles), etc. Some other operations may not form such

Thus, it turned out that invariance of the equation of motion with respect to an arbitrary:

- *translation in time* (time homogeneity) results in the *energy conservation principle*
- *translation in space* (space homogeneity) gives the *total momentum conservation principle*
- *rotation in space* (space isotropy) implies the *total angular momentum conservation principle*.

These may be regarded as the foundations of science. The homogeneity of time allows one to expect that repeating experiments give the same results. The homogeneity of space makes it possible to compare the results of the same experiments carried out in two different laboratories. Finally, the isotropy of space allows one to reject any suspicion that a different orientation of our laboratory bench with respect to distant stars changes the result.

Now, let us try to incorporate this into quantum mechanics.

All symmetry operations (e.g. translation, rotation, reflection in a plane) are isometric, i.e. $\hat{U}^\dagger = \hat{U}^{-1}$ and \hat{U} does not change distances between points of the transformed object (Figs. 2.1 and 2.2).

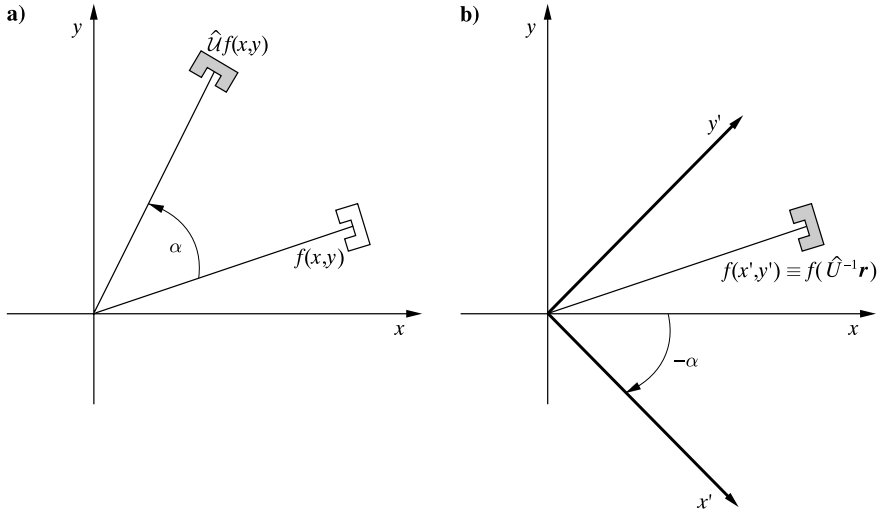
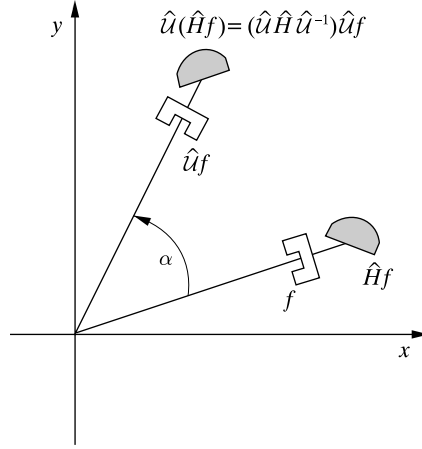


Fig. 2.1. (a) An object is rotated by angle α . (b) The coordinate system is rotated by angle $-\alpha$. The new position of the object in the old coordinate system (a) is the same as the initial position of the object in the new coordinate system (b).

families and then the Noether theorem is no longer valid. This was an important discovery. Symmetry of a theory is much more fundamental than the symmetry of an object. *The symmetry of a theory means that phenomena are described by the same equations no matter what laboratory coordinate system is chosen.*

Fig. 2.2. The f and $\hat{H}f$ represent, in general, different functions. Rotation (by α) of function $\hat{H}f$ gives function $\hat{U}(\hat{H}f)$ and, in consequence, is bound to denote the *rotation* of f (i.e. $\hat{U}f$) and the *transformation* $\hat{U}\hat{H}\hat{U}^{-1}$ of the operator \hat{H} . Indeed, only then does $\hat{U}\hat{H}\hat{U}^{-1}$ acting on the *rotated* function, i.e. $\hat{U}f$ give $\hat{U}\hat{H}\hat{U}^{-1}(\hat{U}f) = (\hat{U}\hat{H})(\hat{U}f)$, i.e. the rotation of the result. Because of $\hat{U}(\hat{H}f) = (\hat{U}\hat{H})(\hat{U}f)$, when verifying the invariance of \hat{H} with respect to transformation \hat{U} , it is sufficient to check whether $\hat{U}\hat{H}$ has the same formula as \hat{H} , but expressed in the new coordinates. Only this $\hat{U}\hat{H}$ will fit to f expressed in the new coordinates, i.e. to $\hat{U}f$. This is how we will proceed shortly.



The operator \hat{U} acting in 3D Cartesian space corresponds to the operator \hat{U} acting in the Hilbert space, cf. eq. (C.2), p. 905. Thus the function $f(\mathbf{r})$ transforms to $f' = \hat{U}f = f(\hat{U}^{-1}\mathbf{r})$, while the operator \hat{A} transforms to $\hat{A}' = \hat{U}\hat{A}\hat{U}^{-1}$ (Fig. 2.2). The formula for \hat{A}' differs in general from \hat{A} , but when it does not, i.e. $\hat{A}' = \hat{A}$, then \hat{U} commutes with \hat{A} .

Indeed, then $\hat{A} = \hat{U}\hat{A}\hat{U}^{-1}$, i.e. one has the commutation relation $\hat{A}\hat{U} = \hat{U}\hat{A}$, which means that \hat{U} and \hat{A} share their eigenfunctions (Appendix B, p. 895).

Let us take the Hamiltonian \hat{H} as the operator \hat{A} . Before writing it down let us introduce *atomic units*. Their justification comes from something similar to laziness. The quantities one calculates in quantum mechanics are stuffed up by some constants: $\hbar = \frac{h}{2\pi}$, where h is the Planck constant, electron charge $-e$, its (rest) mass m_0 , etc. These constants appear in clumsy formulae with various powers, in the nominator and denominator (see Table of units, p. 1062). We always know, however, that the quantity we calculate is energy, length, time or something similar and we know how the unit energy, the unit length, etc. is expressed by \hbar , e , m_0 .

atomic units

ATOMIC UNITS

If one inserts: $\hbar = 1$, $e = 1$, $m_0 = 1$, this gives a dramatic simplification of the formulae. One has to remember though, that these units have been introduced and, whenever needed, one can evaluate the result in other units (see Table of conversion coefficients, p. 1063).

The Hamiltonian for a system of M nuclei (with charges Z_I and masses m_I ,

non-relativistic
Hamiltonian

$I = 1, \dots, M$) and N electrons, in the non-relativistic approximation and assuming point-like particles without any internal structure,⁴ takes [in atomic units (a.u.)] the following form (see p. 18)

$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}, \quad (2.1)$$

where the kinetic energy operators for the nuclei and electrons (in a.u.) read as:

$$\hat{T}_n = -\frac{1}{2} \sum_{I=1}^M \frac{1}{m_I} \Delta_I, \quad (2.2)$$

$$\hat{T}_e = -\frac{1}{2} \sum_{i=1}^N \Delta_i, \quad (2.3)$$

where the Laplacians are

$$\Delta_I = \frac{\partial^2}{\partial X_I^2} + \frac{\partial^2}{\partial Y_I^2} + \frac{\partial^2}{\partial Z_I^2},$$

$$\Delta_i = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2},$$

⁴No internal structure of the electron has yet been discovered. The electron is treated as a point-like particle. Contrary to this nuclei have a rich internal structure and non-zero dimensions. A clear multi-level-like structure appears (which has to a large extent forced a similar structure on the corresponding scientific methodologies):

- Level I. A nucleon (neutron, proton) consists of three (the valence) quarks, clearly seen on the scattering image obtained for the proton. Nobody has yet observed a free quark.
- Level II. The strong forces acting among nucleons have a range of about 1–2 fm (1 fm = 10^{-15} m). Above 0.4–0.5 fm they are attractive, at shorter distances they correspond to repulsion. One need not consider their quark structure when computing the forces among nucleons, but they may be treated as particles *without internal structure*. The attractive forces between nucleons practically do not depend on the nucleon's charge and are so strong that they may overcome the Coulomb repulsion of protons. Thus the nuclei composed of many nucleons (various chemical elements) may be formed, which exhibit a shell structure (analogous to electronic structure, cf. Chapter 8) related to the packing of the nucleons. The motion of the nucleons is strongly correlated. A nucleus may have various energy states (ground and excited), may be distorted, may undergo splitting, etc. About 2000 nuclei are known, of which only 270 are stable. The smallest nucleus is the proton, the largest known so far is ^{209}Bi (209 nucleons). The largest observed number of protons in a nucleus is 118. Even the largest nuclei have diameters about 100000 times smaller than the electronic shells of the atom. Even for an atom with atomic number 118, the first Bohr radius is equal to $\frac{1}{118}$ a.u. or $5 \cdot 10^{-13}$ m, still about 100 times larger than the nucleus.
- Level III. Chemists *can* neglect the internal structure of nuclei. A nucleus *can* be treated as a structureless point-like particle and using the theory described in this book, one is able to predict extremely precisely virtually all the chemical properties of atoms and molecules. Some interesting exceptions will be given in 6.11.2.

and x, y, z stand for the Cartesian coordinates of the nuclei and electrons indicated by vectors $\mathbf{R}_I = (X_I, Y_I, Z_I)$ and $\mathbf{r}_i = (x_i, y_i, z_i)$, respectively.

The operator \hat{V} corresponds to the electrostatic interaction of all the particles (nucleus–nucleus, nucleus–electron, electron–electron):

$$\hat{V} = \sum_{I=1}^M \sum_{J>I}^M \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} - \sum_{I=1}^M \sum_{i=1}^N \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (2.4)$$

or, in a simplified form

$$\hat{V} = \sum_{I=1}^M \sum_{J>I}^M \frac{Z_I Z_J}{R_{IJ}} - \sum_{I=1}^M \sum_{i=1}^N \frac{Z_I}{r_{iI}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}}. \quad (2.5)$$

If the Hamiltonian turned out to be invariant with respect to a symmetry operation \hat{U} (translation, rotation, etc.), this would imply the commutation of \hat{U} and \hat{H} . We will check this in more detail below.

Note that the distances R_{IJ}, r_{iI} and r_{ij} in the Coulombic potential energy in eq. (2.5) witness the assumption of instantaneous interactions in non-relativistic theory (infinite speed of travelling the interaction through space).

2.1.2 INVARIANCE WITH RESPECT TO TRANSLATION

Translation by vector \mathbf{T} of function $f(\mathbf{r})$ in space means the function $\hat{U}f(\mathbf{r}) = f(\hat{U}^{-1}\mathbf{r}) = f(\mathbf{r} - \mathbf{T})$, i.e. an opposite (by vector $-\mathbf{T}$) translation of the coordinate system (Fig. 2.3).

