Intermolecular interactions

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A description is given of the current state of the theory of intermolecular interactions. This includes a general physical picture of these interactions and an analysis of the relative contributions of different types of interaction (electrostatic, resonance, induction, dispersion, relativistic, magnetostatic, and exchange). The leading features of each contribution are discussed. A review is also given of methods available for calculating the potential specific for each range of distances between the interacting systems. Particular attention is devoted to an analysis of approximations used in different theoretical calculations.

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CONTENTS

> *"The space between molecules is thought by some to be filled with air."*
> *A. S. Kompaneets*

INTRODUCTION

Knowledge of the intermolecular interaction potentials[1] is essential for a broad range of problems in physics, chemistry, and biology. The very existence of liquids and solids relies on these intermolecular interactions. The thermodynamic properties of gases and liquids and, in particular, their transport characteristics (the coefficients of thermal conductivity, diffusion, and so on) are determined by the nature of the intermolecular interaction. Intermolecular forces determine most of the properties of crystals, including equilibrium geometry, cohesion energy, phonon spectra, and so on.

The intermolecular interactions are responsible for the formation of chemical complexes involving charge transfer and hydrogen bonding, and lie at the basis of the formation of colloids. Elementary chemical events cannot be investigated unless one knows the processes involving energy transfer between translational and electronic-vibrational degrees of freedom, which depend on the interaction between particles in the course of collisions. The potential surface characterizing the relative trajectories of reagents must be known before one can calculate the rates of chemical reactions.

Intermolecular interactions are also of major importance in biology. It will be sufficient to mention that it is precisely these forces that ensure the stability of such important life-supporting compounds as DNA and RNA.

Modern technology demands data on the macroscopic properties of gases under conditions in which measurements are difficult to perform (ultrasonic velocities, high temperatures $T > 1000°$, ultrahigh pressures in shock waves, and so on). The required gas parameters can be calculated but only if the necessary potential-energy curves have been obtained independently for a broad range of separations. Knowledge of the intermolecular interaction forces is also required in the theory of molecular lasers.

The following are the most important sources of information that we have on molecular forces:

a) scattering experiments performed with atomic or molecular beams, which often provide experimental

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[1] For brevity, we use the single phrase "intermolecular interaction" which is meant to include interatomic interactions that do not result in the formation of a chemical bond.

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data from which the potentials can be directly determined;

b) spectroscopic measurements (vibrational-rotational spectra, predissociation, pressure broadening of spectral lines);

c) data on thermophysical properties of gases and liquids (virial coefficients, viscosity, and transport coefficients generally);

d) data on the properties of crystals (elastic constants, phonon spectra, sublimation energies);

e) experiments on radiation damage in solids (focusing energy, threshold displacement energy, channeling, and so on);

f) experiments on nuclear magnetic resonance in solids and liquids (spin and spin-lattice relaxation time).

Various two-body interaction potentials are used in the analysis of experimental data and the parameters of these potentials are obtained by fitting the theoretical values to the experimental data.[1,2] Depending on the particular system under consideration, the Lennard-Jones, Morse, Kihara, and many other potentials are often used. We note that none of these semiempirical potentials can provide a correct description of the actual intermolecular potential over a broad range of separations. Moreover, a given potential with parameters established on the basis of a particular property is often unsatisfactory for other properties, since different physical properties may be sensitive to different parts of the potential curve.

It is important to emphasize that the intermolecular forces cannot be directly measured. In fact, one measures certain other characteristics such as the angle of scattering, transport coefficients, and so on, which are functionally related to the intermolecular potential. In some experiments, it is possible to solve the so-called inverse problem, namely, to determine the form of the potential from experimental data but, as a rule, only in a restricted range of separations (these are the scattering experiments involving molecular beams and vibrational-rotational spectra of diatomic molecules). When the reliability of the resulting potential is estimated, one must take into account not only the approximate character of the measurements (the experimental uncertainty), but also the approximate nature of the formulas relating the measured characteristics to the molecular potential (the uncertainty of the theoretical approximation).

A very common procedure is to choose a model potential and vary its parameters until a satisfactory fit to the experimental data is achieved. It is then important to remember that different model potentials can often predict the same experimental relationship. The experimental confirmation of the theoretical model must then be regarded as a necessary though not sufficient condition for the validity of the theoretical model. Thus, the magnitude of the second virial coefficient is not very sensitive to the shape of the potential curve or the position of its minimum, and depends only on the ratio of the width to depth of the potential well.[3] Viscosity is also relatively insensitive to the dependence of the potential on distance.

All this demonstrates the importance of theoretical determinations of potential curves. More realistic model potentials can be constructed once the analytical form of these potentials is known, at least qualitatively. Substantial success has in fact now been achieved in the development of a theory of intermolecular interactions.

It is very difficult to illuminate all the questions connected with the theory of intermolecular forces in a single review. We have tried to provide a general physical picture of the interaction between molecules, to analyze the contributions of different types of interaction as far as possible, and to identify among them those that are the most important for each range of separations. Considerable attention is devoted to the analysis of approximations used in different theoretical methods. Unfortunately, lack of space has prevented us from examining such important points as the nonadditivity of intermolecular forces, the choice of model potentials, the determination of potentials from experimental data, and certain other questions. Inclusion of these topics in the review would have resulted in an excessive degree of conciseness.

Before we proceed to the description of modern ideas on the nature of intermolecular forces, it will be instructive to examine the evolution of these concepts. The history of the subject is no different from that of other branches of knowledge in that it shows that many errors and misconceptions had to be resolved before the present level of understanding of molecular interactions was achieved.

1. DEVELOPMENT OF CLASSICAL IDEAS ON INTERMOLECULAR FORCES

The atomistic theory of the structure of matter is due to ancient philosophers. They believed that all bodies consisted of minute indivisible particles (atoms) separated by empty space. Interactions between atoms occured only on direct contact. In his poem, "De Rerum Natura," Lucretius presents the teaching of Epicurus and writes:[4]

> "Once again, things which seem hard, compact,
> Are made of atoms far more closely hooked,
> Are held more closely at their roots,
> (If such a metaphor I dare use)
> By branching particles.
> Of things like these, the diamond takes its stand
> in vanguard rank.
> It's schooled to disregard, despise all blows;
> Furthermore, things that seem hard and tightly packed
> must consist of atoms closely hooked together,
> and linked in a compact body by their branchlike connections.
> In the first rank of this category are diamond-stones,
> with their capacity for stountly swimming blows...
> But liquids, on the other hand, with their fluid nature

must consist of elements that are smooth and round...

