The Fundamentals of Physical Chemistry

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By

Yuliy D. Gamburg

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PREFACE

This textbook of physical chemistry is based on lectures that the author delivered in D. I. Mendeleev University. The relatively small number of hours allocated to the lecture course made it necessary to present the material in a rather concise manner, but at the same time the author sought to stay up to the requirements of both the rigor of the presentation and a fairly representative amount of information. To what extent it was possible, readers can judge.

A student receives some information in the field of physical chemistry at the first stage, when studying general and inorganic chemistry, as well as analytical chemistry. I set the task to write a next-level course that would allow him (her) to study further more thoroughly and without much difficulty such special areas of physical chemistry as thermodynamics, phase equilibria, electrochemistry, surface phenomena, kinetics of chemical reactions, and others.

The author set out to convey to the reader the most important ideas of modern physical chemistry, believing that all the necessary details of each specific section are now easy to find on the Internet. At the same time, the scope of the provided information and the totality of the formulaic material are sufficient to solve the main set of tasks related to the study of this course.

The problems of the structure of matter are presented in a completely concise form (Chapter 1). This is quite enough to understand further material, while a separate book is required for deep acquaintance with these issues. There are many such textbooks, and it is difficult for me to recommend any specific one. It is assumed that most of the content of this chapter is already known to the reader from other courses.

The problems of electrochemistry (chapter 8) are covered briefly here as I have recently authored a specialized textbook *The Fundamentals of Electrochemistry*, which I recommend for a more in-depth study.

A significant part of spectroscopy, quantum and statistical physics, thermodynamics of irreversible processes and colloid chemistry, which are often included in the general physicochemical course, remained outside the textbook. These issues, as I suppose, should be presented as separate disciplines, and moreover after the course of physical chemistry per se.

Dr. Maria R. Ehrenburg was a great help to me when working on the book. She read the entire text carefully and made a number of important remarks. It was a pleasure to work with her.

I hope this book has met the goals I set for it, and that students find it friendly and effective in studying physical chemistry.

Yuliy D. Gamburg

LIST OF SYMBOLS

A	atomic weight
a	thermodynamic activity
a	attraction constant in Frumkin equation
B	adsorption constant
BV	Butler – Volmer equation
C, c	concentration
C_{V}, C_{p}	heat capacities
D	diffusion coefficient
d	density
E	energy
E	potential`
E^{0}	standard potential
E_{eq}	equilibrium potential
e	electron
e	electronic charge
f	fugacity
F	Faraday constant
F	Helmholtz energy
G	Gibbs energy
$\boldsymbol{g}$	number of atoms in the cluster
h	height, thickness
h	Planck's constant
H	enthalpy
I	electric current
$\boldsymbol{I}$	ionic strength
i	current density
i_0	exchange current density
i_{d}	diffusion current density
i_{lim}	limiting current density
$\boldsymbol{J}$	flux
K, k	different constants
$\mathrm{k_B}$	Bolzmann constant
l	length, distance
M	metal
M	molar mass

M^{z+}	ion of metal
m	mass
m_e	mass of electron
N	number of species
N_A	Avogadro number
n	number (of moles etc.)
p	pressure
q	electric charge
Q	heat
R	molar gas constant
R	Ohmic resistance
R	Rydberg constant
R	radius
r	distance along the radius
r	rate of a chemical reaction
S, s	area
S	entropy
T	absolute temperature
t	transport number
t	temperature in the Celsius scale
t	time
U	potential energy, internal energy
V	volume
v	volume per one species
v	velocity
V_m	molar volume of the metal
W	work
w	velocity of a flux
x	distance
x_i	molar fraction
y	distance
y_i	molar fraction (in vapor)
z	electric charge of the species in electron units
z	compressibility coefficient
Z	number of clusters
Z	statistic sum

α	transfer coefficient
β	polarizability $\partial\eta/\partial i$
γ	interface energy
γ	activity coefficient

Γ	adsorption
Γ_∞	limiting adsorption
δ	thickness of the reaction layer
δ_N	Nernst diffusion layer thickness
δ_{Pr}	Prandtl layer thickness
ε	relative permittivity
ε	roughness amplitude
η	overpotential
η_c	cathodic overpotential
η_a	anodic overpotential
θ	coverage
θ	Debye temperature
κ	conductivity
λ	wavelength
λ	molar ionic conductivity
Λ	molar conductivity
μ_i	chemical potential of a species
$\underline{\mu}$	electrochemical potential
ν	viscosity (kinematic)
ν	frequency
π	osmotic pressure
σ	surface tension (specific surface energy)
τ	duration of the process
Φ	form factor
φ	Galvani potential
Ψ	wave function

CHAPTER ONE

INTRODUCTION TO THE STRUCTURE OF MATTER

This introductory chapter summarizes information about the structure of matter that is necessary for a physicochemist along with knowledge of the basics of mathematics, physics and chemistry. It is assumed that most of the material in this chapter is already known to the reader who is starting to study physical chemistry. The most important concepts introduced in the study of quantum chemistry are **highlighted in bold** in the text.