Transformation $\mathbf{r}' = \mathbf{r} + \mathbf{T}$ does not change the Hamiltonian. This is evident for the potential energy \hat{V} , because the translations \mathbf{T} cancel, leaving the interparticle distances unchanged. For the kinetic energy one obtains

$$\frac{\partial}{\partial x'} = \sum_{\sigma=x,y,z} \frac{\partial \sigma}{\partial x'} \frac{\partial}{\partial \sigma} = \frac{\partial x}{\partial x'} \frac{\partial}{\partial x} = \frac{\partial}{\partial x},$$

and all the kinetic energy operators (eqs. (2.2) and (2.3)) are composed of the operators having this form.

The Hamiltonian is therefore invariant with respect to any translation of the coordinate system.

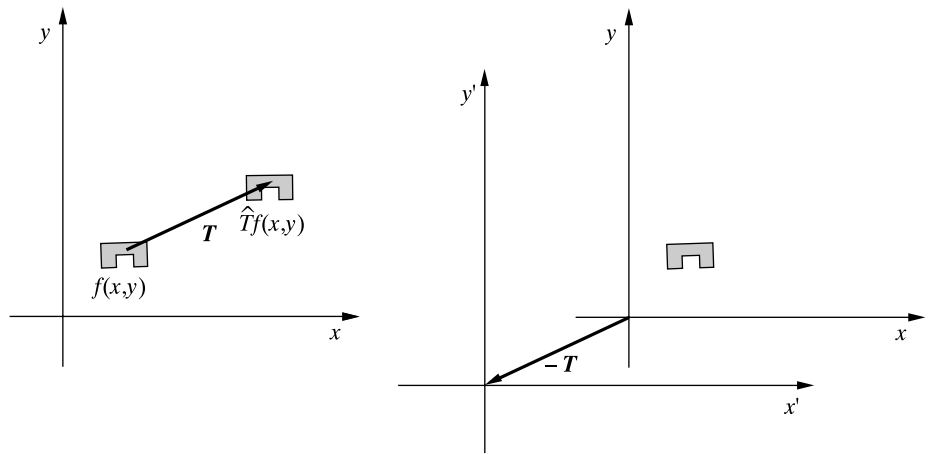


Fig. 2.3. A function f shifted by vector T (symmetry operation \hat{T}), i.e. $\hat{T}f(x, y)$ in the coordinate system (x, y) is the same as function $f(x', y')$, in the coordinate system (x', y') shifted by $-T$.

space
homogeneity

There are two main consequences of translational symmetry:

- No matter, whether the coordinate system used is fixed in Trafalgar Square, or in the centre of mass of the system, one has to solve the same mathematical problem.
- The solution to the Schrödinger equation corresponding to the space fixed coordinate system (SFS) located in Trafalgar Square is Ψ_{pN} , whereas Ψ_{0N} is calculated in the body-fixed coordinate system (see Appendix I) located in the centre of mass at R_{CM} with the (total) momentum p_{CM} . These two solutions are related by $\Psi_{pN} = \Psi_{0N} \exp(ip_{CM} \cdot R_{CM})$. The number $N = 0, 1, 2, \dots$ counts the energy states after the centre-of-mass motion is separated.

This means that the energy spectrum represents a continuum, because the centre of mass may have any (non-negative) kinetic energy $p_{CM}^2/(2m)$. If, however, one assumes that $p_{CM} = \text{const}$, then the energy spectrum is *discrete* for low-energy eigenvalues (see eq. (1.13)).

spectroscopic
states

This spectrum corresponds to the bound states, i.e. those states which do not correspond to any kind of dissociation (including ionization). Higher energy states lead to dissociation of the molecule, and the fragments may have any kinetic energy. Therefore, above the discrete spectrum one has a continuum of states. The states Ψ_{0N} will be called *spectroscopic states*. The bound states Ψ_{0N} are square integrable, as opposed to Ψ_{pN} , which are not because of function $\exp(ipR_{CM})$, which describes the free motion of the centre of mass.

2.1.3 INVARIANCE WITH RESPECT TO ROTATION

The Hamiltonian is also invariant with respect to any rotation in space \hat{U} of the coordinate system about a fixed axis. The rotation is carried out by applying an orthogonal matrix transformation U of vector $\mathbf{r} = (x, y, z)^T$ that describes any particle of coordinates x, y, z . Therefore all the particles undergo the same rotation and the new coordinates are $\mathbf{r}' = \hat{U}\mathbf{r} = U\mathbf{r}$. Again there is no problem with the potential energy, because a rotation does not change the interparticle distances. What about the Laplacians in the kinetic energy operators? Let us see.

isotropy of
space

$$\begin{aligned}
 \Delta &= \sum_{k=1}^3 \frac{\partial^2}{\partial x_k^2} = \sum_{k=1}^3 \frac{\partial}{\partial x_k} \frac{\partial}{\partial x_k} = \sum_{k=1}^3 \left(\sum_{i=1}^3 \frac{\partial}{\partial x'_i} \frac{\partial x'_i}{\partial x_k} \right) \left(\sum_{i=1}^3 \frac{\partial}{\partial x'_i} \frac{\partial x'_i}{\partial x_k} \right) \\
 &= \sum_{i=1}^3 \sum_{j=1}^3 \sum_{k=1}^3 \left(\frac{\partial}{\partial x'_i} \frac{\partial x'_i}{\partial x_k} \right) \left(\frac{\partial}{\partial x'_j} \frac{\partial x'_j}{\partial x_k} \right) \\
 &= \sum_{i=1}^3 \sum_{j=1}^3 \sum_{k=1}^3 \left(\frac{\partial}{\partial x'_i} U_{ik} \right) \left(\frac{\partial}{\partial x'_j} U_{jk} \right) = \sum_{i=1}^3 \sum_{j=1}^3 \sum_{k=1}^3 \left(\frac{\partial}{\partial x'_i} U_{ik} \right) \left(\frac{\partial}{\partial x'_j} U_{kj}^\dagger \right) \\
 &= \sum_{i=1}^3 \sum_{j=1}^3 \left(\frac{\partial}{\partial x'_i} \right) \left(\frac{\partial}{\partial x'_j} \right) \sum_{k=1}^3 U_{ik} U_{kj}^\dagger \\
 &= \sum_{i=1}^3 \sum_{j=1}^3 \left(\frac{\partial}{\partial x'_i} \right) \left(\frac{\partial}{\partial x'_j} \right) \delta_{ij} = \sum_{k=1}^3 \frac{\partial^2}{\partial (x'_k)^2}.
 \end{aligned}$$

Thus, one has invariance of the Hamiltonian with respect to any rotation about the origin of the coordinate system. This means (see p. 955) that the Hamiltonian and the operator of the square of the total angular momentum \hat{J}^2 (as well as of one of its components, denoted by \hat{J}_z) commute. One is able, therefore, to measure simultaneously the energy, the square of total angular momentum as well as one of the components of total angular momentum, and (as it will be shown in (4.6)) one has

$$\hat{J}^2 \Psi_{0N}(\mathbf{r}, \mathbf{R}) = J(J+1) \hbar^2 \Psi_{0N}(\mathbf{r}, \mathbf{R}), \quad (2.6)$$

$$\hat{J}_z \Psi_{0N}(\mathbf{r}, \mathbf{R}) = M_J \hbar \Psi_{0N}(\mathbf{r}, \mathbf{R}), \quad (2.7)$$

where $J = 0, 1, 2, \dots$ and $M_J = -J, -J+1, \dots, +J$.

Any rotation matrix may be shown as a product of “elementary” rotations, each about axes x , y or z . For example, rotation about the y axis by angle θ corresponds to the matrix

$$\begin{pmatrix} \cos \theta & 0 & -\sin \theta \\ 0 & 1 & 0 \\ \sin \theta & 0 & \cos \theta \end{pmatrix}.$$

The pattern of such matrices is simple: one has to put in some places sines, cosines, zeros and ones with the proper signs.⁵ This matrix is orthogonal,⁶ i.e. $U^T = U^{-1}$, which you may easily check. The product of two orthogonal matrices represents an orthogonal matrix, therefore any rotation corresponds to an orthogonal matrix.

2.1.4 INVARIANCE WITH RESPECT TO PERMUTATION OF IDENTICAL PARTICLES (FERMIONS AND BOSONS)

The Hamiltonian has also permutational symmetry. This means that if someone exchanged labels numbering the identical particles, independently of how it was done, they would always obtain the identical mathematical expression for the Hamiltonian. This implies that any wave function has to be symmetric (for bosons) or antisymmetric (fermions) with respect to the exchange of labels between two identical particles (cf. p. 33).

2.1.5 INVARIANCE OF THE TOTAL CHARGE

The total electric charge of a system does not change, whatever happens. In addition to the energy, momentum and angular momentum, strict conservation laws are obeyed exclusively for the total electric charge and the baryon and lepton numbers (a given particle contributes $+1$, the corresponding antiparticle -1).⁷ The charge conservation law follows from the gauge symmetry. This symmetry means the invariance of the theory with respect to partition of the total system into subsystems. Total electric charge conservation follows from the fact that the description of the system has to be invariant with respect to the mixing of the particle and antiparticle states, which is analogous to rotation.

⁵Clockwise and anticlockwise rotations and two possible signs at sines cause a problem with memorizing the right combination. In order to choose the correct one, one may use the following trick. First, we decide that what moves is an *object* (e.g., a function, not the coordinate system). Then, you take my book from your pocket. With Fig. 2.1.a one sees that the rotation of the point with coordinates $(1, 0)$ by angle $\theta = 90^\circ$ should give the point $(0, 1)$, and this is assured only by the rotation matrix: $\begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix}$.

⁶And therefore also unitary (cf. Appendix A, p. 889).

⁷For example, in the Hamiltonian (2.1) it is assumed that whatever might happen to our system, the numbers of the nucleons and electrons will remain constant.

2.1.6 FUNDAMENTAL AND LESS FUNDAMENTAL INVARIANCES

The conservation laws described are of a fundamental character, because they are related to the homogeneity of space and time, the isotropy of space and the non-distinguishability of identical particles.

Besides these strict conservation laws, there are also some approximate laws. Two of these: parity and charge conjugation, will be discussed below. They are rooted in these strict laws, but are valid only in some conditions. For example, in most experiments, not only the baryon number, but also the number of nuclei of each kind are conserved. Despite the importance of this law in chemical reaction equations, this does not represent any strict conservation law as shown by radioactive transmutations of elements.

Some other approximate conservation laws will soon be discussed.

2.1.7 INVARIANCE WITH RESPECT TO INVERSION – PARITY

There are orthogonal transformations which are not equivalent to any rotation, e.g., the matrix of inversion

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix},$$

which corresponds to changing \mathbf{r} to $-\mathbf{r}$ for all the particles and does not represent any rotation. If one performs such a symmetry operation, the Hamiltonian remains invariant. This is evident, both for \hat{V} (the interparticle distances do not change), and for the Laplacian (single differentiation changes sign, double does not). Two consecutive inversions mean an identity operation. Hence,

$$\Psi_{0N}(-\mathbf{r}, -\mathbf{R}) = \Pi \Psi_{0N}(\mathbf{r}, \mathbf{R}), \quad \text{where } \Pi \in \{1, -1\}.$$

Therefore,

the wave function of a stationary state represents an eigenfunction of the inversion operator, and the eigenvalue can be either $\Pi = 1$ or $\Pi = -1$ (this property is called parity, or P).