The decline in the development of science in the Middle Ages was eventually followed by a resurgence of interest in the work of the ancient atomists, but not until the middle of the seventeenth century. Thus, the theories of Galileo are still devoid of any degree of realism. He describes matter in terms of particles in the form of mathematic points separated by empty space, and explains the rigidity of bodies in terms of the "abhorrence of vacuum", i.e., by the resistance of the minute empty spaces to any increase in their size.

The ideas of Descartes have had a major influence on the development of theories of the physical universe. According to Descartes, matter consists of particles of different shape and size. In contrast to the ideas of the ancient philosophers, each particle can now be sub-divided indefinitely. Descartes regards solid bodies as consisting of immobile particles in intimate contact with one another, and describes liquids as consisting of particles that move relative to one another. All the motions are purely mechanical displacements. Descartes' theory does not involve any "latent" interaction forces.

The basic difference between the atomistic theories of Newton and those of his precursors is that he does not restrict himself to purely mechanical interactions. "The parts of all homogeneal hard bodies," writes Newton,[5] "which fully touch one another stick together very strongly. And for explaining how this may be, some have invented hooked atoms... Others tell us that bodies...... stick together by conspiring motions... I had rather infer from their cohesion that their particles attract one another by some force, which in immediate contact is exceeding strong...." Newton then discusses the possibility of attraction with the aid of the forces of gravitation, magnetism, and electricity, but also admits that "there may be other attractions extending to such small distances that they have so far escaped observation." (Compare this with modern ideas on interactions!)

However, neither Newton nor any of his precursors gave a specific expression for the interaction force as a function of distance. The law of interaction between particles of matter was first introduced by the Croatian scientist, R. G. Boscovich (1711-1787). His fundamental work is, in fact, entitled "A Theory of Natural Philosophy Reduced to a Unique Single Law of Forces Existing in Nature."[6] Boscovich assumes than an oscillatory force operates between any two mass points and increases without limit as the particles approach one another. It takes the form of the Newtonian force of attraction $\sim 1/r^2$ at large separations. Boscovich says that he arrived at this idea by thinking about the mechanism of collision. He regards the alternation of attractive and repulsive forces as essential for the explanation of phenomena such as the expansion of gases, absorption, and deformation of plastic materials. Boscovich's law of interaction may be regarded as the first model potential used to explain physical properties.

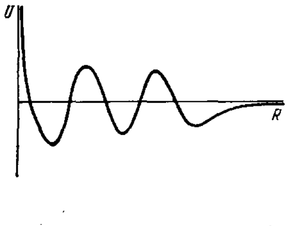

FIG. 1. Universal interaction law proposed by R. Boscovich.

More or less at the same time, the French physicist, A. C. Clairaut (1743) introduced the idea of forces between molecules in order to explain the rise of a liquid in a capillary. The role of molecular forces in capillary phenomena was subsequently discussed by Laplace (1805) and by Gauss (1830). However, the dependence of potential on distance was not specified.

In a series of classical papers on the kinetic theory of gases, Maxwell (1868) introduced the analytic expression $U=kR^{-n}$ for the repulsion between molecules as a function of distance. He used this to obtain expressions for the coefficients of diffusion, thermal conductivity, and viscosity. In the case of viscosity, it was known that it was independent of the gas density and proportional to absolute temperature. The former result can be obtained for any n and had, in fact, been derived for molecules in the form of noninteracting rigid spheres. The second result led Maxwell to the conclusion that $n=4$. Moreover, Maxwell considered that $U=kR^{-n}$ was valid at very small distances as well.

We now know that the repulsive part of the potential is not described by kR^{-4}. In fact, the great Maxwell fell into a logical trap: the fact that a particular assumption leads to a correct result was used to conclude that the assumption was correct without checking to what consequences other assumptions might lead. In this particular case, the fact that viscosity is proportional to temperature can be derived from an infinite number of different potentials $U(R)$.

Maxwell's result was erroneous but, nevertheless, it was very convenient mathematically and enabled him to obtain closed expressions for the different transport characteristics of gases, and this played a major role in the development of kinetic theory.

Different types of model potential were used in subsequent investigations. The forces of attraction which act between neutral atoms and molecules at large distances eventually became known as van der Waals forces. This was connected not with specific studies of the nature of intermolecular forces by van der Waals but with his well-known equation of state (1873)

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT \tag{1.1}$$

which takes into account the difference between a real gas and a perfect gas. The constant a in this equation represents the attraction between the gas molecules. In fact, an increase in a for constant V and T tends to reduce P. The attraction between the molecules should thus reduce the pressure on the walls of the container. The fact that a correction must be introduced for the forces of attraction in order to make the equation of state consistent with experimental data can be regarded as evidence for the existence of forces of attraction between molecules. In addition to phenomenologic approaches based on various model potentials, there were attempts at the end of the nineteenth and beginning of the twentieth century to explain the physical origin of intermolecular forces, in which these forces were related to gravitational forces. However, it was eventually realized that the latter were too weak and they were abandoned. On the other hand, it was becoming clear that atoms and molecules contained electric charges, and this led to the suggestion that intermolecular interactions were of electro-magnetic origin.

Reinganum[7] was the first to represent the interaction between two neutral particles as the interaction between permanent electric dipoles. Electrostatics shows that the energy of interaction between two electric dipoles with dipole moments $\mathbf{d}_1$ and $\mathbf{d}_2$ separated by a distance $\mathbf{R}$ depends on the mutual orientation of the dipoles and is given by

$$U_{dd}=\frac{R^2(\mathbf{d}_1\mathbf{d}_2)-3(\mathbf{d}_1\mathbf{R})(\mathbf{d}_2\mathbf{R})}{R^5} \tag{1.2}$$

If the directions of the two dipoles $\mathbf{d}_1$ and $\mathbf{d}_2$ are characterized by the polar angles θ_1, φ_1 and θ_2, φ_2 and the z axis is taken to lie along the line joining the centers of the dipoles, the formula given by (1.2) assumes the form

$$U_{dd}=-\frac{d_1d_2}{R^3}\left[2\cos\theta_1\cos\theta_2-\sin\theta_1\sin\theta_2\cos(\varphi_1-\varphi_2)\right]. \tag{1.3}$$

