1 Background Knowledge

1.1 The Subject and its Specificity

The importance of intermolecular forces[1] in Nature is very difficult to overestimate. It is sufficient to say that the existence of liquids and solids is due to intermolecular interactions. In the absence of intermolecular interactions our world would be a uniform ideal gas.

A knowledge of the physics of intermolecular interactions is required to solve a wide class of problems in physics, chemistry and biology. The thermodynamic properties of gases and liquids and their kinetic characteristics (the coefficients of heat conductivity, diffusion etc.) are determined by the nature of intermolecular interactions. Intermolecular forces also determine to a large degree the properties of crystals, such as the equilibrium geometry, the binding energy, phonon spectra, etc.

Intermolecular interactions are involved in the formation of complicated chemical complexes, such as charge-transfer and hydrogen-bond complexes. Study of the mechanism of elementary chemical reactions is impossible without knowledge of the exchange processes between the translational and electron-vibration energies, which depend on the interaction of particles under collisions. Knowledge of the potential surface, characterizing the mutual trajectories of the reactants, is necessary to obtain the rates of chemical reactions.

A knowledge of intermolecular interactions is of great importance also in biology. It is enough to say that intermolecular forces account for the stability of such important compounds as DNA and RNA and also play an essential role in muscle contraction. The coagulation theory of colloidal solutions is based on a balance of the repulsive electrostatic forces and the attractive dispersion forces.

The development of modern technology required a knowledge of the macroscopic properties of gases under conditions that are almost inaccessible for experimental measurement (supersonic velocities, high temperatures >1000 K, hyper-high pressures in shock waves). The theoretical prediction of these properties requires a knowledge of the potential energy curves for a wide range of separations, which have to be found in independently.

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[1] Here and in other chapters the term ‘intermolecular forces’ denotes also interatomic forces, which do not lead to the formation of chemical bond. Except for some special cases, no distinction will be made between intermolecular and interatomic interactions.

Intermolecular Interactions I.G. Kaplan

It should be emphasized that intermolecular forces are not measured directly in any experiment. It is other characteristics, such as the deviation angle under scattering, the transport coefficients, etc., which are connected functionally with the intermolecular forces, that are measured. The main source of experimental information about intermolecular interactions are:

- scattering experiments in atomic–molecular beams, which, in some cases, permit the potentials to be obtained directly from the experimental data;
- spectroscopic measurements (vibrational–rotational spectra, predissociation, broadening of lines by pressure, etc.);
- data on thermophysical properties of gases and liquids (virial coefficients, viscosity and transport coefficients, etc.);
- data on crystal properties (elastic constants, phonon spectra, sublimation energy, etc.);
- experiments on the formation of radioactive defects in solids (the focussing energy, the threshold displacement energy, etc.);
- nuclear magnetic resonance experiments in solids and liquids (the time of spin and spin-lattice relaxations).

To process the experimental data, different semiempirical model potentials with parameters obtained by fitting to the experimental data are usually used. The analytical form of these two-body potentials depends upon the system under study and the nature of the problem. Consider, as an example, the widely used (12–6) Lennard-Jones potential:

$$V^{LJ}(R) = \frac{a}{R^{12}} - \frac{b}{R^6} \tag{1.1}$$

This potential (see Section 5.1.2) has two parameters, a and b. At small distances $V^{LJ}(R) > 0$, the repulsive forces dominate; at large distances $V^{LJ}(R) < 0$, the potential becomes attractive. So, at some point R_0, $V^{LJ}(R_0) = 0$. The point R_0 corresponds to the distance where the repulsive forces are compensated by the attractive ones. The potential function (Equation (1.1)) has a minimum, which is found from the condition $dV^{LJ}(R) / dR = 0$ (Figure 1.1) where ε denotes the depth of the potential well. The potential can be expressed via two other independent parameters, R_0 and ε, having obvious physical and geometrical sense. These parameters are connected with the parameters a and b by the following relations:

$$R_0^6 = a/b \quad \text{and} \quad \varepsilon = b^2/4a$$

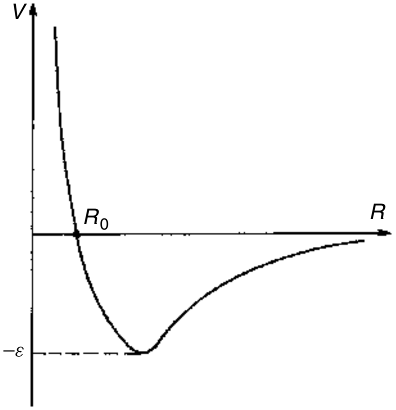

Figure 1.1 The Lennard-Johns model potential (Equation (1.2))

and Equation (1.1) is transformed to:

$$V^{LJ}(R) = 4\varepsilon\left[\left(\frac{R_0}{R}\right)^{12} - \left(\frac{R_0}{R}\right)^{6}\right] \tag{1.2}$$

In general, a model potential can contain n parameters $(p_1,\ p_2, \ldots, p_n)$. To fit these parameters to experimental data, it is necessary to know a theoretical equation that expresses the measured property via a model potential, so that the theoretical equation for the measured property becomes a function of the parameters. Then the procedure that fits these parameters (see Section 5.2) is applied to obtain the best agreement of the calculated values of this function with the measured values.

It should be mentioned that semiempirical potentials cannot describe intermolecular potential adequately for a wide range of separations. A given potential with parameters calibrated for one property, often describes other properties inadequately, since different physical properties may be sensitive to different parts of the potential curve. Hence, to obtain more adequate potentials, the procedure of parameter matching must be carried out using as much of the experimental information as possible on the physical properties of the system under study. The use of high-speed computers brought about the possibility of the application of piecewise potentials that have different analytic form for different ranges of separations (Section 5.1.11).

Model potentials with different analytical forms can lead to the same observed relationship. In this case, experimental agreement with a given analytical dependence of model potential is not a sufficient indication of its correctness but merely a necessary condition. For example, the magnitude of the second virial coefficient is not sensitive to the form of the potential curve and its minimum position; it depends only on the ratio between the width and the depth of the potential well. In the same way, the viscosity coefficient is not sensitive to the dependence of the potential on the separation distance.

When estimating the reliability of the potential obtained, it is necessary to take into account not only the measurement errors but also the approximate nature of the formulae, which connect the measured characteristics with the molecular potential (an error of the theoretical approximation). It is also necessary to bear in mind that the optimized function is a nonlinear function of parameters. As a result, different sets of optimized parameters can give the same precision when fitted to experimental data.