Now the reader will be taken by surprise. From what we have said, it follows that *no molecule has a non-zero dipole moment*. Indeed, the dipole moment is calculated as the mean value of the dipole moment operator, i.e. $\boldsymbol{\mu} = \langle \Psi_{0N} | \hat{\boldsymbol{\mu}} | \Psi_{0N} \rangle = \langle \Psi_{0N} | (\sum_i q_i \mathbf{r}_i) | \Psi_{0N} \rangle$. This integral will be calculated very easily: the integrand is antisymmetric with respect to inversion⁸ and therefore $\boldsymbol{\mu} = \mathbf{0}$.

⁸ Ψ_{0N} may be symmetric or antisymmetric, but $|\Psi_{0N}|^2$ is bound to be symmetric. Therefore, since $\sum_i q_i \mathbf{r}_i$ is antisymmetric, then indeed, the integrand is antisymmetric (the integration limits are symmetric).

Is therefore the very meaning of the dipole moment, a quantity often used in chemistry and physics, a fairy tale? If HCl has no dipole moment, then it is more understandable that H₂ does not have either. All this seems absurd. What about this dipole moment?

Let us stress, that our conclusion pertains to the *total* wave function, which has to reflect the space isotropy leading to the zero dipole moment, because all orientations in space are equally probable. If one applied the transformation $\mathbf{r} \rightarrow -\mathbf{r}$ only to *some* particles in the molecule (e.g., electrons), and not to others (e.g., the nuclei), the wave function will show no parity (it would be neither symmetric nor antisymmetric). We will introduce the Hamiltonian in Chapter 6, which corresponds to immobilizing the nuclei (clamped nuclei approximation) in certain positions in space, and in such a case the wave function depends on the electronic coordinates only. This wave function may be neither symmetric nor antisymmetric with respect to the *partial* inversion transformation $\mathbf{r} \rightarrow -\mathbf{r}$ (for the electrons only). To give an example, let us imagine the HF molecule in a coordinate system, its origin in the middle between the H and F nuclei. Consider a particular configuration of the 10 electrons of the molecule; all close to the fluorine nucleus in some well defined points. One may compute the value of the wave function for this configuration of electrons. Its square gives us the probability density of finding this particular configuration of electrons. Now, imagine the (*partial*) inversion $\mathbf{r} \rightarrow -\mathbf{r}$ applied to all the electrons. Now they will all be close to the proton. If one computes the probability density for the new situation, one would obtain a different value (much, much smaller, because the electrons prefer the fluorine, not the hydrogen). No symmetry or antisymmetry. No wonder therefore that if one computed $\boldsymbol{\mu} = \langle \Psi_{0N} | \hat{\boldsymbol{\mu}} | \Psi_{0N} \rangle$ with such a function (integration is over the electronic coordinates only), the result would differ from zero. This is why chemists believe the HF molecule has a non-zero dipole moment.⁹ On the other hand, if the molecule taken as the example were B₂ (also ten electrons), then the two values have had to be equal, because they describe the same physical situation. This corresponds, therefore, to a wave function with definite parity (symmetric or antisymmetric), and therefore, in this case $\boldsymbol{\mu} = \mathbf{0}$. This is why chemists believe such molecules as H₂, B₂, O₂ have no dipole moment.

Product of inversion and rotation

The Hamiltonian is also invariant with respect to some other symmetry operations like changing the sign of the x coordinates of all particles, or similar operations which are products of inversion and rotation. If one changed the sign of all the x coordinates, it would correspond to a mirror reflection. Since rotational symmetry stems from space isotropy (which we will treat as “trivial”), the mirror reflection may be identified with parity P .

mirror reflection

P symmetry

⁹What therefore do they measure? The answer will be given in Chapter 12.

Enantiomers

A consequence of inversion symmetry is that the wave functions have to be eigenfunctions of the inversion operator with eigenvalues $\Pi = 1$, i.e. the wave function is symmetric, or $\Pi = -1$, i.e. the wave function is antisymmetric. Any asymmetric wave function corresponding to a stationary state is therefore excluded (“illegal”). However, two optical isomers (enantiomers), corresponding to an object and its mirror image, do exist (Fig. 2.4).¹⁰

We ask in a pharmacy for D-glucose, strangely enough the pharmacist is fully cooperative and does not make trouble. We pay a small sum and he gives us something which should not exist¹¹ – a substance with a single enantiomer. We should obtain a substance composed of molecules in their stationary states, which have therefore to have definite parity, either as a sum of the wave functions for the two enantiomers D and L ($\Pi = 1$, cf. Appendix D on p. 948, Example I): $\psi_+ = \psi_D + \psi_L$ or as the difference ($\Pi = -1$): $\psi_- = \psi_D - \psi_L$. The energies corresponding to ψ_+ and ψ_- differ, but the difference is extremely small (quasidegeneracy). The brave shopkeeper has given us something with the wave function $\psi = N(\psi_+ + \psi_-) = \psi_D$ (as result of de-

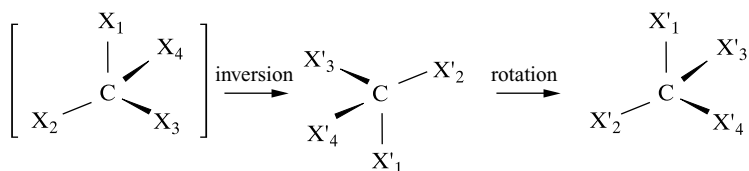
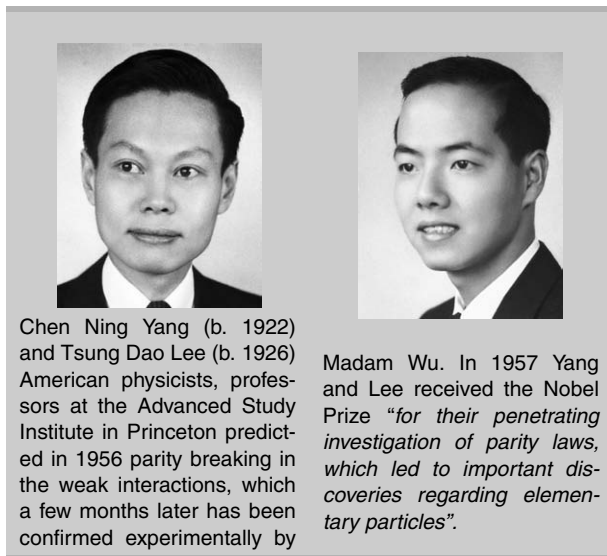


Fig. 2.4. If one superposed the X_1 –C– X_2 and X'_1 –C'– X'_2 fragments of both molecules, the other two substituents could not match: X'_4 in place of X_3 and X'_3 in place of X_4 . The two molecules represent two enantiomeric isomers. A wave function that describes one of the enantiomers does not have a definite parity and is therefore “illegal”.

¹⁰The property that distinguishes them is known as chirality (your hands are an example of chiral objects). The chiral molecules (enantiomers) exhibit optical activity, i.e. polarized light passing through a solution of one of the enantiomers undergoes a rotation of the polarization plane *always in the same direction* (which may be easily seen by reversing the direction of the light beam). Two enantiomeric molecules have the same properties, provided one is checking this by using non-chiral objects. If the probe were chiral, one of the enantiomers would interact with it differently (for purely steric reasons). Enantiomers (e.g., molecular associates) may be formed from chiral or non-chiral subunits.

¹¹More exactly, should be unstable.

coherence), which therefore describes a non-stationary state.¹² As we will see in a moment (p. 82), the approximate lifetime of the state is proportional to the inverse of the integral $\langle \psi_D | \hat{H} | \psi_L \rangle$. If one calculated this integral, one would obtain an extremely small number.¹³ It would turn out that the pharmacy could safely keep the stock of glucose for millions of years. Maybe the reason for decoherence is interaction with the rest of the Universe, maybe even interaction with a vacuum. The very existence of enantiomers, or even the prevalence of one of them on Earth, does not mean breaking parity symmetry. This would happen if one of the enantiomers corresponded to a lower energy than the other.¹⁴

2.1.8 INVARIANCE WITH RESPECT TO CHARGE CONJUGATION

If one changed the signs of the charges of all particles, the Hamiltonian would not change.

C symmetry

This therefore corresponds to exchanging particles and antiparticles.¹⁵ Such a symmetry operation is called the charge conjugation and denoted as C symmetry. This symmetry will not be marked in the wave function symbol (because, as a rule, we have to do with matter, not antimatter), but we will remember. Sometimes it may turn out unexpectedly to be useful (see Chapter 13, p. 702). After Wu's experiment, physicists tried to save the hypothesis that what is conserved is the CP symmetry, i.e. the product of charge conjugation and inversion. However, analysis of experiments with the meson K decay has shown that even this symmetry is approximate (although the deviation is extremely small).

2.1.9 INVARIANCE WITH RESPECT TO THE SYMMETRY OF THE NUCLEAR FRAMEWORK

In many applications the positions of the nuclei are fixed (clamped nuclei approximation, Chapter 6), often in a high-symmetry configuration (cf. Appendix C, p. 903). For example, the benzene molecule in its ground state (after minimizing the energy with respect to the positions of the nuclei) has the symmetry of a regular hexagon. In such cases the electronic Hamiltonian additionally exhibits invariance with respect to some symmetry operations and therefore the wave functions are

¹²Only ψ_+ and ψ_- are stationary states.

¹³This is seen even after attempting to overlap two molecular models physically, Fig. 2.4. The overlap of the wave functions will be small for the same reasons (the wave functions decay exponentially with distance).

¹⁴This is what happens in reality, although the energy difference is extremely small. Experiments with β -decay have shown that Nature breaks parity in weak interactions. Parity conservation law therefore has an approximate character.

¹⁵Somebody thought he had carried out computations for benzene, but he also computed antibenzene. The wave function for benzene and antibenzene are the same.

the eigenstates of these symmetry operations. Therefore, any wave function may have an additional label; the symbol of the irreducible representation¹⁶ it belongs to.

2.1.10 CONSERVATION OF TOTAL SPIN

In an isolated system the *total* angular momentum \mathbf{J} is conserved. However, $\mathbf{J} = \mathbf{L} + \mathbf{S}$, where \mathbf{L} and \mathbf{S} stand for the orbital and spin angular momenta (sum over all particles), respectively. The spin angular momentum \mathbf{S} , a sum of spins of all particles, is not conserved.

However, the (non-relativistic) Hamiltonian does not contain any spin variables. This means that it commutes with the operator of the square of the total spin as well as with the operator of one of the spin components (by convention the z component). Therefore, in the non-relativistic approximation one can simultaneously measure the energy E , the square of the spin S^2 and one of its components S_z .