The energy U_{dd} is a minimum when the two dipoles lie along the z axis ($\theta_1=\theta_2=0, \varphi_1=\varphi_2$):

$$(U_{dd})_{\min}=-\frac{2d_1d_2}{R^3}. \tag{1.4}$$

Reinganum looked upon a medium as a set of parallel dipoles. He then examined the case of free dipoles and took the statistical average over all the orientations. If all directions of the dipoles are equally likely, the result is zero interaction energy, i.e.,

$$\langle U_{dd}\rangle=0, \tag{1.5}$$

where the angle brackets represent averaging over orientations. However, the probability that the dipoles have a particular orientation corresponding to an energy U is determined by the Boltzmann factor $\exp(-U/kT)$, so that, bearing in mind (1.5) and taking U in the form given by (1.3), we obtain the following expression for $U\ll kT$:

$$\langle U_{dd}e^{-U/kT}\rangle\approx\langle U_{dd}\rangle-\frac{1}{kT}\langle U_{dd}^2\rangle=-\frac{2}{3kT}\frac{d_1^2d_2^2}{R^6}. \tag{1.6}$$

It follows that the forces of attraction obtained by Reinganum for his dipoles tend to zero with increasing temperature. These forces were eventually referred to as alignment forces. Since the van der Waals forces are present at high temperatures as well, the introduction of alignment forces did not provide a complete explanation of the nature of intermolecular forces. In addition, the existence of alignment forces required as a precondition that the molecules had permanent dipole moments. It was believed at the time that all molecules had dipole moments. This was based on the investigations of Debye[8] into the theory of dielectric permittivity. Debye based his theory on the properties of five liquids which happened to be polar (alcohols) and came to the conclusion that all molecules were polar.

However, it became clear later that even the simplest homonuclear molecules, such as H_2, N_2, or O_2 did not have a dipole moment. To explain the interaction between them, Debye made the next important step toward an understanding of the nature of intermolecular forces.[9] He assumed that the charges in a molecule were not rigidly fixed but moved under the influence of the field due to the permanent dipole moment of another molecule.

Since not all molecules had dipole moments, Debye considered the case in which the electric dipole moment was induced in a particular molecule by the permanent quadrupole moment of another molecule. To do this, he calculated the electric field $\varepsilon_A(R)$ due to the quadrupole moment D_A of a molecule A at a distance R from it. A molecule B with polarizability α_B placed in this field would interact with molecule A so that the interaction energy would be $U_{AB}=-\vec{\varepsilon}_A\mathrm{d}_B=-\frac{1}{2}\alpha_B\varepsilon_A^2$. By taking into account the fact that molecule A was affected in a similar way by the quadrupole moment of molecule B, and by averaging over all the equally probable orientations, Debye succeeded in obtaining the following temperature-independent expression for the interaction energy:

$$\langle U_{AB}\rangle=-\alpha_A\frac{3}{2}\frac{D_B^2}{R^8}-\alpha_B\frac{3}{2}\frac{D_A^2}{R^8}, \tag{1.7}$$

where D_A and D_B are determined by the components of the quadrupole moment of the molecules. The interaction induced by dipole moments was subsequently examined by Falkenhagen.[10] Forces of the form given by (1.7) are now called the Debye-Falkenhagen induction forces.

Debye considered the induction interaction between molecules with large quadrupole moments, but did not examine the direct electrostatic interaction between the quadrupole moments of the molecules. This was subsequently done by Keesom,[11] who generalized the Reinganum calculations by including the dipole-quadrupole and quadrupole-quadrupole interactions in addition to the dipole-dipole interactions. As in the case of U_{dd}, it was again found that $\langle U_{qd}\rangle=\langle U_{qq}\rangle=0$, but the Boltzmann factor favors the states involving attraction. Alignment forces are occasionally referred to as Keesom forces.

Thus, classical physics has succeeded in explaining, at least qualitatively, two types of interaction: the interaction between molecules with permanent multipole moments and the interaction between permanent and induced moments in molecules. This was done by introducing alignment forces that decreased with increasing temperature and induction forces which were practically independent of temperature. For polar molecules, for example, H_2O, these forces provide the predominant contribution to the intermolecular interaction. However, for other molecules, for example, HCl, they explain only a small proportion of the interaction. Classical theory has also encountered a particular difficulty in the case of the interaction between noble-gas atoms. The electronic shells of these atoms are spherically symmetric, which means that such atoms have neither a dipole nor any other multipole moment. However, the interaction forces between them are of the same order as the interaction forces between polar molecules.

An explanation of the interaction forces between nonpolar molecules, and between the atoms of noble gases, has become possible only since the advent of quantum mechanics. Dispersion forces were first considered by Wang.[12] This was followed by the fundamental papers of London.[13-16] A rigorous theory of intermolecular forces giving a correct description at both small and large distances is based on the quantum-mechanical theory. It will be described below.

2. MODERN QUANTUM-MECHANICAL IDEAS ON INTERMOLECULAR INTERACTION

A. The concept of intermolecular potentials and classification of types of interaction

Intermolecular forces are due to electromagnetic interactions between the electrons and nuclei forming the molecule. The quantum-mechanical character of the motion of these particles must be taken into account when a rigorous theory of intermolecular forces is constructed. Consequently, the problem reduces to a solution of the Schrödinger equation for a system of interacting molecules, and can be solved only approximately. A substantial simplification and clarity are achieved by the fact that the electronic and nuclear motions can be separated, and by the introduction of the concept of potential-energy curves. We shall illustrate this problem by considering the example of two interacting atoms.