In some cases, it is possible to solve the so-called inverse problem, i.e. to determine the potential directly from the experimental data without preliminary premises about its analytical form (as a rule, in a restricted range of distances). Different approaches to this complex problem are described in Section 5.3.

The discussion above emphasizes the importance of the theoretical determination of intermolecular potentials. The knowledge of the analytical dependence, which follows from the theory, permits more reliable model potentials to be constructed.

The basic concepts of the quantum-mechanical theory of intermolecular forces were formulated about 75 years ago. Nevertheless, it was only the last several decades that the number of studies on intermolecular interactions increased rapidly. This development has emerged for two reasons. Firstly, a general development of quantum-chemical methods of calculating the electronic structure of molecules has taken place, partly due to the availability of high-speed computers and the use of more refined mathematical methods. Secondly, more reliable experimental methods have appeared, which have allowed the theoretical predictions to be verified.

Before presenting the modern concepts about the nature of intermolecular forces, it is instructive to follow the evolution of these concepts. The discovery of the laws of intermolecular interactions, as any other discovery, was not a straightforward process. A great number of fallacies and wrong trends occurred along the way.

1.2 A Brief Historical Survey

Development of concepts about the nature of intermolecular forces is linked with the development of ideas about the atom. Concepts about the atomic structure of matter were formulated by the ancient philosophers. According to Democritus (fifth century BC) and to his semilegendary colleague Leukippos, all bodies consist of finest indivisible particles or *atoms*, separated by a vacuum (emptiness). A vacuum is required for the existence of motion. In the absence of a vacuum, the bodies would interfere under collisions, and motion would be impossible. Bodies differ from each other by the form of the atoms, their arrangement and their mutual orientation.

Introducing the concept of atoms required answering the question: In what manner are atoms linked to form different bodies? Since the interaction was considered to occur only by their direct contact, the problem was solved at the level of the simplest mechanical models, such as hooks, notches, and other devices, as described, for example, by Lucretius (first century BC) in his poem De Renum Natura [1].

In the Middle Ages, the problem of the atomic structure of matter did not attract any attention. An interest in science was completely lost and the scholastic mentality dominated. One of widely discussed ‘actual’ problems was: How many angels can be accommodated on the edge of a needle? The interest in the doctrine of the ancient atomistics arose only from the middle of the seventeenth century. This process occurred very gradually. For example, Galileo, who worked successfully in the field of the dynamics of bodies, became very abstract when was discussing the structure of these bodies. He reduced the particles, which compose the matter, to mathematical points separated by a vacuum and explained the strength of bodies as the disgust to vacuum, i.e. as the resistance of small emptinesses to their expansion.

The ideas of Descartes greatly influenced the development of concepts about the internal structure of matter. These ideas were presented in his treatise ‘Les Passions de l’Ame’, finished in 1633 but published only in 1664–1667 after his death. Descartes assumed that matter is equivalent to its extent but that, on the other hand, an extent does not exist without matter (cf. with the modern concept of space and matter!). In contrast to the ancient atomistics, Descartes suggested that matter is, in principle, infinitely divisible. This idea was also accepted by Leibniz, who assumed that there is no last small body because each body, even very small, is a whole world with an infinite number of creations.

According to Descartes, matter consists of particles, which differ from each other in form and size, and that they are also divisible. Descartes suggested that solids consist of fixed bodies, which are densely packed, and that liquids consist of particles, which move relative to each other. All motions are represented exclusively by mechanical displacements. Descartes assumed that ‘hidden’ interactive forces are absent.

Newton is known as the creator of Newton’s laws in classical mechanics and Newton’s gravitational law. But he considered also forces existing in material medium. A principal difference between Newton and his predecessors was in postulating, in addition to mechanical interaction, the existence of gravitational, magnetic and electric forces, as well as other attractions effective only at very small distances [2].

However, the concrete form of the dependence of interatomic forces upon the distance was not discussed neither by Newton nor by his predecessors. The law of the interaction between particles was introduced for the first time by the Croatian physicist Boscovich (1711–1787) in a work entitled ‘Theory of Natural Science Reduced to the Single Law of Forces Existing in Nature’ [3]. According to Boscovich, all bodies consist of point particles. The oscillating force between any two point particles increases infinitely as they approach each other and tends to the Newton gravitational forces $\left(\sim 1/R^2\right)$ at large distances (Figure 1.2). The existence of repulsive and attractive forces and their alternation is necessary, in Boscovichś opinion, in order to explain the physical properties of gases as well as the deformation of plastic bodies. The Boscovich interaction law was the first interatomic potential used to explain physical properties.

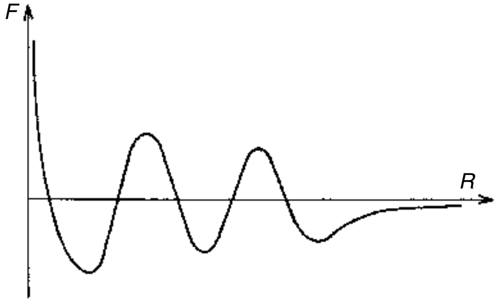

Figure 1.2 The Boscovich universal potential

At approximately the same time, in 1743, the French physicist Clairault introduced the concept of forces interacting between molecules to explain the rising of liquids in capillaries [4]. The studies by Clairault in this field were developed further by Laplace [5] and by Gauss [6]. The intermolecular potential $V(R)$ was used in their papers in a most general functional form. Gauss studied the problem of liquids in capillaries using the principle of virtual work, requiring equilibrium of every mass point under acting forces. He considered three types of forces acting on molecules in liquid: 1. the force of gravity, 2. the mutual attractive forces between the molecules and 3. attractive forces between the molecules of the liquid and the molecules composing the walls of the capillary tube. Gauss showed that for the appearing integrals to be finite, the potential must behave at $R \to \infty$ as $1/R^n$ with n not smaller than six.

The kinetic theory of gases was developed by Clausius [7], Maxwell [8, 9] and Boltzmann [10] in the second half of the nineteenth century. Clausius [7] accepted that molecules repel each other at small distances and attract each other at large distances (at present, this concept is well established). Maxwell presumed that the intermolecular forces are entirely repulsive at all distances. He used an analytical form for the interaction potential, $V\,(R) = A/R^n$, which corresponds to a repulsion, and obtained the expressions for the diffusion, heat capacity and elasticity coefficients. At that time it was known that the elasticity is proportional to the absolute temperature and does not depend on the gas density. The second property can be explained for any value of n, it had been derived previously on the assumption that the molecules are rigid spheres not interacting with each other except on direct contact. For an explanation of the first property, Maxwell concluded that $n = 4$. He assumed that the dependence A/R^4 is also valid at very small distances.