2.1.11 INDICES OF SPECTROSCOPIC STATES

In summary, assumptions about the homogeneity of space and time, isotropy of space and parity conservation lead to the following quantum numbers (indices) for the spectroscopic states:

- N quantizes energy,
- J quantizes the length of total angular momentum,
- M quantizes the z component of total angular momentum,
- Π determines parity:

$$\Psi_{N,J,M,\Pi}(\mathbf{r}, \mathbf{R}).$$

Besides these indices following from the fundamental laws (in the case of parity it is a little too exaggerated), there may be also some indices related to less fundamental conservation laws:

- the irreducible representation index of the symmetry group of the clamped nuclei Hamiltonian (Appendix C)
- the values of S^2 (traditionally one gives the *multiplicity* $2S + 1$) and S_z .

¹⁶Of the symmetry group composed of the symmetry operations mentioned above.

2.2 SCHRÖDINGER EQUATION FOR STATIONARY STATES

It may be instructive to see how Erwin Schrödinger invented his famous equation (1.13) for *stationary states* ψ of energy E (\hat{H} denotes the Hamiltonian of the system)

$$\hat{H}\psi = E\psi. \quad (2.8)$$

Schrödinger surprised the contemporary quantum elite (associated mainly with

Erwin Rudolf Josef Alexander Schrödinger (1887–1961), Austrian physicist, professor at the universities of Jena, Stuttgart, Graz, Breslau, Zurich, Berlin and Vienna. In later years Schrödinger recalled the Zurich period most warmly, in particular, discussions with the mathematician Hermann Weyl and physicist Peter Debye. In 1927 Schrödinger succeeded Max Planck at the University of Berlin, and in 1933 received the Nobel Prize “for the discovery of new productive forms of atomic theory”. Hating the Nazi regime, he left Germany in 1933 and moved to the University of Oxford. However, homesick for his native Austria he went back in 1936 and took a professorship at the University of Graz. Meanwhile Hitler carried out his Anschluss with Austria in 1938, and Schrödinger even though not a Jew, could have been an easy target as one who fled Germany because of the Nazis. He emigrated to the USA (Princeton), and then to Ireland (Institute for Advanced Studies in Dublin), worked there till 1956, then returned to Austria and remained there, at the Vienna University, until his death.

In his scientific work as well as in his personal life Schrödinger did not strive for big goals, he worked by himself. Maybe what characterizes him best is that he was always ready to leave having belongings packed in his rucksack. Among the goals of this textbook listed in the Introduction there is not demoralization of youth. This is why I will stop here, limit myself to the carefully selected information given above and refrain from describing the circumstances, in which quantum mechanics was born. For those students who read the material recommended in the Additional Literature, I provide some useful references: W. Moore, “Schrödinger: Life and Thought”, Cambridge University Press, 1989, and the comments on the book given by P.W. Atkins, *Nature*,



341 (1989), also <http://www-history.mcs.st-andrews.ac.uk/history/Mathematicians/Schrodinger.html>.

Schrödinger's curriculum vitae found in Breslau (now Wrocław):

“Erwin Schrödinger, born on Aug., 12, 1887 in Vienna, the son of the merchant Rudolf Schrödinger and his wife née Lauer. The family of my father comes from the Upper Palatinate and Wirtemberg region, and the family of my mother from German Hungary and (from the maternal side) from England. I attended a so called “academic” high school (once part of the university) in my native town. Then from 1906–1910 I studied physics at Vienna University, where I graduated in 1910 as a doctor of physics. I owe my main inspiration to my respected teacher Fritz Hasenöhr, who by an unlucky fate was torn from his diligent students – he fell gloriously as an attack commander on the battlefield of Vielgereuth. As well as Hasenöhr, I owe my mathematical education to Professors Franz Mertens and Wilhelm Wirtinger, and a certain knowledge of experimental physics to my principal of many years (1911–1920) Professor Franz Exner and my intimate friend R.M.F. Rohrmuth. A lack of experimental and some mathematical skills oriented me basically towards theory.

Presumably the spirit of Ludwig Boltzmann (deceased in 1906), operating especially intensively in Vienna, directed me first towards the probability theory in physics. Then, (...) a closer contact with the experimental works of Exner and Rohrmuth oriented me to the physiological theory of colours, in which I tried to confirm and develop the achievements of Helmholtz. In 1911–1920 I was a laboratory assistant under Franz Exner in Vienna, of course, with $4\frac{1}{2}$ years long pause caused by war. I have obtained my habilitation in 1914 at the University of Vienna, while in 1920 I accepted an offer from Max Wien and became his assistant professor at the new theoretical physics department in Jena. This lasted, unfortunately, only one semester, because I could not refuse a professorship at the Technical University in Stuttgart. I was there also only one semester, because April

1921 I came to the University of Hessen in succession to Klemens Schrafer. I am almost ashamed to confess, that at the moment I sign the present curriculum vitae I am no longer a professor at the University of Breslau, because on Oct. 15. I received my nomination to the University of Zurich. My instability may be recognized exclusively as a sign of my ingratitude!

Breslau, Oct., 5, 1921. Dr Erwin Schrödinger

(found in the archives of the University of Wrocław (Breslau) by Professor Zdzisław Łatajka and Professor Andrzej Sokalski, translated by Professor Andrzej Kaim and the Author. Since the manuscript (see web annex, Supplements) was hardly legible due to Schrödinger's difficult handwriting, some names may have been misspelled.)

Copenhagen and Göttingen) by a clear formulation of quantum mechanics as wave mechanics. January 27, 1926, when Schrödinger submitted a paper entitled “*Quantisierung als Eigenwertproblem*”¹⁷ to *Annalen der Physik*, may be regarded as the birthday of wave mechanics.

Most probably Schrödinger's reasoning was as follows. De Broglie discovered that what people called a particle also had a wave nature (Chapter 1). That is really puzzling. If a wave is involved, then according to Debye's suggestion at the November seminar in Zurich, it might be possible to write the standing wave equation with $\psi(x)$ as its amplitude at position x :

$$v^2 \frac{d^2 \psi}{dx^2} + \omega^2 \psi = 0, \quad (2.9)$$

where v stands for the (phase) velocity of the wave, and ω represents its angular frequency ($\omega = 2\pi\nu$, where ν is the usual frequency) which is related to the wave length λ by the well known formula:¹⁸

$$\omega/v = \frac{2\pi}{\lambda}. \quad (2.10)$$

Besides, Schrödinger knew from the de Broglie's thesis, himself having lectured in Zurich about this, that the wavelength, λ , is related to a particle's momentum p through $\lambda = h/p$, where $h = 2\pi\hbar$ is the Planck constant. This equation is the most

¹⁷Quantization as an eigenproblem. Well, once upon a time quantum mechanics was discussed in German. Some traces of that period remain in the nomenclature. One is the “eigenvalue problem or eigenproblem” which is a German–English hybrid.

¹⁸In other words $\nu = \frac{v}{\lambda}$ or $\lambda = vT$ (i.e. wave length is equal to the velocity times the period). Eq. (2.9) represents an oscillating function $\psi(x)$. Indeed, it means that $\frac{d^2 \psi}{dx^2}$ and ψ differ by sign, i.e. if ψ is above the x axis, then it curves down, while if it is below the x axis, then it curves up.

famous achievement of de Broglie, and relates the corpuscular (p) character and the wave (λ) character of any particle.

On the other hand the momentum p is related to the total energy (E) and the potential energy (V) of the particle through: $p^2 = 2m(E - V)$, which follows, from the expression for the kinetic energy $T = \frac{mv^2}{2} = p^2/(2m)$ and $E = T + V$. Therefore, eq. (2.9) can be rewritten as:

$$\frac{d^2\psi}{dx^2} + \frac{1}{\hbar^2}[2m(E - V)]\psi = 0, \quad (2.11)$$

The most important step towards the great discovery was the transfer of the term involving E to the left hand side. Let us see what Schrödinger obtained:

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V \right] \psi = E\psi. \quad (2.12)$$

This was certainly a good moment for a discovery. Schrödinger obtained a kind of *eigenvalue equation* (1.13), recalling his experience with eigenvalue equations in the theory of liquids.¹⁹ What is striking in eq. (2.12) is the odd fact that an operator $-\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$ amazingly plays the role of the kinetic energy. Indeed, keeping calm we see the following: *something* plus potential energy, all that multiplied by ψ , equals total energy times ψ . Therefore, clearly this *something* must be the kinetic energy! But, wait a minute, the kinetic energy is equal to $\frac{p^2}{2m}$. From this it follows that, in the equation obtained instead of p there is a certain *operator* $i\hbar \frac{d}{dx}$ or $-i\hbar \frac{d}{dx}$, because only then does the squaring give the right answer.

Would the key to the puzzle be simply taking the classical expression for total energy and inserting the above operators instead the momenta? What was the excited Schrödinger supposed to do? The best choice is always to begin with the simplest toys, such as the free particle, the particle in a box, the harmonic oscillator, the rigid rotator or hydrogen atom. Nothing is known about whether Schrödinger himself had a sufficiently deep knowledge of mathematics to be able to solve the (sometimes non-trivial) equations related to these problems, or whether he had advice from a friend

Hermann Weyl (1885–1955), German mathematician, professor at ETH Zurich, then the University of Göttingen and the Institute for Advanced Studies at Princeton (USA), expert in the theory of orthogonal series, group theory and differential equations. Weyl adored Schrödinger's wife, was a friend of the family, and provided an ideal partner for Schrödinger in conver-



sations about the eigenproblem.

versed in mathematics, such as Hermann Weyl.

It turned out that instead of p , $-i\hbar \frac{d}{dx}$ had to be inserted, and not $i\hbar \frac{d}{dx}$ (Postulate II, Chapter 1).

¹⁹Very interesting coincidence: Heisenberg was also involved in fluid dynamics. At the beginning, Schrödinger did not use operators. They appeared after he established closer contacts with the University of Göttingen.

2.2.1 WAVE FUNCTIONS OF CLASS Q

The postulates of quantum mechanics, especially the probabilistic interpretation of the wave function given by Max Born, limits the class of functions allowed (to “class Q”, or “quantum”).

Any wave function

- cannot be zero everywhere (Fig. 2.5.a), because the system *is somewhere* in space;
- has to be continuous, (Fig. 2.5.b). This also means it cannot take infinite values at any point in space²⁰ (Fig. 2.5.c,d);
- has to have a continuous first derivative as well (everywhere in space except isolated points (Fig. 2.5.e,f), where the potential energy tends to $-\infty$), because the Schrödinger equation is a second order differential equation and the second derivative must be defined;
- has to have a uniquely defined value in space,²¹ Fig. 2.5.g,h;
- for bound states has to tend to zero at infinite values of any of the coordinates (Fig. 2.5.i,j), because such a system is compact and does not disintegrate in space. In consequence (from the probabilistic interpretation), the wave function is square integrable, i.e. $\langle \Psi | \Psi \rangle < \infty$.