1.1 Electrons and atoms

The most important statement of modern science is that matter is composed of atoms. Democritus and Lucretius were also convinced of this, but we assert this with greater reason. An atom, in turn, consists of a nucleus and electrons, and owing to the electrical neutrality of the atom, the electric charge of the nucleus is equal to the sum of the charges of electrons (that have an opposite sign). The number of protons Z in the nucleus of an atom is equal to the number of electrons near it, and, in addition to protons, the nucleus also contains neutrons, with the exception of the nucleus of an atom of light hydrogen (protium), which consists of a single proton.

The simplest, although very outdated approach to the problem of electron motion is that Coulomb forces of attraction acting between a positively charged nucleus and negatively charged electrons are balanced by centrifugal forces due to the rotation of electrons around the nucleus. The movement of electrons in any atom occurs in stable orbits, each being characterized by a certain angular momentum. The latter is the product of $\mathrm{m_e v}r$, where $\mathrm{m_e} = 9.109\times10^{-31}$ kg is the mass of the electron, r is its distance from the center of the nucleus, v is the linear velocity of its rotation. At the same time, the integral of the angular momentum of an electron during one period of revolution around the nucleus is different for different orbits, but it is necessarily equal to an integer number n of **Planck's constants** h; this constant ($h \approx 6.626 \times10^{-34}$ J·s) was introduced by Max Planck in 1900 to explain some completely different phenomena, namely the features of thermal radiation. Each orbit is characterized by this number n, as well as by constant energy E, that is, no energy is emitted when moving along the orbit. However, an electron can move from one orbit to another, and during such a transition, the energy difference is absorbed or emitted in the form of a portion ("quantum") of electromagnetic radiation with a frequency v equal to $\Delta E/h$.

The set of frequencies v for all possible transitions in an atom is the spectrum of emission (or absorption) of this type of atoms. Transitions can occur both under the influence of external factors and spontaneously, if energy is emitted at the same time. In other words, the transition to a higher energy level is always forced, the transition to a lower level can be spontaneous.

The entire previous paragraph is a summary of the theory created in 1913 by Niels Bohr. Let's write down these statements ("**Bohr's postulates**") in a formulaic form. First of all,

$$\mathrm{m}_e \mathrm{v}^2/r = Ze^2/(4\pi\varepsilon_0 r^2) \tag{1.1}$$

(this means that the centrifugal force is equal to the Coulombic force). Here e is the charge of the electron ($e \approx 1.6022\times10^{-19}$ C), ε_0 is the electric constant in the SI system ($\varepsilon_0 \approx 8.854\times10^{-12}$ F/m), r is the radius of the orbit, Ze is the charge of the nucleus. From here it is easy to get an expression for the electron velocity v, which turns out to be orders of magnitude less than the velocity of light.

Further, the angular momentum by definition is $\mathrm{mv}r$, and its integral per revolution is $2\pi\times\mathrm{mv}r$. Therefore, the second statement is that the angular momentum of the electron is quantized, i.e.

$$2\pi\times\mathrm{m}_e\mathrm{v}r = nh. \tag{1.2}$$

Hence the following expression is obtained from (1.1) and (1.2) for the radius of the n-th orbit of an electron in a hydrogen atom (i.e. at $Z = 1$)

$$r_\mathrm{n} = n^2h^2\varepsilon_0/(\pi\mathrm{m}_e e^2), \tag{1.3}$$

which, when numerical values of constants are substituted, yields $r_\mathrm{n} \approx 5.29\times10^{-11}n^2$ (in meters). At $n = 1$, this corresponds to the radius of the hydrogen atom in **the ground state** (or, what is the same, the lowest energy equilibrium state).

Using (1.3), it is possible to find the total energy E of an electron in the n-th orbit, which is equal to the difference between its kinetic and potential energies:

$$E = \tfrac{1}{2}\,\mathrm{m}_e \mathrm{v}^2 - e^2/(4\pi\varepsilon_0 r_\mathrm{n}).$$

The kinetic energy of an electron is the energy of its rotation around the nucleus $U = \tfrac{1}{2}\,\mathrm{m}_e\mathrm{v}^2$, and its potential energy $e^2/(4\pi\varepsilon_0 r_\mathrm{n})$ is associated with its presence in the electric field of the nucleus. After substituting the value r_n, we obtain a very important expression

$$E_\mathrm{n} = -\,\mathrm{m}_e e^4/(8\varepsilon_0^2 h^2 n^2). \tag{1.4}$$

This is the energy of a certain stationary quantum state of an electron in a hydrogen atom. The word “quantum” emphasizes the discreteness of such states.