We shall represent the laboratory set of coordinates by $\mathbf{R}'_a$, $\mathbf{R}'_b$ (the coordinates of the nuclei) and $\mathbf{r}'_i$ (the coordinates of the electrons). Since the interaction energy is a function of only the relative separations of the particles, it is natural to transform to the center-of-mass system. This can be done in a number of ways.[17,18] The following is a convenient set of relative coordinates:[19-21]

$$\mathbf{R}=\mathbf{R}'_a-\mathbf{R}'_b, \quad \mathbf{r}_i=\mathbf{r}'_i-\frac{M_a\mathbf{R}'_a+M_b\mathbf{R}'_b}{M_a+M_b}. \tag{2.1}$$

When the motion of the center of mass has been separated out, we obtain the Hamilton for the relative motion

$$H=H_e+K_R, \tag{2.2}$$

where H_e is the Hamiltonian in the approximation of frozen nuclei[2)]

$$H_e=-\frac{1}{2}\sum_i\nabla_i^2-\sum_i\left(\frac{Z_a}{r_{ai}}+\frac{Z_b}{r_{bi}}\right)+\sum_{i<j}\frac{1}{r_{ij}}+\frac{Z_aZ_b}{R}, \tag{2.3}$$

$\mathbf{r}_{ai}$ is the distance of the i-th electron from the a-th nucleus, $\mathbf{r}_{ij}$ is the distance between electrons i, j, and Z_a is the charge of the nucleus a. The operator K_R is made up of the kinetic-energy operator describing the relative motion of the nuclei and the so-called mass-polarization term

$$K_R=-\frac{1}{2\mu}\nabla_R^2-\frac{1}{2(M_a+M_b)}\left(\sum_i\nabla_i\right)^2, \tag{2.4}$$

where $\mu=M_aM_b/(M_a+M_b)$ is the reduced mass of the nuclei. Since the electrons have small mass and, therefore, move much more rapidly than the nuclei, the latter can be regarded as being at rest in the zero-order approximation. Their motion can be taken into account in higher-order approximations. In the zero-order approximation, the wave function for the electron motion, $\psi_n(r,R)$, contains the distance R between the nuclei as a parameter (r represents the set of all the electron coordinates). To each value of R, there corresponds its own electron Schrödinger equation

$$H_e\psi_n(r,R)=E_n(R)\psi_n(r,R), \tag{2.5}$$

where the energy of the n-th state, $E_n(R)$, depends on R.

The solution of the Schrödinger equation for a system with total Hamiltonian given by (2.2)

$$H\Psi(r,R)=E\Psi(r,R) \tag{2.6}$$

can be written as an expansion over the complete set of eigenfunctions $\psi_n(r,R)$ of the Hamiltonian H_e:

$$\Psi(r,R)=\sum_n\chi_n(R)\psi_n(r,R). \tag{2.7}$$

The coefficients of this series are, of course, functions of R. Substituting (2.7) in (2.6), multiplying by $\psi_m^*(r,R)$, and integrating with respect to the electron coordinates, we obtain the following set of equations:

$$\left[-\frac{1}{2\mu}\nabla_R^2+E_m(R)-E\right]\chi_m(R)=\sum_n A_{mn}(R)\chi_m(R), \quad m=1,2,\ldots \tag{2.8}$$

$$A_{mn}(R)=\int\psi_m^*(r,R)\left[\frac{1}{\mu}\nabla_R\psi_n(r,R)\nabla_R-K_R\psi_n(r,R)\right]dv_r. \tag{2.9}$$

The set of equations given by (2.8) is exact. The Born-Oppenheimer approximation[22] (see also Refs. 23-25) corresponds to the separation of the set of equations (2.8) by equating to zero the right-hand sides:

$$\left[-\frac{1}{2\mu}\nabla_R^2+E_m(R)-E\right]\chi_m(R)=0. \tag{2.10}$$

In this approximation, the energy associated with the motion of the electrons, $E_m(R)$, is the potential energy for the motion of the nuclei.

The separation of the electronic and nuclear motions can also be performed by neglecting the off-diagonal terms $A_{mn}(R)$ on the right-hand sides of (2.8) and retaining only the diagonal terms.[26] Equation (2.10) is then replaced by

$$\left[-\frac{1}{2\mu}\nabla_R^2+V_m(R)-E\right]\chi_m(R)=0, \tag{2.11}$$

where the potential energy $W_m(R)$ is given by

$$V_m(R)=E_m(R)-A_{mm}(R). \tag{2.12}$$

The diagonal element $A_{mm}(R)$ can be interpreted as a correction to the potential energy, due to the coupling between the electronic and nuclear motions. Although any approximate method enabling us to separate the nuclear motion from the electronic motion may be referred to as the adiabatic approximation, this phrase is usually taken to represent the approximation defined by (2.11)-(2.12). It is occasionally also referred to as the Born approximation.[3)]

[2)] Here and henceforth, we use the atomic system of units in which $\hbar=e=m=1$.

[3)] We note that the above separation of electronic and nuclear motions is valid only in the case of nondegerate electronic states of the system. In the case of degenerate electronic

The accuracy of both the adiabatic and the Born-Oppenheimer approximations is very high. Precision calculations performed by Kolos and Wolniewicz[29,30] for the ground state of the H_2 molecule have shown that the results based on the adiabatic approximation are accurate to within about $10^{-2}\%$. An analysis of the accuracy of the adiabatic approximation and of the various types of correction to it can be found in the literature.[31-33]

Thus, the motion of the nuclei of the molecules may be looked upon as occurring in the adiabatic potential $V_m(R)$, called the intermolecular interaction potential, or simply the intermolecular potential. Knowing this potential is sufficient to enable us to investigate the behavior of the system of interacting molecules.

A typical intermolecular potential, averaged over the orientations of the molecule, as a function of the distance between the centers of gravity of the molecules is shown in Fig. 2. The curve in Fig. 2 is divided into three regions, namely: the region of small distances (I), in which the potential is repulsive and electron exchange is very important because of the overlap of the electron shells; the region of intermediate distances (II) with the van der Waals minimum, whose position is determined by the balance between repulsive and attractive forces; and the region of large distances (III), in which electron exchange can be neglected and the intermolecular forces are essentially attractive. It is also possible to define the region of ultralarge distances, for which retarded interactions must be taken into account.

Each range of distances is characterized by its own computational approximations which can be used to isolate different types of interaction and estimate their contribution to the overall intermolecular potential. In region III, where the intermolecular interactions are small and electron exchange is negligible, the standard Rayleigh-Schrödinger perturbation theory is valid. First-order perturbation theory yeilds directly the *electrostatic interaction* between the molecules. Higher orders of perturbation theory give the *polarization energy* which results from the polarization of one molecule by the electron cloud of another. In second-order perturbation theory, this subdivides into *induction* and *dispersion* components (this is described in greater detail below). This subdivision can no longer be performed in higher orders. Magnetic interactions are weak and are therefore manifested only in systems in which the electrostatic interaction falls off rapidly with distance (nonpolar molecules with nonzero spins).