2.2.2 BOUNDARY CONDITIONS

The Schrödinger equation is a differential equation. In order to obtain a special solution to such equations, one has to insert the particular boundary conditions to be fulfilled. Such conditions follow from the physics of the problem, i.e. with which kind of experiment are we going to compare the theoretical results? For example:

- for the *bound states* (i.e. square integrable states) we put the condition that the wave function has to vanish at infinity, i.e. if any of the coordinates tends to infinity: $\psi(x = \infty) = \psi(x = -\infty) = 0$;
- for cyclic systems of circumference L , the natural conditions will be: $\psi(x) = \psi(x + L)$ and $\psi'(x) = \psi'(x + L)$, because they ensure a smooth matching of the wave function for $x < 0$ and of the wave function for $x > 0$ at $x = 0$;
- for scattering states (not discussed here) the boundary conditions are more complex.²²

bound states

There is a countable number of bound states. Each state corresponds to eigenvalue E .

²⁰If this happened in any non-zero volume of space (Fig. 2.5.d) the probability would tend to infinity (which is prohibited). However, the requirement is stronger than that: a wave function cannot take an infinite value even at a single point, Fig. 2.5.c. Sometimes such functions appear among the solutions of the Schrödinger equation, and have to be rejected. The formal argument is that, if not excluded from the domain of the Hamiltonian, the latter would be non-Hermitian when such a function were involved in $\langle f | \hat{H} g \rangle = \langle \hat{H} f | g \rangle$. A non-Hermitian Hamiltonian might lead to complex energy eigenvalues, which is prohibited.

²¹At any point in space the function has to have a single value. This plays a role only if we have an angular variable, say ϕ . Then, ϕ and $\phi + 2\pi$ have to give the same value of the wave function. We will encounter this problem in the solution for the rigid rotator.

²²J.R. Taylor, “*Scattering Theory*”, Wiley, New York, 1972 is an excellent reference.

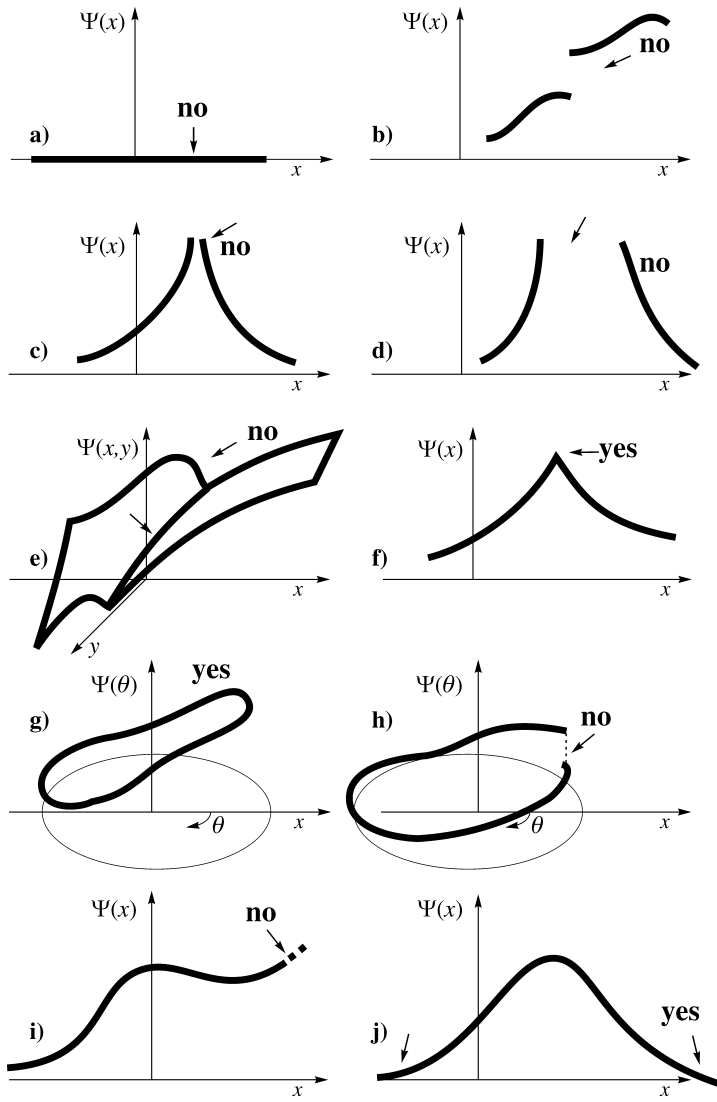
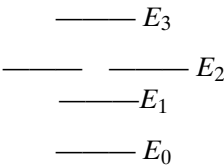


Fig. 2.5. Functions of class Q (i.e. wave functions allowed in quantum mechanics) – examples and counterexamples. A wave function (a) must not be zero everywhere in space (b) has to be continuous (c) cannot tend to infinity even at a single point (d) cannot tend to infinity (e) its first derivative cannot be discontinuous for infinite number of points (f) its first derivative may be discontinuous for a finite number of points (g) has to be defined uniquely in space (for angular variable θ) (h) cannot correspond to multiple values at a point in space (for angular variable θ) (i) for bound states: must not be non-zero in infinity (j) for bound states: has to vanish in infinity.

degeneracy

An energy level may be *degenerate*, that is, more than one wave function may correspond to it, all the wave functions being linearly independent (their number is the *degree of degeneracy*). The eigenvalue spectrum is usually represented by

putting a single horizontal section (in the energy scale) for each wave function:



2.2.3 AN ANALOGY

Let us imagine all the stable positions of a chair on the floor (Fig. 2.6).

Consider a simple chair, very uncomfortable for sitting, but very convenient for a mathematical exercise. Each of the four legs represents a rod of length a , the „seat” is simply a square built of the rods, the back consists of three such rods making a C shape. The potential energy of the chair (in position i) in a gravitational field equals mgh_i , where m stands for the mass of the chair, g gravitational acceleration, and h_i denotes the height of the centre of mass with respect to the floor. We obtain the following energies, E_i , of the stationary states (in units of mga):

- the chair is lying on the support: $E_0 = \frac{4}{11}$;
- the chair is lying inclined: the support and the seat touch the floor $E_1 = \frac{7\sqrt{2}}{22} = 0.45$;
- the chair is lying on the side: $E_2 = \frac{1}{2}$.

Note, however, that we have *two* sides. The energy is the same for the chair lying on the first and second side (because the chair is symmetric), but these are *two* states of the chair, not one. The degree of degeneracy equals *two*, and therefore on the energy diagram we have two horizontal sections. Note how naturally the problem of degeneracy has appeared. The degeneracy of the energy eigenstates of molecules results from symmetry, exactly as in the case of the chair. In some cases,

accidental
degeneracy

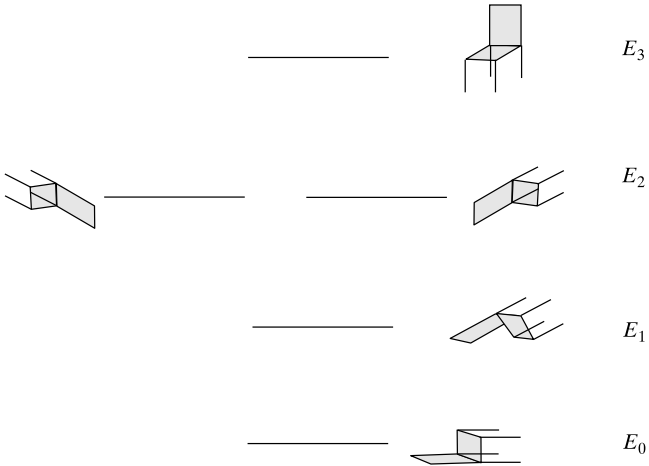


Fig. 2.6. The stable positions of a chair on the floor (arbitrary energy scale). In everyday life we most often use the third excited state.

dynamical
symmetry

one may obtain an *accidental degeneracy*, which does not follow from the symmetry of an object like a chair, but from the properties of the potential field, and is called *dynamical symmetry*.²³

– the chair is in the normal position: $E_3 = 1$.

There are no more stable states of the chair²⁴ and there are only four energy levels, Fig. 2.6. The stable states of the chair are analogues to the stationary quantum states of Fig. 1.8.b,d, on p. 23, while unstable states of the chair on the floor are analogues of the non-stationary states of Fig. 1.8.a,c.

2.2.4 MATHEMATICAL AND PHYSICAL SOLUTIONS

It is worth noting that not all solutions of the Schrödinger equation are physically acceptable.

underground
states

For example, for bound states, all solutions other than those of class Q (see p. 895) must be rejected. In addition, these solutions ψ , which do not exhibit the proper symmetry, even if $|\psi|^2$ does, have also to be rejected. They are called mathematical (non-physical) solutions to the Schrödinger equation. Sometimes such mathematical solutions correspond to a *lower* energy than any physically acceptable energy (known as *underground states*). In particular, such illegal, non-acceptable functions are *asymmetric* with respect to the label exchange for electrons (e.g., symmetric for some pairs and antisymmetric for others). Also, a fully symmetric function would also be such a non-physical (purely mathematical) solution.

2.3 THE TIME-DEPENDENT SCHRÖDINGER EQUATION

What would happen if one prepared the system in a given state ψ , which does not represent a stationary state? For example, one may deform a molecule by using an electric field and then switch the field off.²⁵ The molecule will suddenly turn out to be in state ψ , that is not its stationary state. Then, according to quantum mechanics, the state of the molecule will start to change according to the time evolution equation (time-dependent Schrödinger equation)

$$\hat{H}\psi = i\hbar \frac{\partial \psi}{\partial t}. \quad (2.13)$$

²³Cf. the original works C. Runge, “*Vektoranalysis*”, vol. I, p. 70, ed. S. Hirzel, Leipzig, 1919, W. Lenz, *Zeit. Physik* 24 (1924) 197 as well as L.I. Schiff, “*Quantum Mechanics*”, McGraw Hill (1968).

²⁴Of course, there are plenty of unstable positions of the chair with respect to the floor. The stationary states of the chair have more in common with chemistry than we might think. A chair-like molecule (organic chemists have already synthesized much more complex molecules) interacting with a crystal surface would very probably have similar stationary (vibrational) states.

²⁵We neglect the influence of the magnetic field that accompanies any change of electric field.

The equation plays a role analogous to Newton's equation of motion in classical mechanics. The position and momentum of a particle change according to Newton's equation. In the time-dependent Schrödinger equation the evolution proceeds in a completely different space – in the space of states or Hilbert space (cf. Appendix B, p. 895).

Therefore, in quantum mechanics one has absolute determinism, but in the state space. Indeterminism begins only in our space, when one asks about the coordinates of a particle.