Today, it is well known that the repulsive part of potential is not described by the A/R^4 dependence. As Margenau and Kestner [11] remarked, Maxwell made a logical fallacy: from the fact that some premise led to the correct result, he concluded that the premise was valid, without testing the corollaries resulting from other premises. In the case considered, the proportionality of the elasticity to the temperature can be obtained from an infinite number of different potentials $V(R)$.

Although Maxwell's concept for a analytical form of model potential was erroneous, it represented a mathematically useful expression that allowed closed formulae for various kinetic characteristics of gases to be obtained and played a fundamental role in the subsequent development of the kinetic theory.

Boltzmann's work [10] was stimulated by his doubts on the simplicity of the interaction law proposed by Maxwell. Boltzmann repeated all the calculations using different attractive model potentials. He favored the existence of attractive forces since they provided the condensation of gases. All the models led to results which were similar to those of Maxwell and consistent with experimental data.

The attractive forces, which act between neutral atoms and molecules at large distances, were to be later named as the *van der Waals forces*. This name is not connected with the concrete studies by van der Waals on the nature of intermolecular forces, but with his well-known state equation [12], which accounts for the deviations from the ideal gas behavior:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \tag{1.3}$$

where a is a constant that accounts for the attraction between molecules of gas. That is, at constant volume and temperature, the pressure decreases with increasing a, in agreement with the fact that the attraction between the molecules must reduce the pressure on the vessel walls. The necessity of introducing a correction due to an attraction, in order to make the equation of state consistent with the experimental data, indicates the existence of the attractive forces between molecules.

In subsequent studies, different empirical potentials were used for the explanation of physical properties of gases and liquids. In a series of papers, Sutherland [13, 14] examined some analytical forms of the attractive potential between molecules in the gas phase (in particular, $V(R) \sim -A/R^3$) with parameters determined by fitting to experimental data. This kind of phenomenological approach became typical for subsequent studies in this field. The semiempirical procedure of fitting the potential parameters using experimental data has appeared to be very useful and was developed in the twentieth century, beginning with the paper by Lennard-Jones [15]. The well-known Lennard-Jones potential:

$$V(R) = \frac{\lambda}{R^n} - \frac{\mu}{R^m} \tag{1.4}$$

has been applied widely in studies on gases and condensed matter.

Towards the end of the nineteenth century and at the beginning of the twentieth century, in addition to the phenomenological approaches based on the application of empirical potentials, attempts were made to elucidate the physical nature of intermolecular forces. Some authors connected the intermolecular forces with gravitational ones. For instance, the Newton potential was corrected by a screening factor:

$$V(R) = -G\frac{m_1 m_2}{R} \exp\left(-\frac{R}{a}\right) \tag{1.5}$$

However, the small magnitude of the gravitational forces has resulted in a rejection of their use in the theory of intermolecular forces. Appearing at the same time, the data about the existence of electrical charges in atoms and molecules led to an assumption about the electromagnetic nature of intermolecular forces.

Reinganum [16] was the first to consider the interaction of two neutral molecules as the interaction of two permanent electric dipoles. According to the electrostatic theory, the interaction energy of two electric dipoles with moments $\mathbf{d}_1$ and $\mathbf{d}_2$, respectively, which are located at a distance R from each other, depends on their mutual orientation and has the following form:

$$E_{dd} = \frac{1}{R^5}\left[R^2\left(\mathbf{d}_1 \bullet \mathbf{d}_2\right) - 3(\mathbf{d}_1 \bullet \mathbf{R})(\mathbf{d}_2 \bullet \mathbf{R})\right] \tag{1.6}$$

Introducing the spherical angles $\theta_1, \varphi_1, \theta_2, \varphi_2$, characterizing the directions of dipoles $\mathbf{d}_1$ and $\mathbf{d}_2$, with the z-axis along a line connecting their centers, Equation (1.6) becomes:

$$E_{dd} = -\frac{d_1 d_2}{R^3}\left[2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos(\varphi_1 - \varphi_2)\right] \tag{1.7}$$

The energy E_{dd} becomes positive (corresponds to the repulsive forces), if one of the dipole moments is perpendicular to the z-axis, and has a minimum corresponding to the attractive forces with the value:

$$(E_{dd})_{\min} = -\frac{2d_1 d_2}{R^3} \tag{1.8}$$

for the dipole orientation along the z-axis. Reinganum carried out a statistical calculation of dipole–dipole interactions, averaging all the orientations. Such an average, under the condition that all orientations are equally probable, leads to the zeroth interaction energy:

$$\langle E_{dd}\rangle = 0 \tag{1.9}$$

where the bracket notation denotes an average over orientations. But the probability of the dipole orientation, corresponding to the energy E, is determined by the Boltzmann factor $\exp(-E/kT)$. Taking this into account and E_{dd} in the form of Equation (1.7), one obtains, at the condition $E_{dd} \ll kT$:

$$\left\langle E_{dd}\exp\left(-\frac{E_{dd}}{kT}\right)\right\rangle = \langle E_{dd}\rangle - \frac{1}{kT}\left\langle E_{dd}^2\right\rangle = -\frac{2}{3kT}\frac{d_1^2 d_2^2}{R^6} \tag{1.10}$$

So, the attraction forces between dipoles, obtained by Reinganum, decrease as the temperature increases and approach zero at high temperature. These forces were called *orientational forces*.

Intermolecular forces exist also at high temperatures. Therefore, the introduction of the orientational forces does not provide a complete answer to the question of the nature of intermolecular forces. Moreover, the existence of orientation forces requires the existence of permanent dipole moments in molecules. In fact, it was assumed at that time that all atoms and molecules possess dipole moments. This concept was strengthened by the early Debye studies on the theory of the dielectric permittivity [17]. According to that theory, the molecular dipoles align in an electric field. Debye verified his theory on five liquids, which accidentally occurred to be polar (alcohols), and arrived at the amusing (but not for his time!) conclusion that all molecules are polar.

In later studies it was found, however, that the simplest homoatomic molecules, such as hydrogen (H_2), nitrogen (N_2) and oxygen (O_2) molecules, have no dipole moments. In order to explain the interaction between non-dipole molecules, it was Debye [18] who made the next important step towards the understanding the nature of intermolecular forces. He assumed that the charges in a molecule are not fixed rigidly, but are able to move under the influence of the field produced by a permanent moment of the other molecule.