It follows from (1.4) that during the transition from orbit n_1 to orbit n_2, the energy change (quantum of radiation) is

$$\Delta E = [\mathrm{m}_e e^4/(8\varepsilon_0^2 h^2)](1/n_1^2 - 1/n_2^2]. \tag{1.5}$$

Since $\Delta E = h\nu$, the corresponding frequency of electromagnetic radiation $\nu = \Delta E\,/h$ is

$$\nu = [\mathrm{m}_e e^4/(8\varepsilon_0^2 h^3)]\cdot(1/n_1^2 - 1/n_2^2], \tag{1.6}$$

and the inverse wavelength is λ^{-1}, that is, ν/c, where c is the speed of light,

$$\lambda^{-1} = [\mathrm{m}_e e^4/(8\varepsilon_0^2 h^3\, c)](1/n_1^2 - 1/n_2^2], \tag{1.7}$$

Equation (1.7) defines the electromagnetic spectrum (a set of frequencies for all possible pairs of n_i and n_j) of a given type of atoms (in the visible, ultraviolet and infrared regions). The expression $\mathrm{m}_e e^4/(8\varepsilon_0^2 h^3)$ is **the Rydberg constant** $R \approx 1.097\times10^7$ m^{-1}, that coincides with the value experimentally found from spectral measurements (already very accurate at the beginning of the 20-th century). This coincidence is a strong argument in favor of Bohr’s theory.

We recommend to perform all these calculations yourself, with the substitution of numerical values and paying attention to the dimensions and orders of the values obtained. So, the formula (1.4), after substituting all the constants, should take the form $E = -\,13.6/n^2$ (in terms of electron volts). In the case of a hydrogen atom (n = 1), this energy is equal in absolute magnitude to the energy required to detach an electron from an atom (**ionization energy**) and, like the Rydberg constant, coincides with the experimentally found value. The corresponding electrical potential, expressed in volts, is called **the ionization potential**.

The presented theory, as we see, explains quantitatively a number of phenomena, in particular, the nature of atomic spectra (emission spectra). At the same time, it cannot explain the reason for the discreteness of stable orbital radii and, accordingly, electron energies, as well as the reason for this stability.

It was established after Bohr's work, that all the above facts are a consequence of a deeper law of nature, which follows from the discreteness of states and is described by **the Schrödinger equation**. Erwin Schrödinger published it in 1926. This second-order differential equation is one of the foundations of **quantum mechanics** and in the simplest one-dimensional and time-independent case for a particle with mass m has the form

$$-\,[h^2/(8\pi^2\mathrm{m})]\ \mathrm{d}^2\mathit{\Psi}/\mathrm{d}x^2 = (E - U)\ \mathit{\Psi}, \tag{1.8}$$

where the square of the function $\mathit{\Psi}^2\mathrm{d}V$ characterizes the probability of finding a particle in a state with a given energy E in a given elementary volume $\mathrm{d}V$. Quantity U represents the potential energy in the external field. If $\mathit{\Psi}$ is a complex number, then the probability is $\mathit{\Psi}\ \mathit{\Psi}^*\mathrm{d}V$, where $\mathit{\Psi}^*$ is a conjugate complex number (such a product is always a real number). To calculate the probability of finding an electron in a certain area of space, it is necessary perform integration over this area. The function $\mathit{\Psi}$ is normalized, that is, its integral over the entire space $\int \mathit{\Psi}\ \mathit{\Psi}^*\mathrm{d}V = 1$.

The solutions of this equation exactly correspond to the behavior of real elementary particles in a variety of experimental and natural conditions. The function $\mathit{\Psi}$ is traditionally called **the wave function**.

In the case of an electron in the electric field of a nucleus with a charge Ze, its potential energy depends on the distance from the nucleus r and is $U = Z\,e^2/(4\pi\varepsilon_0 r^2)$.

The Schrödinger equation leads to the same strictly defined, discrete values of the electron energy as equation (1.4). However, the discreteness in this case is quite understandable: solutions of equations of type 1.8 ("wave equations") in limited areas of space exist only for strictly defined energy values. This is similar to the fact that **the string equation** also gives a certain set of frequencies of sinusoidal vibrations, since an integer number of half wavelengths must fit in the length of the string. It is for this reason that a stretched string emits a pleasant sound to the ear, rather than a continuous frequency spectrum (white noise).

Indeed, by simply substituting the values Ψ and $d^2\Psi/dx^2$ in (1.8), it is easy to verify that the solutions of equation (1.8) are sinusoidal functions of the form

$$\Psi = a \sin (2\pi/\lambda)\, x \tag{1.9}$$

These solutions describe the so-called **De Broglie waves**, and at the same time, an integer number of half-waves should fit in the field of particle motion, and the wavelength is $\lambda = h/(mv) = h/(2mE)^{1/2}$. The De Broglie wave is not a mathematical fiction, such waves do actually exist, as evidenced, for example, by electron diffraction patterns, which closely resemble light diffraction patterns.

Another difference between the quantum theory and Bohr's theory is that the probability $\Psi\Psi^*$ yields not orbits (trajectories) which are lines in space (circles in Bohr's theory, ellipses later in Sommerfeld theory), but **orbitals**, which are regions in space where the corresponding particles with the energy E do exist. At the same time, there are places with both high and low probabilities of finding a particle (in our case, an electron); although, of course, the loci corresponding to the highest probability represent the very lines of Bohr's theory, although with more complex shapes. In addition, the condition must be met according to which the integral probability value over the entire volume is equal to one (normalization condition). The probabilistic interpretation of the function Ψ was given by Max Born in the same year 1926 on the basis of an earlier (1916) work by Albert Einstein and is closely related to **the uncertainty relation** of Werner Heisenberg (Heisenberg's **indeterminacy principle**), which states that

$$\Delta x\, \Delta p_x \approx h \tag{1.10}$$

(Δx is the standard deviation of the particle coordinate, Δp_x is the standard deviation of the x- component of its momentum). This means that the more precisely we define one of the conjugate parameters, the less accurately the second one is determined, and the measure of uncertainty is the Planck's constant. Such a pair of observable quantities can also be energy and time, angle and angular momentum. Their product always has the dimension [J×s]. The ratio of uncertainties is the law of nature that causes the above-mentioned "blurring" of orbits.