2.3.1 EVOLUTION IN TIME

As is seen from eq. (2.13), knowledge of the Hamiltonian and of the wave function at a given time (left-hand side), represents sufficient information to determine the time derivative of the wave function (right-hand side). This means that we may compute the wave function after an infinitesimal time dt :

$$\psi + \frac{\partial \psi}{\partial t} dt = \psi - \frac{i}{\hbar} \hat{H} \psi dt = \left[1 + \left(-i \frac{t}{N\hbar} \right) \hat{H} \right] \psi,$$

where we have set $dt = t/N$ with N (natural number) very large. Thus, the new wave function results from action of the operator $[1 + (-i \frac{t}{N\hbar}) \hat{H}]$ on the old wave function. Now, we may pretend that we did not change any function and apply the operator again and again. We assume that \hat{H} is time-independent. The total operation is nothing but the action of the operator:

$$\lim_{N \rightarrow \infty} \left[1 + \left(-i \frac{t}{N\hbar} \right) \hat{H} \right]^N.$$

Please recall that $e^x = \lim_{N \rightarrow \infty} [1 + \frac{x}{N}]^N$.

Hence, the time evolution corresponds to action on the initial ψ of the operator $\exp(-\frac{it}{\hbar} \hat{H})$:

$$\psi' = \exp\left(-\frac{it}{\hbar} \hat{H}\right) \psi. \quad (2.14)$$

Our result satisfies the time-dependent Schrödinger equation,²⁶ if \hat{H} does not depend on time (as we assumed when constructing ψ').

Inserting the spectral resolution of the identity²⁷ (cf. Postulate II in Chapter 1)

²⁶One may verify inserting ψ' into the Schrödinger equation. Differentiating ψ' with respect to t , the left-hand-side is obtained.

²⁷The use of the spectral resolution of the identity in this form is not fully justified. A sudden cut in the electric field may leave the molecule with a non-zero translational energy. However, in the above spectral resolution one has the stationary states computed in the centre-of-mass coordinate system, and therefore translation is not taken into account.

one obtains²⁸

$$\begin{aligned}\psi' &= \exp\left(-i\frac{t}{\hbar}\hat{H}\right)1\psi = \exp\left(-i\frac{t}{\hbar}\hat{H}\right)\sum_n |\psi_n\rangle\langle\psi_n|\psi\rangle \\ &= \sum_n \langle\psi_n|\psi\rangle \exp\left(-i\frac{t}{\hbar}\hat{H}\right)|\psi_n\rangle = \sum_n \langle\psi_n|\psi\rangle \exp\left(-i\frac{t}{\hbar}E_n\right)|\psi_n\rangle.\end{aligned}$$

This is how the state ψ will evolve. It will be similar to one or another stationary state ψ_n , more often to those ψ_n which overlap significantly with the starting function (ψ) and/or correspond to low energy (low frequency). If the overlap $\langle\psi_n|\psi\rangle$ of the starting function ψ with a stationary state ψ_n is zero, then during the evolution no admixture of the ψ_n state will be seen, i.e. *only those stationary states that constitute the starting wave function ψ contribute to the evolution.*

2.3.2 NORMALIZATION IS PRESERVED

Note that the imaginary unit i is important in the formula for ψ' . If “ i ” were absent in the formula, then ψ' would be unnormalized (even if ψ is). Indeed,

$$\begin{aligned}\langle\psi'|\psi'\rangle &= \sum_n \sum_m \langle\psi|\psi_m\rangle\langle\psi_n|\psi\rangle \exp\left(-i\frac{t}{\hbar}E_n\right) \exp\left(+i\frac{t}{\hbar}E_m\right) \langle\psi_m|\psi_n\rangle \\ &= \sum_n \sum_m \langle\psi|\psi_m\rangle\langle\psi_n|\psi\rangle \exp\left(-i\frac{t}{\hbar}(E_n - E_m)\right) \delta_{mn} = \langle\psi|\psi\rangle = 1.\end{aligned}$$

Therefore, the evolution preserves the normalization of the wave function.

2.3.3 THE MEAN VALUE OF THE HAMILTONIAN IS PRESERVED

The mean value of the Hamiltonian is a time-independent quantity. Indeed,

$$\begin{aligned}\langle\psi'|\hat{H}\psi'\rangle &= \left\langle \exp\left(-i\frac{t}{\hbar}\hat{H}\right)\psi \left| \hat{H} \exp\left(-i\frac{t}{\hbar}\hat{H}\right)\psi \right. \right\rangle \\ &= \left\langle \psi \left| \exp\left(i\frac{t}{\hbar}\hat{H}\right)\hat{H} \exp\left(-i\frac{t}{\hbar}\hat{H}\right)\psi \right. \right\rangle \\ &= \left\langle \psi \left| \hat{H} \exp\left(i\frac{t}{\hbar}\hat{H}\right) \exp\left(-i\frac{t}{\hbar}\hat{H}\right)\psi \right. \right\rangle = \langle\psi|\hat{H}\psi\rangle,\end{aligned}$$

because $\exp(-i\frac{t}{\hbar}\hat{H})^\dagger = \exp(i\frac{t}{\hbar}\hat{H})$ (Appendix B, p. 895) and, of course, $\exp(i\frac{t}{\hbar}\hat{H})$ commutes with \hat{H} . The evolution of a non-degenerate stationary state has a trivial time dependence through the factor $\exp(-i\frac{t}{\hbar}E_n)$. If a stationary state is degenerate then it may evolve in a non-trivial way, but at a given time the wave function is always a linear combination of the wave functions corresponding to this energy

²⁸We used here the property of an analytical function f , that for any eigenfunction ψ_n of the operator \hat{H} one has $f(\hat{H})\psi_n = f(E_n)\psi_n$. This follows from the Taylor expansion of $f(\hat{H})$ acting on eigenfunction ψ_n .

level only. However, starting from a non-stationary state (even if the mean energy is equal to the energy of a stationary state), one never reaches a pure stationary state during evolution.

Until a coupling of the system with an electromagnetic field is established, the excited states have an infinite lifetime. However, in reality the excited states have a *finite* lifetime, emit photons, and as a result the energy of the system is lowered (although *together with the photons* the energy remains constant). Quantitative description of spontaneous photon emission has been given by Einstein.

2.3.4 LINEARITY

The most mysterious feature of the Schrödinger equation (2.13) is its linear character. The world is non-linear, because effect is never strictly proportional to cause. However, if $\psi_1(x, t)$ and $\psi_2(x, t)$ satisfy the time dependent Schrödinger equation, then their arbitrary linear combination also represents a solution.²⁹

2.4 EVOLUTION AFTER SWITCHING A PERTURBATION

Let us suppose that we have a system with the Hamiltonian $\hat{H}^{(0)}$ and its stationary states $\psi_k^{(0)}$:

$$\hat{H}^{(0)}\psi_k^{(0)} = E_k^{(0)}\psi_k^{(0)}, \quad (2.15)$$

that form the orthonormal complete set³⁰

$$\psi_k^{(0)}(x, t) = \phi_k^{(0)}(x) \exp\left(-i\frac{E_k^{(0)}}{\hbar}t\right), \quad (2.16)$$

where x represents the coordinates, and t denotes time.

Let us assume, that at time $t = 0$ the system is in the stationary state $\psi_m^{(0)}$. At $t = 0$ a drama begins: one switches on the perturbation $V(x, t)$ that in general depends on all the coordinates (x) and time (t), and after time τ the perturbation is switched off. Now we ask question about the probability of finding the system in the stationary state $\psi_k^{(0)}$.

²⁹Indeed, $\hat{H}(c_1\psi_1 + c_2\psi_2) = c_1\hat{H}\psi_1 + c_2\hat{H}\psi_2 = c_1i\hbar\frac{\partial\psi_1}{\partial t} + c_2i\hbar\frac{\partial\psi_2}{\partial t} = i\hbar\frac{\partial(c_1\psi_1 + c_2\psi_2)}{\partial t}$.

³⁰This *can* always be assured (by suitable orthogonalization and normalization) and follows from the Hermitian character of the operator $\hat{H}^{(0)}$.

After the perturbation is switched on, the wave function $\psi_m^{(0)}$ is no longer stationary and begins to evolve in time according to the time-dependent Schrödinger equation $(\hat{H}^{(0)} + \hat{V})\psi = i\hbar \frac{\partial \psi}{\partial t}$. This is a differential equation with partial derivatives with the boundary condition $\psi(x, t=0) = \phi_m^{(0)}(x)$. The functions $\{\psi_n^{(0)}\}$ form a complete set and therefore the wave function $\psi(x, t)$ that fulfils the Schrödinger equation at any time can be represented as a linear combination with time-dependent coefficients c :

$$\psi(x, t) = \sum_{n=0}^{\infty} c_n(t) \psi_n^{(0)}. \quad (2.17)$$

Inserting this to the left-hand side of the time-dependent Schrödinger equation one obtains:

$$(\hat{H}^{(0)} + \hat{V})\psi = \sum_n c_n (\hat{H}^{(0)} + \hat{V})\psi_n^{(0)} = \sum_n c_n (E_n^{(0)} + V)\psi_n^{(0)},$$

whereas its right-hand side gives:

$$i\hbar \frac{\partial \psi}{\partial t} = i\hbar \sum_n \left[\psi_n^{(0)} \frac{\partial c_n}{\partial t} + c_n \frac{\partial \psi_n^{(0)}}{\partial t} \right] = \sum_n \left[i\hbar \psi_n^{(0)} \frac{\partial c_n}{\partial t} + c_n E_n^{(0)} \psi_n^{(0)} \right].$$

Both sides give:

$$\sum_n c_n \hat{V} \psi_n^{(0)} = \sum_n \left(i\hbar \frac{\partial c_n}{\partial t} \right) \psi_n^{(0)}.$$

Multiplying the left-hand side by $\psi_k^{(0)*}$ and integrating result in:

$$\sum_n c_n V_{kn} = i\hbar \frac{\partial c_k}{\partial t}, \quad (2.18)$$

for $k = 0, 1, 2, \dots$, where

$$V_{kn} = \langle \psi_k^{(0)} | \hat{V} | \psi_n^{(0)} \rangle. \quad (2.19)$$

The formulae obtained are equivalent to the Schrödinger equation. These are differential equations, which we would generally like, provided the summation is not infinite, but in fact it is.³¹ In practice, however, one has to keep the summation finite.³² If the assumed number of terms in the summation is not too large, then problem is soluble using modern computer techniques.

³¹Only then the equivalence to the Schrödinger equation is ensured.

³²This is typical for expansions into the complete set of functions (the so called *algebraic approximation*).

2.4.1 THE TWO-STATE MODEL

Let us take the *two-state model* (cf. Appendix D, p. 948) with two orthonormal eigenfunctions $|\psi_1^{(0)}\rangle = |1\rangle$ and $|\psi_2^{(0)}\rangle = |2\rangle$ of the Hamiltonian $\hat{H}^{(0)}$

$$\hat{H}^{(0)} = E_1^{(0)}|1\rangle\langle 1| + E_2^{(0)}|2\rangle\langle 2|$$

with the perturbation ($v_{12} = v_{21}^* = v$):

$$V = v_{12}|1\rangle\langle 2| + v_{21}|2\rangle\langle 1|.$$

This model has an exact solution (even for a large perturbation V). One may introduce various time-dependences of V , including various regimes for switching on the perturbation.