Since dipoles did not appear to be universal, Debye studied the induction of the dipole electric moment in one molecule by the permanent quadrupole moment of the other molecule. He evaluated the electrical field $D_A(R)$ created by the quadrupole moment Q_A of molecule A at a distance R from it, $D_A = Q_A/R^4$. This field induces a dipole moment $\mathbf{d}_B$ in molecule B, $\mathbf{d}_B \sim \alpha_B \mathbf{D}_A$, where α_B is the polarizability of molecule B. The interaction energy of the induced dipole moment $\mathbf{d}_B$ with the electric field $\mathbf{D}_A$ is equal to $E_{qd} = -\mathbf{d}_B \bullet \mathbf{D}_A = -\alpha_B D_A^2$. Taking into account that a similar effect on molecule A is produced by the quadrupole moment of molecule B and carrying out an averaging over all the equally probable mutual orientations, Debye obtained the following expression for the interaction energy:

$$\langle E_{qq} \rangle = -\frac{2}{3}\left(\alpha_A \frac{Q_B^2}{R^8} + \alpha_B \frac{Q_A^2}{R^8}\right) \tag{1.11}$$

where the quantities Q_A and Q_B are components of the quadrupole moments of the molecules A and B, respectively. It is evident that Expression (1.11) does not depend on the temperature. Therefore, it provides an attractive interaction even at high temperatures when the effect of the orientational forces is almost zero. The induction interaction, induced by dipole moments, was studied later by Falkenhagen [19], who found it to be proportional to $1/R^6$. The forces of this type were then called the *Debye–Falkenhagen induction forces*.

While studying the induction interactions of molecules with quadrupole moments, Debye did not, however, consider the direct electrostatic interaction of quadrupole moments of molecules. This was done by Keesom [20] who generalized Reinganum's calculations by considering, in addition to the dipole–dipole interaction, the dipole-quadrupole and quadrupole-quadrupole ones. Sometimes the orientational forces are named the *Keesom forces*, although it is more correct to call them the *Reinganum–Keesom forces.*

Thus, classical physics has been able to explain, at least qualitatively, two types of interactions: the interactions between molecules with permanent multipole moments and the interactions between permanent and induced moments in molecules. This was achieved by introducing orientational forces that decrease with increasing temperature, and induction forces that do not depend on temperature.

In the case of some polar molecules, e.g. water, these forces make a considerable contribution to the intermolecular interaction. Although they constitute only a small part of the interaction for some other molecules, such as hydrogen chloride.

However, classical physics has completely failed to explain the origin of interaction among rare gas atoms. The electron shells of these atoms are spherically symmetric, which means that such atoms possess neither dipole nor other multipole moments, although the attractive forces in these systems are not negligible. At that time it was already known that at low temperatures rare gases undergo the transitions in liquid and solid states. In the framework of classical physics, one has been also unable to obtain the analytic form of a repulsion law at short distances.

The systematic and correct theory of intermolecular forces, which describes their behavior both at short and large distances, could be constructed only after the development of quantum mechanics between 1925 and 1927 (Bohr, Heisenberg, Schrödinger, Born, Dirac, Pauli). In 1927, Heitler and London [21] carried out the quantum-mechanical calculation of the potential curve for the simple system consisting of two hydrogen atoms. The Heitler–London calculation laid the foundation of the quantum theory of valence. As follows from their results, the repulsive behavior of the potential curve at short distances is determined by the antisymmetry of the wave function with respect to the permutations of electrons that stems from the Pauli exclusion principle. It causes the appearance of the specific *exchange interaction*. The repulsive exchange forces decrease exponentially with the distance.

In the same year, Wang [22] considered the quantum-mechanical attraction arising between two hydrogen atoms at large distances. He showed that it is proportional to $1/R^6$. These forces were called the *dispersion forces* and have a pure quantum-mechanical origin. The general theory of the dispersion forces was formulated in 1930 by Fritz London [23, 24]. The theory of dispersion forces resolved the problem of origin of the attraction between rare gas atoms. The leading term in the dispersion interactions for all systems falls down with distance as $1/R^6$. The dispersion forces are called also the *London forces,* or the *van der Waals forces*.

In 1948, while working on the problems of the coagulation theory of colloidal solutions, the Dutch theoretical physicists Casimir and Polder [25] took into account the retarding effects of the interaction between colloidal particles at large distances. They revealed that in this case, instead of the dependence $1/R^6$, there is a more rapid decrease of the dispersion forces with the distance, namely, the $1/R^7$–law (*the Casimir–Polder interaction).* In the same year, Casimir [26] found the analytical expression for the forces between two parallel metallic plates studying the zero-point energy of the vacuum electromagnetic field between plates. Finally, Lifshitz [27, 28] has created the general theory of the attractive van der Waals forces between macroscopic bodies with arbitrary permittivity.

At this point it is reasonable to conclude our brief historical survey of the evolution and main advances in the theory of intermolecular interactions. Their detailed account and the contemporary achievements are presented in the following parts of this book.

1.3 The Concept of Interatomic Potential and Adiabatic Approximation

A consistent theory of intermolecular forces can only be developed on the basis of quantum-mechanical principles. Because of the quantum nature of the electronic and nuclear motions, the solution of the intermolecular interaction problem reduces to solving the Schrödinger equation for a system of interacting molecules. Such a problem may be solved only after adopting some approximations. A substantial simplification may be achieved because of the possibility of separating the electronic and nuclear subsystems and introducing the concept of the *adiabatic potential*. This approach, denoted as the *adiabatic approximation,* is based on a large difference between the masses of electrons and nuclei (the detailed derivation is presented in Section A3.1).

Within the adiabatic approach, the electron subsystem is studied with fixed nuclei. In the Schrödinger equation, the nuclear kinetic energy operator is neglected and the nuclear coordinates are treated as fixed parameters. The Schrödinger equation splits into two: one for the electron motion with fixed nuclei and the other for the nuclear motion with the electron energy as the potential energy.

Below, we represent the basic equations for the system of two atoms A and B with N_A and N_B electrons, respectively, and the total number of electrons in the system $N = N_A + N_B$. Let us denote the set of $3N$ electron coordinates as r and the distance between nuclei as R. The total wave function in the adiabatic approximation is written as a simple product:

$$\Psi_{m\nu}(r, R) = \chi_{m\nu}(R)\Psi_m(r, R) \tag{1.12}$$

where we denote the wave function describing the nuclear motion as $\chi_{m\nu}(R)$ and the wave function of the N-electron system in a quantum state m as $\Psi_m(r, R)$; for each electronic quantum state m there is a corresponding set of nuclear quantum states ν.