Our task does not include any detailed presentation of quantum mechanics, so we refer the reader to any relevant course, and then we present only the most important results for our subject. So, it is necessary to know that the Schrödinger equation cannot be solved precisely for many-electron systems due to the difficulty of accounting for interelectronic repulsion.

The exact solution of the Schrödinger equation can be obtained only in simple cases, such as an electron in a hydrogen atom, an electron in a potential well, or a particle passing through a potential barrier. For example, if an electron moves between two walls located at a distance l from each other, then the wave function vanishes at each wall (since $\Psi = 0$ outside this space). An integer number n of half wavelengths of De Broglie waves should fit between the walls: $2l/\lambda = n$. But the wave function of a stationary state is a standing wave, that is, two waves running towards each other (one traveling wave is non-stationary). The absolute magnitude of the momentum of such a wave is equal to $p = h/\lambda = nh/2l$. This momentum corresponds to the energy $p^2/2\mathrm{m} = n^2h^2/8\mathrm{m}l^2$. These are the quantum energy levels in this case.

Another simple system of this type is a **one-dimensional harmonic oscillator**. It is a particle of mass m that oscillates along a given x-axis under the action of an elastic or quasi-elastic force (that is, a force proportional to the distance from the equilibrium point, like a spring). In this case, $U = kx^2/2$, so the Schrödinger equation takes the form

$$-\,[h^2/(8\pi^2\mathrm{m})]\ \mathrm{d}^2\Psi/\mathrm{d}x^2 = (E - kx^2/2)\ \Psi \qquad (1.11)$$

In this system, the set of energy levels is a series of $E_\mathrm{n} = h\nu_\mathrm{o}(n + \frac{1}{2})$, where $\mathrm{n} = 0, 1, 2, 3$, etc. These levels are located at equal distances from each other, and the minimum energy is $h\nu_\mathrm{o}/2$ (that is, the energy does not vanish under any conditions; this is a quantum effect). For a state with minimal energy, the classical probability of detecting a particle in an equilibrium position is equal to unity.

In many-electron atoms, each electron moves in a field created not only by the nucleus, but also by other electrons. If, for example, by analogy with the hydrogen atom, we calculate the ionization energy of an atom with an arbitrary Z using formula (1.4), we will get an incorrect result, since the interaction of an electron with the nucleus is shielded by the presence of other electrons.

In this regard, ingenious **approximate methods** (Hartree –Fock, Thomas – Fermi, density functional methods) have been developed and are widely used for multi-electron systems. These methods use such well-known mathematical techniques as the variational method, the perturbation method and others. Currently, this is a very important part of quantum mechanics. The most commonly used approach is the self-consistent field method assuming that an electron moves in some average field created by the nucleus and all electrons except the one under consideration. In this case, it is advisable to introduce the effective charge of the nucleus (Z_{eff}), replacing Z with Z_{eff} in equation (1.4).

The number n introduced above is called the main quantum number.

Further development of the theory led to the understanding that since an electron has three degrees of freedom, there should also be **three quantum numbers** determining its energy. For example, for an electron located in a rectangular box with sides L_x, L_y, L_z, it is necessary to enter the quantum numbers n_x, n_y, n_z.

For the movement of an electron in an atom, a secondary or azimuthal quantum number l was introduced in addition to the main quantum number. For each value of n, it can assume values from zero to $(n - 1)$ and is often denoted by small letters, respectively, s at $l = 0$, p at $l = 1$, then d, f, g, h. Hence the designations of electrons such as 1s, 2p and others; for example, 3d electrons are characterized by quantum numbers $n = 3$, $l = 2$.

The azimuthal quantum number is explained as follows.

Let's write down the Schrödinger equation for the hydrogen atom. The energy of the electron in this atom, as we saw above, is $U - e^2/(4\pi\varepsilon_0 r_n)$, therefore

$$-\,[h^2/(8\pi^2 m_e)]\,d^2\Psi/dx^2 = [U - e^2/(4\pi\varepsilon_0 r_n)]\,\Psi, \qquad (1.12)$$

But such a record does not directly reflect the dependence of the amplitude on the rotational motion of the electron along the sphere (**rotator**). It is necessary to separate the radius-dependent part from the angle-dependent one in the Schrödinger equation. To do this, we will change to spherical coordinates and express the wave function as $\Psi(r,\theta,\varphi) = R(r)\cdot\Theta(\theta)\cdot\Phi(\varphi)$, where $R(r)$ is a multiplier depending on the radius, and $\Theta(\theta)\times\Phi(\varphi)$ is a multiplier depending on the angles θ and φ on the sphere (latitude and longitude). Then a term appears in the solution due to the centrifugal force mv^2/r, or p^2/r^3, where $p = mv$. The solution of the equation, which we omit, shows that permissible values for this momentum are discrete:

$$p = [h/(2\pi)]\times([l(l + 1)]^{1/2} \qquad (1.13)$$

where l can assume non-negative values, such as 0, 1, 2, etc. Quantity l is the azimuthal quantum number. This number, therefore, has a rotational nature.