The differential equations (2.18) for the coefficients $c_1(t)$ and $c_2(t)$ are (in a.u., $\omega_{21} = E_2^{(0)} - E_1^{(0)}$)

$$\begin{aligned} c_1 v \exp(i\omega_{21}t) &= i \frac{\partial c_2}{\partial t}, \\ c_2 v \exp(-i\omega_{21}t) &= i \frac{\partial c_1}{\partial t}. \end{aligned}$$

Let us assume as the initial wave function $|2\rangle$, i.e. $c_1(0) = 0$, $c_2(0) = 1$. In such a case one obtains

$$\begin{aligned} c_1(t) &= -\frac{i}{a} \exp\left(-i\frac{\omega_{21}}{2}t\right) \sin(avt), \\ c_2(t) &= \frac{1}{a} \exp(i\omega_{21}t) \cos\left[-avt + \text{arcSec}\left(\frac{1}{a}\right)\right], \end{aligned}$$

where $a = \sqrt{1 + (\frac{\omega_{21}}{2v})^2}$, and Sec denotes $\frac{1}{\cos}$.

Two states – degeneracy

One of the most important cases corresponds to the degeneracy $\omega_{21} = E_2^{(0)} - E_1^{(0)} = 0$. One obtains $a = 1$ and

$$\begin{aligned} c_1(t) &= -i \sin(vt), \\ c_2(t) &= \cos(vt). \end{aligned}$$

A very interesting result. The functions $|1\rangle$ and $|2\rangle$ may be identified with the ψ_D and ψ_L functions for the D and L enantiomers (cf. p. 68) or, with the wave functions 1s, centred on the two nuclei in the H_2^+ molecule. As one can see from the last two equations, the two wave functions oscillate, transforming one to the

oscillations

other with an oscillation period $T = \frac{2\pi}{\nu}$. If ν were very small (as in the case of D- and L-glucose), then the oscillation period would be very large. This happens to D- and L-enantiomers of glucose, where changing the nuclear configuration from one to the other enantiomer means breaking a chemical bond (a high and wide energy barrier to overcome). This is why the drugstore keeper can safely stock a single enantiomer for a very long time.³³ This however may not be true for other enantiomers. For example, imagine a pair of enantiomers that represent some intermolecular complexes and a small change of the nuclear framework may cause one of them to transform into the other. In such a case, the oscillation period may be much, much smaller than the lifetime of the Universe, e.g., it may be comparable to the time of an experiment. In such a case one could observe the oscillation between the two enantiomers. This is what happens in reality. One observes a spontaneous racemization, which is of dynamical character, i.e. a single molecule oscillates between D and L forms.

2.4.2 FIRST-ORDER PERTURBATION THEORY

If one is to apply first-order perturbation theory, two things have to be assured: the perturbation V has to be small and the time of interest has to be small (switching the perturbation in corresponds to $t = 0$). This is what we are going to assume from now on. At $t = 0$ one starts from the m -th state and therefore $c_m = 1$, while other coefficients $c_n = 0$. Let us assume that to first approximation this will be true even *after* switching the perturbation on, and we will be interested in the tendencies in the time-evolution of c_n for $n \neq m$. These assumptions (based on first-order perturbation theory) lead to a considerable simplification³⁴ of eqs. (2.18):

$$V_{km} = i\hbar \frac{\partial c_k}{\partial t} \quad \text{for } k = 1, 2, \dots, N.$$

In this, and the further equations of this chapter, the coefficients c_k will depend implicitly on the initial state m .

The quantity V_{km} depends on time for two or even three reasons: firstly and secondly, the stationary states $\psi_m^{(0)}$ and $\psi_k^{(0)}$ of eq. (2.16) are time-dependent, and thirdly, in addition the perturbation V may also depend on time. Let us highlight the time-dependence of the wave functions by introducing the frequency

$$\omega_{km} = \frac{E_k^{(0)} - E_m^{(0)}}{\hbar}$$

and the definition

$$v_{km} \equiv \langle \phi_k^{(0)} | \hat{V} | \phi_m^{(0)} \rangle.$$

³³Let us hope no longer than the sell-by date.

³⁴For the sake of simplicity we will not introduce a new notation for the coefficients c_n corresponding to a first-order procedure. If the above simplified equation were introduced to the left-hand side of eq. (2.18), then its solution would give c accurate up to the second order, etc.

One obtains

$$-\frac{i}{\hbar} v_{km} e^{i\omega_{km}t} = \frac{\partial c_k}{\partial t}.$$

Subsequent integration with the boundary condition $c_k(\tau = 0) = 0$ for $k \neq m$ gives:

$$c_k(\tau) = -\frac{i}{\hbar} \int_0^\tau dt v_{km}(t) e^{i\omega_{km}t}. \quad (2.20)$$

The square of $c_k(\tau)$ represents (to the accuracy of first-order perturbation theory), the probability that at time τ the system will be found in state $\psi_k^{(0)}$. Let us calculate this probability for a few important cases of the perturbation \hat{V} .

2.4.3 TIME-INDEPENDENT PERTURBATION AND THE FERMI GOLDEN RULE

From formula (2.20) we have

$$c_k(\tau) = -\frac{i}{\hbar} v_{km} \int_0^\tau dt e^{i\omega_{km}t} = -\frac{i}{\hbar} v_{km} \frac{e^{i\omega_{km}\tau} - 1}{i\omega_{km}} = -v_{km} \frac{e^{i\omega_{km}\tau} - 1}{\hbar\omega_{km}}. \quad (2.21)$$

Now let us calculate the probability density $P_m^k = |c_k|^2$, that at time τ the system will be in state k (the initial state is m):

$$\begin{aligned} P_m^k(\tau) &= |v_{km}|^2 \frac{(-1 + \cos \omega_{km}\tau)^2 + \sin^2 \omega_{km}\tau}{(\hbar\omega_{km})^2} = |v_{km}|^2 \frac{(2 - 2\cos \omega_{km}\tau)}{(\hbar\omega_{km})^2} \\ &= |v_{km}|^2 \frac{(4 \sin^2 \frac{\omega_{km}\tau}{2})}{(\hbar\omega_{km})^2} = |v_{km}|^2 \frac{1}{\hbar^2} \frac{(\sin^2 \frac{\omega_{km}\tau}{2})}{(\frac{\omega_{km}}{2})^2}. \end{aligned}$$

In order to undergo the transition from state m to state k one has to have a large v_{km} , i.e. a large coupling of the two states through perturbation \hat{V} . Note that probability P_m^k strongly depends on the time τ chosen; the probability oscillates as the square of the sine when τ increases, for some τ it is large, for others it is just zero. From Example 4 in Appendix E, p. 951, one can see that for large values of τ one may write the following approximation³⁵ to P_m^k :

$$P_m^k(\tau) \cong |v_{km}|^2 \pi \frac{\tau}{\hbar^2} \delta\left(\frac{\omega_{km}}{2}\right) = \frac{2\pi\tau}{\hbar^2} |v_{km}|^2 \delta(\omega_{km}) = \frac{2\pi\tau}{\hbar} |v_{km}|^2 \delta(E_k^{(0)} - E_m^{(0)}),$$

where we have used twice the Dirac delta function property that $\delta(ax) = \frac{\delta(x)}{|a|}$.

³⁵Large when compared to $2\pi/\omega_{km}$, but not too large in order to keep the first-order perturbation theory valid.

As one can see, P_m^k is proportional to time τ , which makes sense only because τ has to be relatively small (first-order perturbation theory has to be valid). Note that the Dirac delta function forces the energies of both states (the initial and the final) to be equal, because of the time-independence of V .

A time-independent perturbation is unable to change the state of the system when it corresponds to a change of its energy.

A very similar formula is systematically derived in several important cases. Probably this is why the probability per unit time is called, poetically, the Fermi golden rule:³⁶

FERMI GOLDEN RULE

$$w_m^k \equiv \frac{P_m^k(\tau)}{\tau} = |v_{km}|^2 \frac{2\pi}{\hbar} \delta(E_k^{(0)} - E_m^{(0)}). \quad (2.22)$$

2.4.4 THE MOST IMPORTANT CASE: PERIODIC PERTURBATION

Let us assume a time-dependent periodic perturbation

$$\hat{V}(x, t) = \hat{v}(x) e^{\pm i\omega t}.$$

Such a perturbation corresponds, e.g., to an oscillating electric field³⁷ of angular frequency ω .

Let us take a look at successive equations, which we obtained at the time-independent \hat{V} . The only change will be, that V_{km} will have the form

$$V_{km} \equiv \langle \psi_k^{(0)} | \hat{V} | \psi_m^{(0)} \rangle = v_{km} e^{i(\omega_{km} \pm \omega)t}$$

instead of

$$V_{km} \equiv \langle \psi_k^{(0)} | \hat{V} | \psi_m^{(0)} \rangle = v_{km} e^{i\omega_{km}t}.$$

The whole derivation will be therefore identical, except that the constant ω_{km} will be replaced by $\omega_{km} \pm \omega$. Hence, we have a new form of the Fermi golden rule for the probability per unit time of transition from the m -th to the k -th state:

³⁶E. Fermi, *Nuclear Physics*, University of Chicago Press, Chicago, 1950, p. 142.

³⁷In the homogeneous field approximation, the field interacts with the dipole moment of the molecule (cf. Chapter 12) $V(x, t) = V(x) e^{\pm i\omega t} = -\hat{\boldsymbol{\mu}} \cdot \boldsymbol{\mathcal{E}} e^{\pm i\omega t}$, where $\boldsymbol{\mathcal{E}}$ denotes the electric field intensity of the light wave and $\hat{\boldsymbol{\mu}}$ is the dipole moment operator.

FERMI GOLDEN RULE

$$w_m^k \equiv \frac{P_m^k(\tau)}{\tau} = |v_{km}|^2 \frac{2\pi}{\hbar} \delta(E_k^{(0)} - E_m^{(0)} \pm \hbar\omega). \quad (2.23)$$

Note, that V with $\exp(+i\omega t)$ gives the equality $E_k^{(0)} + \hbar\omega = E_m^{(0)}$, which means that $E_k^{(0)} \leq E_m^{(0)}$ and therefore one has emission from the m -th to the k -th states. On the other hand, V with $\exp(-i\omega t)$ forces the equation $E_k^{(0)} - \hbar\omega = E_m^{(0)}$, which corresponds to absorption from the m -th to the k -th state.

Therefore, a periodic perturbation is able to make a transition between states of different energy.

Summary

The Hamiltonian of any isolated system is invariant with respect to the following transformations (operations):

- any translation in time (homogeneity of time)
- any translation of the coordinate system (space homogeneity)
- any rotation of the coordinate system (space isotropy)
- inversion ($\mathbf{r} \rightarrow -\mathbf{r}$)
- reversing all charges (charge conjugation)
- exchanging labels of identical particles.

This means that the wave function corresponding to a stationary state (the eigenfunction of the Hamiltonian) also has to be an eigenfunction of the:

- total momentum operator (due to the translational symmetry)
- total angular momentum operator and one of its components (due to the rotational symmetry)
- inversion operator
- any permutation (of identical particles) operator (due to the non-distinguishability of identical particles)
- \hat{S}^2 and \hat{S}_z operators (for the non-relativistic Hamiltonian (2.1) due to the absence of spin variables in it).