The electronic wave function $\Psi_m(r, R)$ has to satisfy the Schrödinger equation for the electronic motion:

$$H_e\Psi_m(r, R) = E_m(R)\Psi_m(r, R) \tag{1.13}$$

with the Hamiltonian:

$$H_e = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\left(\frac{Z_a e^2}{r_{ai}} + \frac{Z_b e^2}{r_{bi}}\right) + \sum_{i<j}\frac{e^2}{r_{ij}} + \frac{Z_a Z_b e^2}{R} \tag{1.14}$$

where r_{ai} and r_{bi} are the distances between electron i and nuclei a and b, having the charges Z_a and Z_b, respectively, and R is the fixed interatomic distance (see

Equation (A3.8)). The wave function $\Psi_m(r, R)$ describes the electronic motion at fixed nuclear coordinates or at an infinitely slow change of nuclear coordinates (adiabatic change). So, the eigenvalues E_m of Equation (1.13) depend upon the value of parameter R. The solution of Equation (1.13) at different values of R allows to obtain the function $E_m(R)$. This function plays the role of the potential energy in the Schrödinger equation for the nuclear motion, which in the so-called *Born–Oppenheimer approximation* [29] is presented as:

$$\left[-\frac{\hbar^2}{2\mu}\nabla_R^2 + E_m(R)\right]\chi_{m\nu}(R) = E_{m\nu}\chi_{m\nu}(R) \tag{1.15}$$

As was noted by Born [30, 31], the adiabatic potential energy $E_m\,(R)$ can be corrected by adding the diagonal contribution of the electron-nuclear interaction *(vibronic interaction)* (see Section A3.1). In this *Born adiabatic approximation*, the Schrödinger equation for the nuclear motion is written as:

$$\left[-\frac{\hbar^2}{2\mu}\nabla_R^2 + V_m\,(R)\right]\chi_{m\nu}\,(R) = E_m\chi_{m\nu}\,(R) \tag{1.16}$$

$$V_m\,(R) = E_m\,(R) - W_{mm}\,(R) \tag{1.17}$$

The adiabatic potential energy $V_m\,(R)$ is named the *interatomic potential.* The second term in Equation (1.17), $W_{mm}\,(R)$, is called *adiabatic correction.* The methods for calculating it are given in references [32–38]. Because of calculation difficulties, the adiabatic correction is often neglected and the interatomic potential is approximated by the energy $E_m\,(R)$ found in solution of the Schrödinger equation for the electronic motion at different values of the interatomic distance R (Equation (1.13)).

In the vicinity of the minimum of the potential energy, the nuclear motion can be separated in the *vibration* motion of nuclei and the *rotation* motion of the system as a whole. The nuclear wave function is factorized as:

$$\chi_{m\nu}(R) = \Lambda_{m\nu}(Q)\Theta^J_{MK}(\vartheta) \tag{1.18}$$

where ν enumerates the vibrational states, Q is the normal coordinate, J is the rotational angular moment, M and K are its projections on z-axes of the laboratory frame and molecular frame, respectively, and ϑ is the set of the Euler angles. Vibrational energy levels $E_{m\nu}$ for some electronic quantum state m are depicted in Figure 1.3.

The knowledge of interatomic potentials is necessary for studying the behavior of interacting atoms (molecules) at different distances and at different temperatures. But it must be kept in mind that the adiabatic approximation is not valid for degenerate electronic states, which are often the case for excited electronic states. It is also a bad approximation when the electronic terms are close to each other. In these cases the electron-nuclear interaction terms in the coupled equations (Equation (A3.13)) cannot be neglected. The adiabatic potential loses its physical meaning as the potential energy for the nuclear motion. The physical and chemical phenomena associated with the degeneracy and quasi-degeneracy of electronic

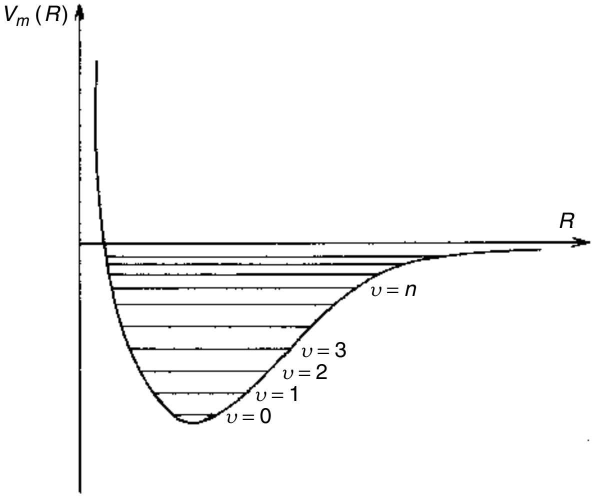

Figure 1.3 Vibrational energy levels in a potential well formed in an electronic quantum state (m)

states are called the *Jahn–Teller effect* [39–43]. In Jahn–Teller systems, the adiabatical approach cannot be applied and the role of the vibronic interactions becomes crucial. Among such systems a very important role is played by molecular systems with potential surfaces characterized by so-called *conical intersections* [44], in which the nonadiabatic coupling terms are singular at isolated points. In the last decade, conical intersection effects have attracted great attention in theoretical and experimental studies as an essential aspect of various electronically nonadiabatic processes (see reviews by Baer [45] and Yarkony [46], and references therein).

For the nondegenerate ground electronic state, the adiabatic approximation works surprisingly well. The discussion of the accuracy of the adiabatic approximation is presented in reviews by Kołos [47] and Rychlewski [48]. For a good check, a most precisely calculated molecular system has to be chosen. The best choice is the hydrogen molecule. On one hand, it is the simplest molecular system for which the numerous precise theoretical and experimental studies have been performed. On the other hand, it contains the lightest nuclei; so, it can be expected that the obtained error of the adiabatic approximation will be an upper limit.

In Table 1.1, the most precise theoretical and experimental values of the dissociation energy and the ionization potential for the hydrogen molecule are presented. The discrepancy is smaller than the experimental error. It is a great success of computational chemistry based on quantum-mechanical concepts of chemical bonding. It should be stressed that this excellent agreement between theory and experiment is a result of more than six decades of research on both sides–theoretical and experimental. Thus, the calculations for hydrogen are the most trustworthy and can be used to check the adiabatic approximation.