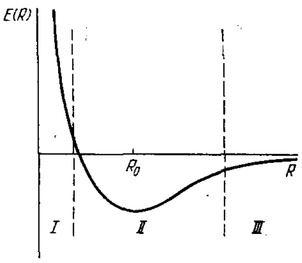

FIG. 2. Typical form of intermolecular potential: *I*—small distances; *II*—intermediate distances; *III*—large distances; R_0 is the van der Waals minimum.

For distances R for which the time R/c taken by the interaction to propagate is of the same order as the time $\sim\hbar/I$ of electronic transitions (I is the ionization potential), i.e., for $R\sim\hbar c/I$ it is essential to take into account the retardation of the interaction. This effect begins to be appreciable usually for $R\gtrsim 400a_0$. In this range of distances, one has to use field perturbation theory in which both the states of the interacting molecules and the states of the electromagnetic field have to be taken into account.

Electron exchange must be taken into account for $R \lesssim 15a_0$. The energy terms in first-order perturbation theory, which appear as a result of the antisymmetrization of the total wave function for the system of interacting molecules, are called the *exchange energy*. Corrections for exchange in higher-order perturbation theory are usually referred to as the *exchange-polarization energy*. At intermediate distances, in addition to exchange interactions, we also have interactions connected with *charge transfer* from one molecule to another.

At still shorter distances, i.e., for $R\lesssim 4a_0$, the molecules lose their individuality and the interacting system must be regarded as a single quasimolecule.

Table I shows the classification of the various types of interaction. Spin magnetic interactions are placed only in the last column because they can be neglected at all other distances (see, however, Sec. F).

The above classification of intermolecular interactions is, to some extent, conventional since it is based on an approximate analysis. The question is whether this type of classification is physically significant. The fact is that nature is not aware of our computational methods and the true potential curve contains contributions due to all types of interaction.

Fortunately, the answer to this question is in the affirmative. The representation of the interaction energy

TABLE I. Classification of types of interaction.

Small distances	Intermediate distances	Large distances	Ultralarge distances
Interactions in quasimolecule: 1. Coulomb 2. Exchange	1. Electrostatic 2. Exchange 3. Exchange-polarization 4. Charge transfer	1. Electrostatic multipole-multipole 2. Polarization: a) induction b) dispersion 3. Resonance 4. Relativistic, magnetic	1. Electromagnetic, retarded 2. Spin, magnetic

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states, the electronic and nuclear motions cannot be separated because the terms $A_{nm}(R)$ in (2.8) cannot be neglected. The energy $E_m(R)$ can then no longer be interpreted as the potential function for the motion of the nuclei. The states of the system, often referred to as the electronic-vibrational (of vibronic) states are obtained by solving a set of equations analogous to (2.8), the order of which is equal to the degree of degeneracy of the electronic level. Further details can be found in the literature.[27,28]

by the sum of different terms enables us to isolate terms that provide the greatest contribution in a given range of distances. As we shall see later, each term has a perfectly specific physical interpretation. This means that we can relate it to particular physical characteristics of molecules (polarizability, dipole and quadrupole moments, and so on). This, in turn, enables us to perform a qualitative estimate of the strength of the intermolecular interaction for different classes of molecules without having recourse to a complicated quantitative computation.

Let us consider the various types of molecular interaction in detail.

B. Direct electrostatic interaction

The energy of the electrostatic interaction in first-order perturbation theory is defined as the average of the electrostatic interaction operator over the quantum-mechanical distribution of the molecular changes.

After the separation of the motion of the center of mass [see (2.2)], the Hamiltonian for a system of two interacting molecules can be written as the sum of the Hamiltonians for the isolated molecules $H_0 = H_A + H_B$ plus the energy U of their electrostatic interaction:

$$H_e = H_0 + U, \tag{2.13}$$

$$U = -\sum_a \sum_{j=1}^{n_B} \frac{Z_a}{r_{aj}} - \sum_b \sum_{i=1}^{n_A} \frac{Z_b}{r_{bi}} + \sum_{i=1}^{n_A} \sum_{j=1}^{n_B} \frac{1}{r_{ij}} + \sum_{a,b} \frac{Z_a Z_b}{R_{ab}}, \tag{2.14}$$

where a, b labels the nuclei and i, j the electrons in the molecules A and B, respectively.

At large distances, the energy U may be regarded as a small perturbation. If we neglect electron exchange, the zero-order wave functions are given by simple products of the wave functions for the isolated molecules:

$$H_0 \psi_n^A \psi_m^B = (\varepsilon_n^A + \varepsilon_m^B)\, \psi_n^A \psi_m^B = E_{nm}^{(0)} \psi_n^A \psi_m^B, \tag{2.15}$$

where n, m is the set of quantum numbers characterizing the states of the isolated molecules.

The direct electrostatic interaction energy is defined by first-order perturbation theory and is given by

$$E_{\rm el}^{(1)} = \langle \psi_n^A \psi_m^B \,|\, U \,|\, \psi_n^A \psi_m^B \rangle. \tag{2.16}$$

At large distances between the molecules, the electrostatic energy may be satisfactorily represented by the sum of the first few terms of the expansion of $E_{\rm el}^{(1)}$ into a series in powers of $1/R$. This expansion is based on the introduction of the multipole moments of the charge distribution. At distances that are large in comparison with the linear dimensions of the system, the potential corresponding to the field produced by the system of charges can be written as an expansion in terms of the multipole moments. In Cartesian coordinates, the first three terms of this expansion at a point characterized by radius vector $\mathbf{R}$ are:

$$\varphi = \sum_i \frac{e_i}{|\mathbf{R} - \mathbf{r}_i|} = \frac{\sum_i e_i}{R} + \frac{\mathbf{d}\mathbf{R}}{R^3} + \frac{1}{6} \sum D_{\alpha\beta} \left(\frac{X_\alpha X_\beta}{R^5} - \frac{\delta_{\alpha\beta}}{R^3} \right) + \dots, \tag{2.17}$$

$$\mathbf{d} = \sum_i e_i \mathbf{r}_i, \quad D_{\alpha\beta} = \sum_i e_i (3 x_{i\alpha} x_{i\beta} - r_i^2 \delta_{\alpha\beta}), \dots, \tag{2.18}$$

where the sum over i is the sum over all charges of the system, $x_{i\alpha}, X_\alpha$ are the Cartesian coordinates corresponding to the position vectors $\mathbf{r}_i, \mathbf{R}, \mathbf{d}$ is the dipole moment of the system, and $D_{\alpha\beta}$ are the components of the quadrupole moment tensor of the system of charges. In their general form, the multipole moments written in terms of spherical polars are expressed in terms of irreducible tensor operators.[34,35]

In the case of electrically neutral systems, the expansion given by (2.17) begins with the term corresponding to the first nonzero 2^l-pole moment. We note that only the first nonzero moment is independent of the choice of the origin of the coordinate system.[36] The values of l for the ground state of the molecules belonging to different point symmetry groups are listed in Table II.