The necessity of introduction of the third (magnetic) quantum number mi is due to the fact that an electron rotating around a nucleus has a magnetic moment, like any charged body rotating around a certain centrum. The magnitude of this moment is equal to the projection of the momentum of rotation on the z axis, namely, $[h/2\pi]\times m$. The number m entered here can take both positive and negative values from zero to $\pm l$, a total of $(2l + 1)$ values, including zero. In the absence of a magnetic field, the electron energy does not depend on m_{i}, but in a magnetic field it can assume all $(2l + 1)$ values, causing the splitting of spectral lines (the Zeeman effect).

The ratio of the magnetic moment m to the momentum p is the cosine of the angle between the moment and the z axis, that is

$$\cos\alpha = m\,([l\,(l + 1)]^{-1/2} \tag{1.14}$$

This equation means that only certain **discrete directions** of the angle α are allowed (and not just certain energies). This fact is called **spatial quantization**.

We emphasize once again that all the above discrete solutions are simply due to the fact that an integer number of half wavelengths of De Broglie waves must be placed in the field of motion of a particle (in this case, an electron). Planck's constant h is often found in equations in combination with $1/(2\pi)$, as can be seen from equation (1.13). Therefore, for convenience, this ratio is denoted as $\hbar = h/2\pi$.

Finally, the study of atomic spectra showed that it is necessary to introduce another extremely important – the fourth – quantum number which does not follow from the solution of the Schrödinger equation. It is associated with the fact that the particles have their **own (intrinsic) angular momentum**, which Goldsmith and Uhlenbeck in 1925 called "**spin**".

The theory of spin was developed by Wolfgang Pauli and Paul Dirac in 1925-1928. At the same time, Dirac created a mathematical formalism that made it possible to significantly deepen the content of quantum physics by describing the magnetic properties of atoms and the fine structure of spectra (the Zeeman effect mentioned above).

The spin value s is measured in units equal to $\hbar$, and can be $s = 0$, ½, 1 and other integer and half-integer positive values for various particles. Spin is positive, but its projection can be either a positive or a negative number. In the theory of atomic structure, the projection of the spin moment onto the quantization axis (the spin quantum number m_{s}), is often used. For an electron, it can take only two values: +1/2 and -1/2.

As Pauli showed in 1940, the statistical behavior of particle systems (particle energy distribution) depends on whether spin is an integer or a half-integer. Particles with an integer spin are called **bosons** (they obey Bose statistics), and those with a half-integer spin are **fermions** (they obey Fermi statistics). The difference between these statistics is that fermions with the same spin tend to be located separately (which is equivalent to the repulsive forces between them), while bosons, on the contrary, tend to hold together, which is equivalent to the forces of attraction. For these reasons, the energy distributions of bosons and fermions differ from the classical Maxwell distribution, in which the number of particles with energy E is proportional to $\exp(-E/k_BT)$.

At the same time, the principle of indistinguishability of identical particles is valid: any permutation of such identical particles causes no change in the system. This principle is based on the requirement of a certain permutation symmetry of the wave function in a system of identical particles. Namely, for particles with integer spin, that is, for bosons, the wave function should be symmetric, i.e. it should not change at all when the coordinates and projections of the spins are rearranged, whereas for fermions, it should change sign in the case of such a permutation, i.e., it should be antisymmetric.

The projection of spin of an electron is always either +½ or –½, for other particles it may be different, but always integer or half-integer. The concept of spin has proven to be very fruitful in the study of various systems, the components of which can be in two, and only two states. A spin projection is often denoted by a vertical arrow pointing either up or down: ↑ or ↓.

Note that the electron's own magnetic momentum due to spin slightly (by 0.1%) exceeds the minimum magnetic moment – the Bohr magneton $e\hbar/(2\mathrm{m}_ec)$ – associated with the movement of an electron around the nucleus. Quantum electrodynamics explains this difference with high precision.

Along with the numerical designation of quantum numbers, in the case of electrons in an atom, letter designations are also used. The layers with n = 1, 2, 3 and 4 correspond to the capital letters K, L, M, N, and the lowercase letters s, p, d, f, g correspond to the sublevels (shells) with l = 0, 1, 2, 3, 4.

So, if certain quantum numbers are given, then there can be only one electron in a given atom in a given state (that is, with a given set of quantum numbers). This is **the Pauli principle**. In another way, it is formulated as follows: there can be not more than two electrons at a given energy sublevel (see below), and, moreover, their spin must be opposite. This is precisely due to the fact that electrons have a half-integer spin, that is, they are fermions, and they do not let their own kind into an occupied orbital. In other words, for electrons, the wave function is antisymmetric with respect to permutations (this is actually the Pauli principle).

It is the Pauli principle that makes it possible to understand the arrangement of elements in the periodic table.