Table 1.1 Comparison of theoretical calculations with experimental values for the hydrogen molecule in (in cm^{-1})

	Theory	Experiment	Discrepancy
a) Dissociation energy			
Kołos–Rychlewski [49]	36 118.049		0.006 ± 0.08
Wolniewicz [50]	36 118.069		0.004 ± 0.008
		36 118.11 ± 0.08[a]	
b) Ionization potential			
Kołos–Rychlewski [49]	124 417.471		0.017 ± 0.017
Wolniewicz [50]	124 417.491		0.003 ± 0.017
		124 417.488 ± 0.017[b]	

[a] Reference [51]
[b] Reference [52]

According to the calculation of the nonadiabatic corrections to the hydrogen ground state dissociation energy by Wolniewicz [50, 53], the nonadiabatic correction to the lowest vibrational level $\Delta D_0\,(\nu = 0)^{nonad} = 0.50\ \text{cm}^{-1}$ and the maximum nonadiabatic correction was found for the vibrational level $\nu = 9$, $\triangle D_0\,(\nu = 9)^{nonad} = 5.20\ \text{cm}^{-1}$. The precise value of D_0 is equal to $36\,118.069\ \text{cm}^{-1}$ [50]. Hence, the relative error of the adiabatic approximation in the ground state of the hydrogen molecule is $\Delta D_0^{nonad}/D_0 = 10^{-5}$ to 10^{-4}. From this follows that the accuracy of the adiabatic approximation is very high. It is considerably higher than the value of the small parameter $\left(m_e/M_p\right)^{\frac{1}{4}} = 0.15$, on which the Born–Oppenheimer adiabatic approximation [29] was based. For molecules with heavier atoms one can expect even larger precision. But it is difficult to check because of calculation problems.

For two atoms, the interatomic potential is represented by a potential curve $V(R)$. In the ground electronic state of two-atom systems, the interatomic potential $V_0(R)$ usually has a minimum. The depth of potential well, E_0, depends upon a system under study. In covalent bonded molecules, the well depth is equal to several electron-volts (eV) in the van der Waals dimers of noble gas atoms, it is equal to 10^{-2} to 10^{-3} eV. The ratio of the well depths in helium and hydrogen molecules (the two extreme cases) is about 10^{-4}. The helium dimer was observed experimentally only recently [54]. It is the most weakly bound molecule known at present. Its dissociation energy ($D_0 = E_0 - (1/2)\hbar\omega_0$) is equal to 1.2 mK $\simeq 10^{-7}$ eV, while in hydrogen the dissociation energy $D_0 = 4.48$ eV. Also the great difference is in the optimal (equilibrium) distances: from 1.4 a_0 in the hydrogen molecule to 5.6 a_0 in the helium dimer.

The potentials describing the interaction between two molecules may be, as in the two-atom case, represented by a potential curve depending only on one variable, if the interaction is averaged over all molecular orientations in space. This potential, $V(R)$, where R is the distance between the centers of masses of the molecules, is named the *potential of intermolecular interaction*, or briefly, the *intermolecular potential*. When the interacting molecules are fixed in space, the intermolecular potential, $V(R,\vartheta)$, depends on a set of Euler's angles, ϑ, which determines the mutual orientation of the molecules. In addition, the interaction depends on the electronic state of the interacting systems. Therefore, for any pair of molecules there is a set of intermolecular potentials, $V_m(R, \vartheta)$, where m labels the quantum states of the systems.

For three atoms taking part in a substitution reaction:

$$A + BC \longrightarrow AB + C \tag{1.19}$$

the adiabatic potential is represented by a potential surface depending on three interatomic separations:

$$V_m = V_m(R_{AB}, R_{BC}, R_{AC}) \tag{1.20}$$

If two of the interatomic separations remain constant, the resulting potential curve represents a cross section of this surface. Similarly to a two-atom case, in a three-atom system there is a set of potential surfaces that depends on the quantum states of the reacting atoms.

In a system with three (or more) atoms, there is the problem of nonadditivity. It is necessary to study the deviations from the additive approach, in which the potential of the system can be presented as a sum of pair potentials V_{ab}:

$$V\,(ABC\ldots) = \sum_{a<b} V_{ab} \tag{1.21}$$

This problem will be discussed in Chapter 4.

As shown in the preceding text, the concept of interatomic potential is based on the adiabatic approximation. Some authors studying the pairwise atom–atom potentials consider them as a classical concept. This is an incorrect statement. Even in the case where the motion of atoms is treated classically, as it is often done in the molecular dynamic studies, the interatomic potentials applied in these approaches have a quantum mechanical origin. The analytical form of numerous semiempirical model potentials (see Chapter 5) is based on the analytical expressions for different types of intermolecular forces (exchange, dispersion etc.) found by an approximate solution of the Schrödinger equation in the adiabatic approximation.

It should be noted that the adiabatic approximation may be invalid in high-energy collisions if the magnitude of energy is so high that the nuclear kinetic energy operator cannot be neglected. In this case, the electrons will not be able to adjust adiabatically to the nuclear rearrangement. In the theory of atomic collisions [55, 56] it is shown that the adiabatic approximation is valid only for large values of the so-called the Massey parameter ζ_{mn}:

$$\zeta_{mn} = \omega_{mn} a/v \tag{1.22}$$

where ω_{mn} is the frequency of electronic transitions between states m and n, v is the velocity of the atomic motion, and a is the distance at which the adiabatic electronic wave function undergoes essential changes. Parameter a is defined as a characteristic distance such that a shift by a results in an appreciable change of the matrix element with a semiclassical analogue of the nonadiabatic operator. The essence of the Massey criterion may be reduced to a requirement for the collision time, $\sim a/v$, to be much larger than the transition time, $\sim \omega_{mn}^{-1}$, between the adiabatic terms of the interacting system. When the equality (Equation (1.22)) breaks down, a large probability of nonadiabatic transitions exists, that is, the mixing of adiabatic terms of the system takes place.

In the early 1960s, the validity of applying the adiabatic approximation in elastic atomic collisions was discussed in connection with the high-energy helium (He) collision experiments by Armdur and Bertrand [57]. The experimental repulsive part of the He–He potential at distances $R \simeq 0.5$ Å was 9 eV lower than published theoretical values. The accurate quantum-mechanical calculation, with the inclusion of configuration interaction, carried out by Philipson [58], led to a lowering of the theoretical curve by 2 to 3 eV only. It was suggested that the adiabatic approximation breaks down in the experiment since the energy of the helium atoms was of order of 1000 eV. However, inclusion of nonadiabatic corrections resulted in an insignificant lowering of the theoretical curves, due to some compensating factors [59]. It is instructive that the reason for the discrepancy was found to be in the experimental measurements. After revising all the details of the experiment, Armdur [60] obtained a good agreement between the new experimental curve and the curve calculated by Philipson. Thus, the experimental data in such elastic atomic collisions, at least in the range of energies of a few keV, are described adequately within the frame of the adiabatic approximation. But it can be expected that the adiabatic approach will break down for higher collision energies.