To ensure that a molecule has zero dipole moment in the ground state, it is sufficient to demand that it should have neither more than one symmetry axis, or a mirror rotation axis, or a center of symmetry. Such molecules include all the homonuclear diatomic molecules, ethylene, benzene, and many other molecules, for which the first nonzero moment is the quadrupole moment. The potential due to molecules of this type is proportional to $1/R^3$. In the case of the ground state of molecules with cubic symmetry, the first nonzero moment is the octupole moment (CH_4, SF_6, and so on) and the corresponding potential is $\sim 1/R^4$. Finally, for systems with spherical symmetry (atoms in the s state), all the multipole moments are zero. The most complete tables of dipole moments for different classes of molecular compounds are given in Ref. 37. Table III lists the mean values of quadrupole moments for a number of molecules.[38]

The energy of electrostatic interaction between two molecules may be looked upon as the potential energy of the charges belonging to one of the molecules in the field produced by the other:

$$U = \sum_i e_i \varphi(\mathbf{r}_i). \tag{2.19}$$

If the two molecules are at a large distance from one another, the potential $\varphi(\mathbf{r}_i)$ will be a slowly varying function of position in the region occupied by the first molecule. If we take the potential at some point 0 of this space, we can conveniently expand (2.19) into a series in powers of $\mathbf{r}_i$. The terms of this series will be characterized by the multipole moments of the first molecule, namely,

$$U = \left(\sum_i e_i \right) \varphi_0 + \mathbf{d}\, (\mathrm{grad}\, \varphi)_0 + \frac{1}{6} \sum_{\alpha\beta} D_{\alpha\beta} \left(\frac{\partial^2 \varphi}{\partial x_\alpha \partial x_\beta} \right)_0 + \dots \tag{2.20}$$

We now substitute the multipole expansion (2.17) for the potential φ in (2.20). The first term in (2.20) will then give the monopole-multipole interactions, the second will give the dipole-multipole interactions, and so on. Buckingham[36] has given an analysis of the number of

TABLE II. Values of l for the first nonzero $2l$-pole moment in the ground state of molecules of different symmetry.

Point group	C_n	C_{nv}	C_s	C_{nh} $n > 1$	S_n	D_n	D_{nd}	D_{nh}	T_d	O_h	K_h
l	1	1	1	2	2	2	2	2	3	3	Нет

TABLE III. Quadrupole moments of nonpolar molecules (in atomic units).

Molecule	H_2	N_2	O_2	CO	NO	CC_2	N_2O	C_2H_4
Quadrupole moment	0.6	1.6	1.0	2.1	2.0	4.1	4.2	3.2

independent constants in (2.20) for the different point symmetry groups encountered in the case of molecules.

For electrically neutral polar molecules, the first term in the interaction energy is the dipole-dipole term giving a $\sim 1/R^3$ dependence. The expression for this term is given by (1.2)–(1.3). In first-order perturbation theory, the inclusion of quantum-mechanical effects reduces only to the inclusion of the distribution of the charges in space. To determine the dipole-dipole interaction energy, the expression given by (1.2) must be substituted in operator form into the matrix element (2.16):

$$E_{dd}^{(1)}=\frac{(\mathbf{d}_{nn}^{A}\mathbf{d}_{mm}^{B})}{R^{3}}-\frac{3(\mathbf{d}_{nn}^{A}\mathbf{R})(\mathbf{d}_{mm}^{B}\mathbf{R})}{R^{5}}, \qquad (2.21)$$

where

$$\mathbf{d}_{nn}^{A}=\langle\psi_{n}^{A}|\mathbf{d}|\psi_{n}^{A}\rangle. \qquad (2.22)$$

According to Table II, the expectation value of the dipole moment is zero in the ground state, with the exception of molecules with point symmetry C_n and C_{nv}. The mean dipole moment may no longer be zero in the excited states of such molecules. States in which the average dipole moment is not zero can be obtained by decomposing the symmetric product of the corresponding irreducible representation with itself into irreducible parts.[39-41]

The electrostatic interaction between homonuclear diatomic molecules is described by the quadrupole-quadrupole term $\sim 1/R^5$, and the interaction between methane molecules is described by the ocupole-octupole term $\sim 1/R^7$. Table IV shows the distance dependence of the multipole-multipole interaction energy.

As already noted, the multipole expansion is valid for large distances between the interacting systems. The necessary condition for its validity is the absence of overlap between the charge distributions. Moreover, the quantum-mechanical "smearing out" of the charges ensures that this overlap will always occur. Since it decreases exponentially with distance, an expression for the interaction energy in the form of a multipole series implies that exponentially decreasing terms have been neglected. It is also important to emphasize that the multipole series converges only asymptotically to the true interaction energy. This means that exact convergence occurs only for $R\rightarrow\infty$. For finite R,[a] further increase in the number of expansion terms beyond a certain number will lead to the divergence of the series. The question of convergence of the multipole expansion will be considered below in Sec. 3A.

TABLE IV. Distance dependence of different multipole-multipole interactions.

	Monopole	Dipole	Quadrupole	Octupole	Hexadecupole
Monopole	$1/R$	$1/R^2$	$1/R^3$	$1/R^4$	$1/R^5$
Dipole	$1/R^2$	$1/R^3$	$1/R^4$	$1/R^5$	$1/R^6$
Quadrupole	$1/R^3$	$1/R^4$	$1/R^5$	$1/R^6$	$1/R^7$
Octupole	$1/R^4$	$1/R^5$	$1/R^6$	$1/R^7$	$1/R^8$
Hexadecupole	$1/R^5$	$1/R^6$	$1/R^7$	$1/R^8$	$1/R^9$

The strength of the multipole-multipole interactions depends on the mutual orientation of the molecules. When all the mutual orientations of the molecules are equally probable, the average of the interaction energy over their distribution is zero:

$$\langle U_{dd}\rangle=\langle U_{qq}\rangle=\ldots=0. \qquad (2.23)$$

However, the interaction energy does depend on orientation, and this means that orientations corresponding to lower energies are the more probable. The result of this is that the average orientation energy evaluated by taking into account the Boltzmann distribution is not zero. The expression for $\langle U_{dd}e^{-U_{dd}/KT}\rangle$ for $U_{dd}\ll kT$ turns out to be the same as the classical expression obtained by Reinganum and given by (1.6).