If we consider the distribution of electrons across shells as their number Z increases, then they cannot "cluster", but gradually occupy orbitals in atoms with an increasingly high sum of quantum numbers $n + l$, since lower levels turn out to be fully occupied. Successive electron shells (energy levels) are formed, which are characterized by the number n: first, the level $n = 1$ is filled, then $n = 2$, $n = 3$, etc. The levels vary greatly in terms of energy; they consist of sublevels (shells), such as 2*s*, or 2*p*, the difference in energy between which is much smaller. As the energy levels increase, the average distance of electrons from the nucleus also increases.

For a visual representation of the atomic orbital, a kind of "cloud" is depicted with a density varying from point to point, and as you move from the densest part to the surface of the cloud, the density decreases to almost zero. As a result, some shape of the cloud is revealed, although without a clearly defined surface (in images, the orbital is usually shown from the maximum up to some low density). An electron cloud provides some probability of where the electron is located, not the exact location. Instead, it serves as a map indicating the likely regions where an electron can be found in an atom or molecule. The spatial regions occupied by *s*-electrons have spherical symmetry, *p*-electrons are dumbbell–shaped, and in the case of *d*-, *f*-, etc., more complex configurations arise.

Consider as an example the neon atom Ne^{10}, which has the structure $1s^2 2s^2 2p^6$, that is, it contains a pair of 1*s* electrons (with opposite spins), a pair of 2*s* electrons and three pairs of 2*p* electrons; there are no unpaired electrons in this atom, and the first two shells are completely filled.

An element with one more electron in it already requires a transition to the next shell, that is, this electron falls into the 3*s* sublevel. This is an atom having $Z = 11$, that is, sodium. The last electron (unpaired) determines the valence of a sodium atom equal to one. This electron is relatively weakly bound to the nucleus, and the atom easily gives it away, forming a positively charged sodium ion. In other words, sodium has a low first ionization energy. Indeed, from the tables it can be found that the first ionization energy of sodium is 5.14 e*V*, while for neon this value is 21.56 e*V*: it is much more difficult to remove an electron from filled levels. Therefore, neon is chemically inert.

In conclusion, as another example, we will give the distribution of electrons by levels in the radium atom:

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6 7s^2$. From this series, the nature of the construction of electronic shells is quite clear: the first four levels are completely filled, there are unfilled sublevels on the 5th and 6th, and the fact that the last two atoms are on the seventh level means that radium stands in the second group of the seventh period of the periodic table and has a valence of 2 in compounds.

So, the lowest energy orbitals get filled by the electrons first. After the lower energy orbitals are filled, the electrons move on to higher levels. **The**

Hund’s rules of filling the shells are observed for the ground states. The first one is the most important: the total spin should be the maximum. More strictly, the lowest energy corresponds to maximum number of unpaired electrons with equal spin (either +½ or −½). After that, the value of the quantum number *l* should be the largest one (the second rule). The sequence of filling the sublevels at the first five levels is as follows: 1*s* → 2*s* → 2*p* → 3*s* → 3*p* → 4*s* → 3*d* → 4*p* → 5*s* → 4*d* → 5*p*. This distribution of electrons explains many features of changes in the properties of atoms as the number of electrons in them increases, in particular, the periodicity of properties, which allowed D. I. Mendeleev to create a periodic table of elements.

It is quite remarkable that quantum theory, which only originated at the very beginning of the 20th century, had already acquired an almost complete form by 1940 and was able to explain many experimental facts in various fields of physics and chemistry.

1.2 Molecules and chemical bonding

The number of different substances is orders of magnitude greater than the number of elements, of which there are about 100. This is a consequence of the fact that two or more identical or different atoms combine to form molecules. Indeed, there should already be $\frac{1}{2} \times 10^4$ different hypothetical diatomic molecules, and there should be orders of magnitude more triatomic ones. The formation of molecules is the result of **chemical bonding** between atoms. The chemical bonding and the structure of molecules are the subject of **quantum chemistry**. Our task was not to present the basics of quantum chemistry, as well as quantum mechanics, so we will limit ourselves to considering its most important results.

There are several types of chemical bonds.

Let’s start with a typical example of an **ionic (electrovalent, heteropolar) bond**: an alkali metal ion and a halogen ion. As mentioned above, atoms such as sodium, potassium and similar ones (that is, having one electron on the outer shell) have a low first ionization potential and easily release this electron, forming positive ions. On the other hand, halogen atoms, such as: fluorine, chlorine, bromine, and iodine have an external electron shell in which there is a single vacant place (in the periodic table, such atoms are located directly in front of inert (noble) gases having a completely filled, closed shell). Halogen atoms accept a free electron, forming negative ions.

As a result, both ions form closed stable shells (shells of inert gases) and at the same time are attracted to each other by electrostatic (Coulombic) forces, forming ionic compounds of the NaCl type. Such compounds are salts, they have a binding energy of the order of hundreds of kJ/mol; the word "halogen" means "giving birth to salt". In the gaseous and liquid state, they are molecules, whereas in the solid state they form crystal lattices of ions built in one or another correct order. Thus, sodium chloride has a lattice in which sodium and chlorine ions alternate in each line, while the cesium chloride lattice consists of two identical sublattices of chlorine and cesium shifted by half the diagonal of the cube with respect to each other (Fig. 1-1).