Such a wave function corresponds to the energy belonging to the energy continuum.³⁸ Only after separation of the centre-of-mass motion does one obtain the spectroscopic states (belonging to a discrete spectrum) $\Psi_{N,J,M,\Pi}(\mathbf{r}, \mathbf{R})$, where $N = 0, 1, 2, \dots$ denotes the number of the electronic state, $J = 0, 1, 2, \dots$ quantizes the total angular momentum,

³⁸Because the molecule as a whole (i.e. its centre of mass) may have an arbitrary kinetic energy. Sometimes it is rewarding to introduce the notion of the *quasicontinuum* of states, which arises if the system is enclosed in a large box instead of considering it in infinite space. This simplifies the underlying mathematics.

M , $-J \leq M \leq J$, quantizes its component along the z axis, and $\Pi = \pm 1$ represents the parity with respect to the inversion. As to the invariance with respect to permutations of identical particles: an acceptable wave function has to be antisymmetric with respect to the exchange of identical fermions, whereas it has to be symmetric when exchanging bosons.

The time-independent Schrödinger equation $\hat{H}\psi = E\psi$ has been “derived” from the wave equation and the de Broglie equation. Solving this equation results in the stationary states and their energies. This is the basic equation of quantum chemistry. The prevailing weight of research in this domain is concentrated on solving this equation for various systems.

The time-dependent Schrödinger equation $\hat{H}\psi = i\hbar \frac{\partial \psi}{\partial t}$ represents the time evolution of an arbitrary initial wave function. The assumption that translation in time is a unitary operator leads to preserving the normalization of the wave function and of the mean value of the Hamiltonian. If the Hamiltonian is time-independent, then one obtains the formal solution to the Schrödinger equation by applying the operator $\exp(-\frac{it}{\hbar}\hat{H})$ to the initial wave function. The time evolution of the stationary state $\psi_m^{(0)}$ is most interesting in the case of suddenly switching the perturbation \hat{V} . The state is no longer stationary and the wave function begins to change as time passes. Two cases have been considered:

- time-independent perturbation
- periodic perturbation.

Only in the case of a time-dependent perturbation may the system change the energy state.

Main concepts, new terms

symmetry of the Hamiltonian (p. 57)
 invariance of theory (p. 58)
 translational symmetry (p. 61)
 spectroscopic state (p. 62)
 rotational symmetry (p. 63)
 baryon number (p. 64)
 lepton number (p. 64)
 gauge symmetry (p. 64)
 inversion (p. 65)
 symmetry P (p. 65)
 enantiomers (p. 67)
 symmetry C (p. 68)
 charge conjugation (p. 68)
 stationary state (p. 70)

Schrödinger equation (p. 70)
 bound state (p. 73)
 wave function “matching” (p. 73)
 mathematical solution (p. 76)
 physical solutions (p. 76)
 wave function evolution (p. 76)
 time-evolution operator (p. 77)
 algebraic approximation (p. 80)
 two-state model (p. 81)
 first-order perturbation theory (p. 82)
 time-independent perturbation (p. 83)
 Fermi golden rule (p. 84)
 periodic perturbation (p. 84)

From the research front

The overwhelming majority of research in the domain of quantum chemistry is based on the solution of the time-independent Schrödinger equation. Without computers it was possible to solve (in an approximate way) the equation for H_2^+ by conducting a hall full of secretaries with primitive calculators for many hours (what a determination!). Thanks to computers, such problems became easy as early as the 1960s. Despite enormous progress in computer science,³⁹ by the end of the 1980s the molecules studied were rather small when compared

³⁹A boss of the computer industry reportedly declared that if progress similar to that in his branch would occur in the car industry, a Mercedes would cost 1\$ and would take one gallon of gas to go

to the expectations of experimentalists. They could be treated only as models, because they were usually devoid of the substituents theoreticians considered irrelevant in the behaviour of the molecule. The last years of the twentieth century were marked by the unprecedented delivery by theoreticians of powerful high-tech efficient tools of quantum chemistry available to everybody: chemists, physicists, etc. Also to those who knew little of the underlying theory. The software computes millions of integrals, uses sophisticated mathematics, literally the whole arsenal of quantum chemistry, but users need not know about it. It is sufficient to make ... a mouse click on a quantum chemistry method icon.⁴⁰ Despite such progress, the time-dependent Schrödinger equation is rarely solved. For the time being, researchers are interested mainly in stationary states. The quality of results depends on the size of the molecules investigated. Very accurate computations (accuracy ~ 0.01 kcal/mol) are feasible for the smallest molecules containing a few electrons, less accurate ones use first principles (*ab initio methods*) and are feasible for hundreds of atoms (accuracy to a few kcal/mol). Semiempirical quantum calculations⁴¹ of even poorer accuracy are applicable to thousands of atoms.

oscillations

Ad futurum...

The numerical results routinely obtained so far indicate that, for the vast majority of chemical problems (yet not all, cf. Chapter 3) there is no need to search for a better tool than the Schrödinger equation. Future progress will be based on more and more accurate solutions for larger and larger molecules. The appetite is unlimited here, but the numerical difficulties increase much faster than the size of the system. However, progress in computer science has systematically opened new possibilities, always more exciting than previous ones. Some simplified alternatives to the Schrödinger equation (e.g., such as described in Chapter 11) will also become more important.

Undoubtedly, methods based on the time-dependent Schrödinger equation will also be developed. A typical possible target might be to plan a sequence of laser pulses,⁴² such that the system undergoes a change of state from ψ_1 to ψ_2 ("*state-to-state reaction*"). The way we carry out chemical reactions, usually by rather primitive heating, may change to a precise transformation of the system from state to state.

state-to-state

It seems that the essence of science comes down to the fundamental question "*why?*" and a clear answer to this question follows from a deep understanding of Nature's machinery. We *cannot* tell a student: "well, this is what the computer says", because it implies that the computer understands, but what about you and me? Hence, interpretation of the results will be of crucial importance (a sort of Bader analysis, cf. Chapter 11). Progress here seems to be rather modest for the time being.

around the Earth. Somebody from the car sector answered that if cars were produced like computers, they would break down twice a day.

⁴⁰I hope all students understand that a quantum chemist has to be equipped with something more than a strong forefinger for clicking.

⁴¹In such calculations many integrals are approximated by simple formulae (sometimes involving experimental data), the main goal of which is efficiency.

⁴²I.e. a sinusoidal impulse for each of the sequences: switching on time, duration, intensity, phase. For contemporary laser technique it is an easy task. Now chemists should consider transforming reagents to products. The beginnings of such an approach are already present in the literature (e.g., J. Manz, G.K. Paramonov, M. Polášek, C. Schütte, *Isr. J. Chem.* 34 (1994) 115).

Additional literature

R. Feynman, *The Character of Physical Law*, Cox and Wyman, Ltd, London, (1965).

The best recommendation is that the Feynman's books need no recommendation.

J. Ciosłowski, in "Pauling's Legacy: Modern Modelling of the Chemical Bond", Elsevier, *Theor. Comput. Chem.*, 6 (1999) 1, eds. Z.B. Maksić, W.J. Orville-Thomas.

A concise presentation of the symmetry requirements.

Questions

- If the Hamiltonian \hat{H} is invariant with respect to a unitary operation \hat{U} , then:
 - a) the stationary states are the eigenfunctions of \hat{U} and \hat{H} ; b) $\hat{U}\hat{H} + \hat{H}\hat{U} = 0$; c) $\hat{U}\hat{H}\hat{U} = \hat{H}$; d) $\hat{U} = 1$.
- The symmetry broken in the wave function for an optical isomer is:
 - a) rotation; b) inversion; c) charge conjugation; d) permutational symmetry.
- The spectroscopic states represent:
 - a) such states of a molecule, that the optical transitions between them are especially intensive; b) the ground and the first excited states; c) the states that arise after switching on the electric field; d) the wave functions of the Hamiltonian that are calculated in the centre-of-mass coordinate system.
- Degeneracy of the energy levels comes from:
 - a) symmetry of the problem; b) requirement that the wave functions are of class Q; c) energy conservation rule; d) angular momentum conservation rule.
- The time evolution operator in the Schrödinger equation (time-independent Hamiltonian \hat{H}) is equal to:
 - a) $\exp(-\frac{i\hat{H}}{t})$; b) $\exp(-\frac{i\hat{H}}{t})$; c) $\exp(-\frac{t}{\hbar}\hat{H})$; d) $\exp(-\frac{i\hat{H}}{\hbar}t)$.
- If one prepares the system in state ψ_D (one of the two non-stationary states ψ_D and ψ_L of equal energy), the system will:
 - a) go to state ψ_L and remain in it; b) remain in ψ_D ; c) oscillate between ψ_D and ψ_L ; d) evolve to state $\psi_D \pm \psi_L$.
- During time evolution of the wave function $\psi(t)$ of the system (the initial function is normalized, \bar{E} stands for the mean value of the time-independent Hamiltonian)
 - a) $|\psi(t)| = 1$, $\bar{E} = \text{const}$; b) $\int |\psi(t)|^2 = 1$, and \bar{E} decreases; c) $\int |\psi(t)|^2 d\tau = 1$, and $\bar{E} = \text{const}$; d) \bar{E} lowers, while the wave function stays normalized.
- The Dirac delta $\delta(x)$ has the following properties:
 - a) $\int_1^\infty f(x)\delta(x) dx = f(0)$ and $\delta(ax) = \delta(x)/|a|$; b) $\int_{-\infty}^\infty f(x)\delta(x) dx = f(0)$ and $\delta(ax) = \frac{\delta(x)}{|a|}$; c) $\int_{-\infty}^{-1} f(x)\delta(x) dx = f(0)$ and $\delta(ax) = \delta(x)|a|$; d) $\int_{-\infty}^\infty f(x)\delta(x) dx = f(0)$ and $\delta(ax) = \delta(x)/a$.
- The state of the system corresponds to the energy $E_m^{(0)} < E_k^{(0)}$. During a short time period τ one applies a homogeneous time-independent electric field of intensity \mathcal{E} . The probability that after time τ the system will have energy $E_k^{(0)}$ is equal to:
 - a) $1/2$; b) 0 ; c) 1 ; d) $\frac{1}{\mathcal{E}^2}$.

10. The state of the system corresponds to energy $E_m^{(0)} < E_k^{(0)}$. During a short time period τ one applies a periodic perturbation of amplitude $V(x)$, corresponding to the matrix elements denoted by v_{km} . The probability that after time τ the system will have energy $E_k^{(0)}$ is proportional to:

a) $|v_{km}|$ and τ ; b) $|v_{km}|^{-2}$ and $\tau^{\frac{1}{2}}$; c) $|v_{km}|^2$ and τ^{-1} ; d) $|v_{km}|^2$ and τ .

Answers

1a, 2b, 3d, 4a, 5d, 6c, 7c, 8b, 9b, 10d