In collision experiments with the helium beam [57], the helium atoms stayed in the ground electronic state. So, it was the elastic scattering process. The adiabatic approximation is not adequate for most of inelastic scattering processes (the charge exchange, predissociation etc.) even at low energy. For a non-negligible probability of transition from some electronic state to another, the adiabatic potential curves have to be located at a transition point R sufficiently close to each other. Hence, the system will correspond to quasi-degenerate case and it is the vibronic interaction that causes such kind of inelastic transitions. This was realized in 1932 in three independent studies: Landau [61], Zener [62] and Stueckelberg [63].

Thus, the adiabatic representation, in which the electronic Hamiltonian matrix is diagonal, cannot be a satisfactory basis for study most inelastic scattering processes. At present in these studies, the so-called *diabatic representation* is used. It was introduced by Lichten [64] and rigorously formulated by Smith [65]. The diabatic electronic states are defined by an unitary transformation chosen in a such manner that the first derivative couplings in coupled equations for the nuclear motion, Equation (A3.13), become sufficiently small to be neglected. In the diabatic representation, the electronic Hamiltonian matrix is nondiagonal. Its nondiagonal elements are responsible for the transitions from one adiabatic electronic state to another.

Analyzing the atom–atom collisions, Smith [65] considered the case with a single internal coordinate. The multidimensional case was analyzed by Baer [66] and Mead and Truhlar [67]. One of the last derivations of the adiabatic-to-diabatic transformation can be found in Reference [45]. To study the topological effects in scattering processes and nonadiabatic phenomena in many-atomic molecules, the extended versions of the Born–Oppenheimer equations were developed [68–70]; see also Reference [45]. Vibronic dynamics is now a well elaborated and active field of investigation [46, 71, 72].

1.4 General Classification of Intermolecular Interactions

The classification of intermolecular interactions depends on the distance between interacting objects; although it must be kept in mind that all types of intermolecular interactions have the same physical nature: namely, the electromagnetic one. Various types of intermolecular interactions are presented in Figure 1.4. They are

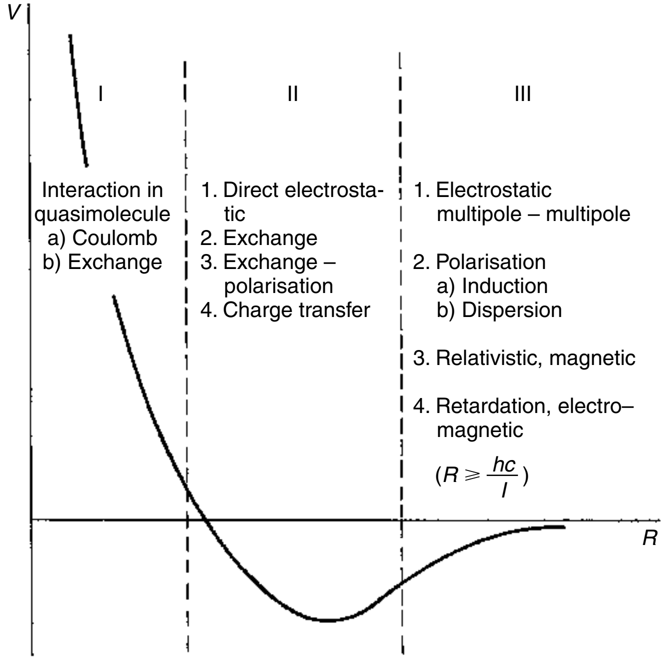

Figure 1.4 Classification of intermolecular interactions

classified according to the three ranges of interatomic separation for a typical interatomic potential. These three ranges are:

> I. A range of short distances at which the potential has a repulsive nature and the electronic exchange, due to the overlap of the molecular electronic shells, dominates.
>
> II. A range of intermediate distances with the van der Waals minimum, which is a result of the balance of the repulsive and attractive forces.
>
> III. A range of large distances at which the electronic exchange is negligible and the intermolecular forces are attractive.

Range I

In this region, the perturbation theory (PT) for calculating the intermolecular interactions cannot be applied. To some extent, the interacting atoms (molecules) lose their individuality because of a large overlap of their electronic shells. The same variational methods, which are used for molecular calculations, can be applied to the calculation of the total energy of interacting system, which can be considered as a ‘supermolecule’. The interaction energy is found as a difference:

$$E_{int} = E_{tot} - \sum_{a=1}^{n} E_a \tag{1.23}$$

where E_a is the energy of isolated subsystems (molecules or atoms) that have to be calculated at the same approximation as a whole system. In this region we can separate only two types of interaction energies: the *Coulomb energy* and the *exchange energy*. If we put to zero all integrals containing the exchange or overlap of electron densities, we obtain E_{Coul}. Then, the exchange energy is defined as the difference:

$$E_{exch} = E_{int} - E_{Coul} \tag{1.24}$$

Range II

Both repulsive and attractive forces exist in this region. This causes the minimum of intermolecular potential energy and provides a stability of the system. The magnitude of the interaction energy is much smaller than the self-energy of the interacting molecules and the PT can be applied; although the electron exchange, appearing as a consequence of the antisymmetry of the total wave function, is still large. The standard perturbation Rayleigh–Schrödinger and Brillouin–Wigner theories (see Section A3.3) are developed for the zero-order wave function taken as a simple product of the wave functions of interacting atoms (molecules). In the intermediate distance region, the antisymmetric zero-order wave function has to be dealt with. This leads to essential modifications of the standard perturbation schemes. The approaches developed were named *Symmetry Adapted Perturbation Theories* (SAPT): they are discussed in Section 3.2.1 (for details see References [73–75]).

The exchange energy is separated only in the first order of SAPT. The decomposition of E_{int} into a perturbation series can be written as:

$$E_{int} = \varepsilon_{el}^{(1)} + \varepsilon_{exch}^{(1)} + \sum_{n=2}^{\infty} \varepsilon_{pol.exch}^{(n)} \tag{1.25}$$

$\varepsilon_{el}^{(1)}$ is the classical electrostatic interaction energy between two (or more) systems of charges. The only difference to the classical expression is in the charge distribution: instead of point charges, $\varepsilon_{el}^{(1)}$ contains distributed electron densities. $\varepsilon_{exch}^{(1)}$ is the exchange energy in the first order of PT. Its origin is based on the Pauli principle demanding the antisymmetrization of many-electron wave functions. Because of antisymmetrization, electrons have the probability of being located on each interacting atoms (molecules); so, they are delocalized. This is a specific quantum-mechanical effect. Thus, the exchange interaction exists only in the framework of the quantum-mechanical description. In the second and higher orders of SAPT, the exchange effects cannot be separated from the polarization energy. In various formulations of SAPT, the different expressions for the exchange–polarization energy $\varepsilon_{pol.exch}^{(2)}$ are elaborated [73].