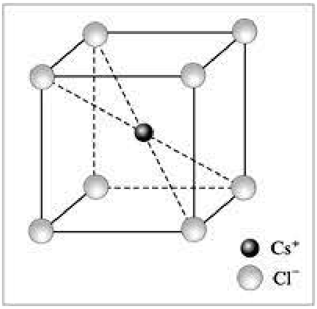
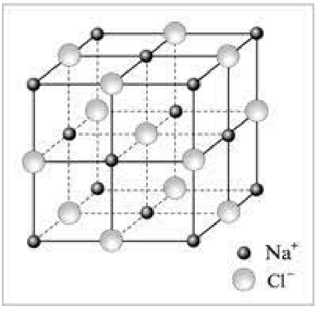


Fig. 1-1 Crystal lattices of CsCl and NaCl.



Solid salts are dielectrics, while liquid (molten) salts have good electrical conductivity due to their decomposition (dissociation) into individual ions. This also applies to salt solutions in dielectric solvents, where molecules dissociate into solvated ions, that is, solvent molecules are attached to ions. Another important property of salts is their ability to absorb infrared radiation.

Along with singly-charged ions of alkali metals and halogens, there are also double-charged positive ions (Mg^{2+}, Ca^{2+}, Zn^{2+}, Cu^{2+}, Sr^{2+} and Ba^{2+} cations), double-charge negative ions (anions) of sulfur and some others. Polyatomic ions also exist such as, e.g., ammonium, sulfate, nitrate, hydroxide and many others. Obviously, if a compound is formed between ions with different charges, then it contains cations and anions in quantities inversely proportional to their charges (which corresponds to the principle of electrical neutrality of molecules). An example is the salt calcium chloride $CaCl_2$, consisting of one double-charged calcium ion and two single-charged chlorine ions.

To be precise, there is no “pure” ionic bond, that is, a complete transition of an electron from one atom to another is almost never observed. This means that, in fact, the ionic bond should be considered as the limiting case of a **covalent polar bond**.

Covalent (homeopolar) bonding is the most common case. Atoms in molecules of simple gases (H_2, Cl_2), such compounds as H_2O, NH_3, CH_4, CO_2, HCl and many others are connected by covalent bonds. It is believed that a covalent bond occurs between atoms that do not differ much from each other in electronegativity.

The appearance of a covalent bond between atoms is due to the fact that all or part of the electrons of two or more atoms become common to them. In other words, the nuclei of these atoms become common centers of attraction for several electrons located on the outer shells. As a result of the overlap of individual electronic orbitals, new orbitals arise that no longer relate to the atom, but to the entire molecule (molecular orbitals, MO). MO are formed as a result of the combination of atomic orbitals (AO). The total number of MO is equal to the total number of AO from which they were formed. Each molecular orbital has a certain energy characterized by a corresponding ionization potential.

Methods for calculating such systems have been developed: a method in which molecular orbitals are considered as linear combinations of atomic orbitals (MO LCAO), in which it is postulated that the wave function can be represented as

$$\Psi_i = C_1\Psi_1 + C_2\Psi_2 + \ldots + C_k\Psi_k, \qquad (1.15)$$

where Ψ_k is the wave function for the k-th orbital, C are numerical coefficients.

There is also a valence bond method and a number of special calculation methods. They are based on the idea that the binding of atoms is achieved during the formation of a molecule as a result of the formation of one or more pairs of electrons with opposite (antiparallel) spins from those electrons that have been present in the atomic orbitals of individual atoms. In this case, the electronic configuration of each of the atoms changes slightly.

The positively charged ions seem to be attracted to this electron pairs. More precisely, the electron pairs turn out to be smeared over the entire space of the molecule, but regions of enhanced electron density appear between the nuclei of atoms in comparison with other regions of space. This draws the nuclei together, which leads to the formation of a chemical bond.

The presence of an electron pair between interacting atoms reduces the total energy of the system. It is believed that this change in energy caused by the overlap of atomic orbitals is due to some additional interaction, denoted as **the exchange interaction**, since it is determined by those terms in general expressions for the energy of the system that are responsible for the permutations of particles. Therefore, this interaction is closely related to the spin of electrons. It is important to note that the exchange interaction manifests itself only with the direct convergence of atoms, that is, it is short-range in contrast to the long-range Coulomb interaction. The energy of the long-range interaction of a system of N particles is proportional to the number of different pairs that can be composed of these particles, i.e. $\frac{1}{2}N(N-1) \approx N^2/2$ (for large N), while the energy of the exchange interaction is proportional to the number of the nearest neighbors, and therefore tends to saturation.

The concept of the exchange interaction, which is convenient for many calculations, reflects the fact that when a molecule is formed, the electrons of an atom enter the near-nuclear space of another atom, that is, the electrons are shared, and their permutation symmetry is taken into account.

Since electrons are fermions, the wave function consisting of the spatial and spin parts must be antisymmetric with respect to their permutation. In this case, either the spatial or the spin part must be antisymmetric. From the point of view of chemical bonds, the symmetric wave function is a so–called bonding orbital, the antisymmetric one is an antibonding one. In other words, when two atoms are combined into a molecule, two atomic orbitals (having identical symmetry and close energies) are transformed into two molecular orbitals: one with lower energy and the other with higher energy. The transition of an electron to the first of them leads to the formation of a bond, the transition to the second yields no bond.