C. Polarization interactions

Forces that are due to the polarization of one molecule by the electron cloud of another are called *polarization forces*. They are described by second and higher orders of perturbation theory. The expression for the interaction energy between two molecules in ground states, in second-order perturbation theory, is[39]

$$E_{\mathrm{pol}}^{(2)}=-\sum_{m,\,n}{}'\frac{|\langle\psi_{n}^{A}\psi_{m}^{B}|U|\psi_{0}^{A}\psi_{0}^{B}\rangle|^{2}}{(\varepsilon_{n}^{A}-\varepsilon_{0}^{A})+(\varepsilon_{m}^{B}-\varepsilon_{0}^{B})}=E_{\mathrm{ind}}^{(2)}+E_{\mathrm{disp}}^{(2)}. \qquad (2.24)$$

The prime on the summation sign indicates that the quantum numbers n and m cannot simultaneously assume values corresponding to the ground states of the isolated molecules. The sum over n, m can be split into two parts which have different physical interpretations and are therefore given different designations. Let us consider them separately.

1) Induction forces:

$$E_{\mathrm{ind}}^{(2)}=-\sum_{m\neq 0}\frac{|\langle\psi_{0}^{A}\psi_{m}^{B}|U|\psi_{0}^{A}\psi_{0}^{B}\rangle|^{2}}{\varepsilon_{m}^{B}-\varepsilon_{0}^{B}}-\sum_{n\neq 0}\frac{|\langle\psi_{n}^{A}\psi_{0}^{B}|U|\psi_{0}^{A}\psi_{0}^{B}\rangle|^{2}}{\varepsilon_{n}^{A}-\varepsilon_{0}^{A}}. \qquad (2.25)$$

The first term corresponds to the electrostatic interaction between the charges of molecule A with the electron density distribution

$$\rho_{00}^{A}(i)=n_{A}\int|\psi_{0}^{A}(1\,\ldots\,i\,\ldots\,n_{A})|^{2}\,dv^{(i)}, \qquad (2.26)$$

and the charge distribution of molecule B with the electron density distribution

$$\rho_{m0}^{B}(j)=n_{B}\int\psi_{m}^{B}(1\,\ldots\,j\,\ldots\,n_{B})^{*}\,\psi_{0}^{B}(1\,\ldots\,j\,\ldots\,n_{B})\,dv^{(j)}. \qquad (2.27)$$

Since we are considering the interaction between molecules in ground states, the change in the electron-density distribution in molecule B must be induced by the field due to molecule A. Similarly, the second term in (2.25) corresponds to the interaction between molecule B in the electronic ground state and the induced electron density distribution in molecule A.

The induction energy is always negative for molecules in the electronic ground state, i.e., it correspond to an attraction. For electronically excited states, induction energy may correspond to either attraction or repulsion.

At large distances between the molecules, the induction force can be represented by a multipole series obtained by expanding U in (2.25) in powers of $1/R$. The first term in the series corresponds to the interaction between the induced dipoles and the field due to the inducing molecule. The dependence on $1/R$ is determined by the square of the corresponding dipole-multipole interaction and can be readily obtained from Table IV. Thus, for the interaction between an ion and a neutral molecule, the dominant term is $1/R^4$; for the interaction between a polar molecule and an arbitrary neutral molecule, the dominant term is $\sim 1/R^6$; the interaction between the quadrupole moment of one molecule and the induced dipole moment in another is $\sim 1/R^8$, and so on.

In the dipole-dipole approximation, the energy of induction interaction between two polar molecules is obtained by substituting (1.2) in (2.25) and averaging over the dipole orientations. The result is:

$$E^{(2)}_{\text{ind}}(d-d) = -\frac{2}{3R^6}(d^A_{00})^2 \sum_{m\neq 0} \frac{|\mathbf{d}^B_{m0}|^2}{\varepsilon^B_m - \varepsilon^B_0} - \frac{2}{3R^6}(d^B_{00})^2 \sum_{n\neq 0} \frac{|\mathbf{d}^A_{n0}|^2}{\varepsilon^A_n - \varepsilon^A_0}. \tag{2.28}$$

The sum in this expression can be readily expressed in terms of the mean statistical polarizability of the molecule

$$\alpha(0) \equiv \alpha_0 = \frac{2}{3} \sum_{n\neq 0} \frac{|\mathbf{d}_{n0}|^2}{\varepsilon_n - \varepsilon_0} \tag{2.29}$$

which can be measured. The result is an expression which is identical with the classical induction interaction between two dipoles:

$$E^{(2)}_{\text{ind}}(d-d) = -\frac{1}{R^6}\left[(d^A_{00})^2 \alpha^B_0 + (d^B_{00})^2 \alpha^A_0\right]. \tag{2.30}$$

Induction forces are very important in ion-molecule systems as well. In the case of neutral molecules, induction forces are usually very small with the exception of certain classes of molecules with large induced dipole moments, for example, long molecules with conjugated bonds, a number of biopolymers.

2) *Dispersion forces.* The interaction that remains after the polarization energy (2.24) is subtracted from (2.25) was called by London the dispersion interaction:

$$E^{(2)}_{\text{disp}} = -\sum_{m,\, n\neq 0} \frac{|\langle \psi^A_n \psi^B_m | U | \psi^A_0 \psi^B_0 \rangle|^2}{(\varepsilon^A_n - \varepsilon^A_0) + (\varepsilon^B_m - \varepsilon^B_0)}. \tag{2.31}$$

The matrix element $U_{nm,00}$ in this expression corresponds to the electrostatic interaction between two mutually induced electron density distributions:

$$U_{nm,00} = \int \rho^A_{n0}(i)\, \rho^B_{m0}(j) \frac{1}{r_{ij}}\, dv_i\, dv_j. \tag{2.32}$$

Dispersion energy does not have a classical analog and is determined by quantum-mechanical fluctuations in the electron density. The instantaneous charge distribution corresponding to the instantaneous dipole (plus subsequent multipole)moment of a given molecule induces dipole moments in the other molecule. The interaction between these molecules is, in fact, responsible for the dispersion energy. For molecules in the ground state, this is always negative, i.e., it corresponds to attraction.