Range III

In this region, exchange effects can be neglected. Usually, it is valid for R $\gtrsim 15a_0$. The different types of intermolecular interactions are classified in the frame of the standard Rayleigh–Schrödinger perturbation theory. In the second order of PT, the polarization energy splits on the induction $\varepsilon_{ind}^{(2)}$ and dispersion $\varepsilon_{disp}^{(2)}$ energies. In higher orders, some mixed term $\varepsilon_{ind.disp}$, which results from coupling of the induction and dispersion energies, appears. In the third order of PT, $\varepsilon_{ind,disp}^{(3)}$ was analyzed by Jeziorski *et al.* [74]. Thus, at distances where the exchange effects are negligible, the PT expansion can be written:

$$E_{int} = \varepsilon_{el}^{(1)} + \sum_{n=2}^{\infty} \left[\varepsilon_{ind}^{(n)} + \varepsilon_{disp}^{(n)} \right] + \sum_{n=3}^{\infty} \varepsilon_{ind.disp}^{(n)} \tag{1.26}$$

What is important is that at these distances the multipole expansion of the electrostatic potential is valid. The interaction operator can be expanded in the multipole series. As a result, $\varepsilon_{el}^{(1)}$ represents a direct multipole–multipole electrostatic energy. At sufficiently large distances, only the first term in the multipole expansion is enough to describe the interaction. For polar molecules, it is the dipole term. In this approximation, the electrostatic energy $\varepsilon_{el}^{(1)}$ is given by the classical expression (Equation (1.6)), but the dipole moments have to be calculated with the molecular (atomic) electron densities.

The physical sense of the induction energy $\varepsilon_{ind}^{(2)}$ is the same as in classical physics (see discussion in Section 1.2). The dispersion energy is a pure quantum-mechanical phenomenon. It originates in the quantum-mechanical fluctuations of electronic density. The instant redistribution of electron density leads to the nonzero mean dipole moment even in the cases when the permanent dipole moment is equal to zero (nonpolar molecules, noble gas atoms). This instant dipole moment induces a dipole and more higher moments in the other molecule. In the second order of PT, the multipole expansion of the dispersion energy $\varepsilon^{(2)}_{disp}$ is usually written in the following form:

$$\varepsilon^{(2)}_{disp} = -\sum_{n=6}^{\infty} \frac{C_n}{R^n} \tag{1.27}$$

For atoms, the sum in Equation (1.27) contains only even powers, whereas in the case of the interaction between molecules, it may also contain odd powers of n (see Sections 3.1.2 and 3.1.3). The coefficients C_n are named as *dispersion coefficients*. For their calculation, quite sophisticated quantum-mechanical methods are elaborated [73]. In the higher orders of PT, the interpretation of different terms in Equation (1.26) becomes more complex. The dispersion energy in the third order of PT, $\varepsilon^{(3)}_{disp}$, will be discussed in Chapter 4. This is the well-known Axilrod–Teller–Mutto dispersion energy [76, 77].

Magnetic interactions exist at all distances, but in ranges I and II they are often negligible in comparison with larger electrostatic interactions. On the other hand, magnetic interactions are precisely detected by measurements of the energy level splitting in a magnetic field in the well-elaborated methodics of electron and nuclear paramagnetic resonances. In some special cases, the magnetic interactions become the largest at sufficiently large distances. This is the case for oriented nonpolar molecules possessing the quadrupole moment as the first nonvanishing multipole moment and having, in the ground state, the total electronic spin $S \neq 0$. The first term in the multipole expansion of different electrostatic intermolecular interactions for these molecules has the following distance dependence:

$\sim\frac{1}{R^5}$ in the electrostatic energy $\varepsilon^{(1)}_{el}$ (the quadrupole–quadrupole interaction).

$\sim\frac{1}{R^6}$ in the dispersion energy $\varepsilon^{(2)}_{disp}$ (the dipole–dipole interaction).

$\sim\frac{1}{R^8}$ in the induction energy $\varepsilon^{(2)}_{ind}$ (the quadrupole–induced dipole interaction).

The magnetic spin–spin interaction is relativistic one and has a dipole-dipole distance behavior. It is $\sim\alpha^2/R^3$, where $\alpha = 1/137$ is the fine structure constant. Although α^2 is small, it is evident that the magnetic interactions become predominant with increasing intermolecular distance. The described situation is realized for oxygen molecules absorbed on some surface. The oxygen molecule, as all homonuclear diatomic molecules, has no dipole moment and its ground state is triplet, that is, the total electronic spin $S = 1$ [78].

At distances at which the propagation time of the interaction, R/c, is of the same order as the average time of the electronic transitions, which is proportional to $\hbar/I_1$ (where I_1 is the first ionization potential), that is, $R \sim \hbar c/I$, the *retardation effect* should be taken into account. Usually, this effect becomes appreciable at $R \gg 500$ bohrs.

Consideration of the retardation effect is important in the coagulation theory of colloid solutions, where interactions between macroscopic bodies should be taken into account. In such cases, the London term for the dispersion interactions, $\sim 1/R^6$, must be replaced with the Casimir–Polder term, $1/R^7$ (see Section 2.5).

The classification of the intermolecular interactions presented in the preceding text is arbitrary to a large extent since it is based on expressions of the perturbation theory and the following question may arise: has such classification any physical sense? Nature does not know about our perturbation theory and other approximation methods, and real potentials do contain contributions from all types of interactions.

Fortunately, the answer to such a question is positive. The representation of the interaction energy as a sum of various components permits the terms giving the greatest contribution in a given range to be separated. Each term in the multipole electrostatic interactions or in the dispersion energy series has a clear physical sense. The magnitude of the multipole interactions depends upon the values of multipole moments, the induction and dispersion forces are proportional to the molecular polarizabilities, and so on. These physical quantities can be obtained from experiments. So, each term is related to real physical properties of atoms or molecules. Often it allows the magnitude of intermolecular interactions to be estimated qualitatively without complex quantitative calculations.

In the next chapter the different types of intermolecular interactions are discussed in detail.

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