An electron in a bonding (energetically more advantageous than the initial AO) molecular orbital, is located with a higher probability between the nuclei, and contributes to their chemical binding. In an antibonding MO (less advantageous than the initial ones), the electron is located with a higher probability behind the nuclei (not between them), which results in certain mutual repulsion of the nuclei. In other words, the electron density between the nuclei is increased on the bonding orbital, and decreased on the antibonding one.

A molecule is stable only if the number of electrons in the bonding orbitals exceeds the number of electrons in the antibonding ones. In this regard, the concept of orbital population is introduced as the total electron density sharing between the atoms entering the molecule. In addition to these two types of MO, there are also non-bonding orbitals; the electrons in them do not participate in the formation of a chemical bond. This corresponds to the case when the atomic orbital enters a molecule without changing its energy.

The simplest system in which the exchange interaction plays an important role is a two-electron system, as, for example, in a hydrogen molecule or in a helium atom. When a diatomic H_2 molecule is formed, two MO are formed between the H atoms, one of the orbitals being bonding, the other antibonding.

It is necessary to note such a feature as **the hybridization of orbitals** (this concept is introduced in the theory of valence bonds). For instance, the carbon atom has 4 electrons at the outer sublevels, including (in an excited state) one 2*s* electron and three 2*p* electrons. It would seem that they should provide four bonds, one of which is different from the others, in particular, in terms of energy. But in reality, all four bonds are equivalent. This is explained by the fact that their total electron density during the formation of, for example, a CH_4 (methane) molecule is divided into four equivalent parts, differing only in spatial orientation. This is called sp^3-hybridization. By analogy with atomic *s*-, *p*-, *d*-, *f*- orbitals, molecular orbitals are denoted by the corresponding Greek letters σ-, π-, δ-, φ-.

The hybridization of atomic orbitals is not a real physical process, but only a convenient mathematical model that allows us to explain the distribution of electron density in molecules during the formation of a covalent bond. For example, in *sp*-hybridization, when hybrid orbitals are formed from one *s*-electron and one *p*-electron, their wave functions Ψ_1 and Ψ_2 are formed from the initial wave functions of the electrons Ψ_s and Ψ_p as

$$\Psi_1 = (1/\sqrt{2})(\Psi_s + \Psi_p),$$

$$\Psi_2 = (1/\sqrt{2})(\Psi_s - \Psi_p).$$

Obviously, the total probability of finding electrons in orbitals, proportional to the squares of the wave functions, remains the same. In the case of other types of hybridization, the corresponding formulas are slightly more complicated.

The interaction of atoms in molecules, unlike the interaction of ions, is described by more complex potentials than the Coulomb potential. One of them is the **Morse potential**

$$E = E_0\,(1 - e^{-a\rho})^2 \tag{1.16}$$

The type of this function is shown in Fig. 1-2.

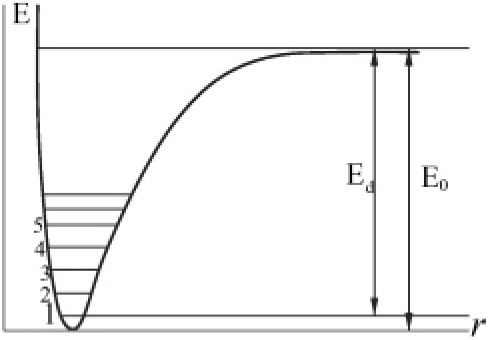


Fig. 1-2 View of the Morse function. Discrete vibrational levels are shown.

Here, E_0 represents the well depth (or the dissociation energy of the molecule), a is a constant (related to the frequency of vibrations), $\rho = r - r_0$, where r is the distance between the atoms, and r_0 is the distance corresponding to the minimum energy of the molecule. The minimum energy corresponds to the most stable state of the molecule. The energy in molecules is quantized, as in atoms (figure 1-2 shows energy levels). Therefore, the dissociation energy E_d is slightly different from the well depth. Therefore, during the transitions of electrons from one level to another, as in atoms, photons are emitted and molecular spectra arise. Study of such spectra allows establishing the structure and properties of molecules.

As a rule, one of the two electrons forming a chemical bond belongs to one atom and the other one comes from the other atom. However, it is not uncommon for both electrons to originally belong to the same atom. In this case the first atom is **a donor of the electron** and the second is **an acceptor**. This is how, for example, one of the bonds in the ammonium ion NH_4^+ is formed. At the same time, all four bonds are equivalent.

In the case when a molecule is formed from two identical atoms, the system turns out to be symmetrical; it is a nonpolar covalent bond. In other cases (due to the difference in the electronegativity of atoms), the bonding orbital is shifted towards an atom with a higher electronegativity (polar covalent bond). Several electronegativity scales have been developed that are close to each other. With a sufficiently large difference in the electronegativity of two elements, the polar covalent bond between them tends to a purely ionic one, which, as already mentioned, is the limiting case of a covalent polar bond. In intermediate cases, the concept of an effective