TABLE V. Dispersion energy and coefficients C_n for two H atoms in the 1s state according to Kolos[42] (C_n is in atomic units, energy is in cm^{-1}).

R, in units of	C_6, Dipole-dipole	C_8, Dipole, quadrupole	Dipole-octupole C_{10}	Quadrupole-quadrupole
	6.499	124.4	2150.6	1135.2
	C_6/R^6	C_8/R^8	C_{10}/R^{10}	
8	5.44	1.63	0.67	
9	2.68	0.63	0.21	
10	1.43	0.27	0.07	

The multipole expansion of dispersion energy begins with the term $\sim 1/R^6$. It is usually written in the form

$$E^{(2)}_{\text{disp}} = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \ldots \tag{2.33}$$

The first term corresponds to the dipole-dipole interaction, the second to the dipole-quadrupole interaction, and the third contributes both as the dipole-octupole and the quardupole-quadrupole interaction. Both these contributions must be taken into account when the term proportional to $\sim 1/R^{10}$ is calculated. This is confirmed by precision calculations performed by Kolos[42] for two hydrogen atoms (Table V). Since hydrogen atoms in the ground state have no electric multipole moments, their interaction energy in the ground state is of the dispersion type (see, however, Sec. F).

As already noted in Sec. B, the multipole expansion converges to the exact energy only asymptotically. For finite R, the terms in the series $\sum_n (C_n/R^n)$ begin to increase in absolute magnitude beginning with a certain n. Nevertheless, this does not mean that the multipole series becomes useless. For sufficiently large R, the sum of the first few terms of the series is a good approximation to the energy. It follows from Table V that, for $R \gtrsim 10a_0$, the dispersion energy can be estimated from the first term, C_6/R^6, to within about 20%. This is the explanation for the large number of papers devoted to methods of calculating the coefficients C_6 and C_8 (Refs. 43–45; see also Ref. 55). For spherically symmetric systems, or for arbitrary systems after averaging over the orientations, the exact expression for C_6 is[4)]

$$C_6 = \frac{2}{3} \sum_{n,\, m\neq 0} \frac{|d^A_{n0}|^2 |d^B_{m0}|^2}{\omega^A_{n0} + \omega^B_{m0}}. \tag{2.34}$$

This can be readily expressed in terms of the oscillator strengths f_{n0} of isolated molecules:

$$f^A_{n0} = \frac{2}{3} \omega^A_{n0} |d^A_{n0}|^2, \tag{2.35}$$

and, in particular:

$$C_6 = \frac{3}{2} \sum_{n,\, m\neq 0} \frac{f^A_{n0} f^B_{m0}}{\omega^A_{n0} \omega^B_{m0} (\omega^A_{n0} + \omega^B_{m0})}. \tag{2.36}$$

Calculations based on this expression require a knowledge of the oscillator strengths for all the transitions to both the discrete and continuous spectra. Direct

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[4)] In the atomic system of units, the transition frequency is $\omega_{n0} = \varepsilon_n - \varepsilon_0$.

utilization of (2.36) in practical calculations is therefore difficult. However, this formula is convenient as a basis for deriving approximate expressions. The best known is the London formula, widely used for qualitative estimates. To derive this formula, we express the mean statistical polarizability α_0 (2.29) in terms of the oscillator strengths (2.35):

$$\alpha_0 = \sum_{n \neq 0} \frac{f_{n0}}{\omega_{n0}^2}. \tag{2.37}$$

For many molecules, it is possible to identify a narrow frequency band within which the oscillator strengths are much greater than elsewhere. The sums in (2.37) and (2.36) can then be replaced by a single term, and this leads to the well-known London formula

$$C_6 = \frac{3}{2} \alpha_0^A \alpha_0^B \frac{\omega_{K0}^A \omega_{l0}^B}{\omega_{K0}^A + \omega_{l0}^B}. \tag{2.38}$$

The frequencies ω_{K0}^A and ω_{l0}^B may be looked upon as empirical parameters. To be specific, they are usually replaced with the first ionization potentials, and the London formula is written in the form

$$C_6 = \frac{3}{2} \alpha_0^A \alpha_0^B \frac{I_1^A I_1^B}{I_1^A + I_1^B}. \tag{2.39}$$

This expression can be readily used to perform qualitative estimates of C_6, and the values obtained thereby are usually the lower limits for C_6. However, for two hydrogen atoms, the exact value of the dispersion energy is obtained by replacing I_1 by $\sim 5I_1/6$. The recommended values of C_6 and C_8 in the case of inert gases are listed in Table VI. For comparison, the last column lists the values of C_6 calculated from the London formula (2.39).

The Casimir-Polder integral identity[56] can be used to transform the exact formula (2.36) into an integral over dynamic polarizabilities, taken as functions of an imaginary argument[44,56]

$$C_6 = \frac{3}{\pi} \int_0^{\infty} \alpha^A (i\omega)\, \alpha^B (i\omega)\, d\omega, \tag{2.40}$$

where

$$\alpha (z) = \int_{\omega_{10}^2}^{\infty} \frac{df(\varepsilon)}{\varepsilon^2 - z^2} \tag{2.41}$$

is a generalization to the complex plane of the well-known expression for the Kramers-Heisenberg expression for the dynamic polarizability

$$\alpha (\omega) = \sum_{n=1}^{\infty} \frac{f_{n0}}{\omega_{n0}^2 - \omega^2}. \tag{2.42}$$

The formula given by (2.40) has been used in recent years to perform quite accurate calculations of C_6 for a number of atoms and simple molecules.[51,52] Nesbet[53] used Chebyshev estimates of the dynamic polarizability integral to obtain a value of C_6 for He-He. Tulub[54] used the Markov-Krein theorem,[57] well known in the theory of moments, to determine the extremal values of the integral given by (2.40). For polar molecules, polarization forces have both dispersion and induction components. Their ratio can be easily estimated from (2.30) and (2.39). For identical molecules, we have[58]

$$\frac{E_{\mathrm{disp}}}{E_{\mathrm{ind}}} = \frac{3}{8} I \frac{\alpha}{d^2}. \tag{2.43}$$

TABLE VI. Recommended values of the constants C_6 and C_8 for inert-gas atoms (atomic units).

System	C_6 [52]	C_8 [52]	I_1, эв	α_0, a_0^3	C_6 according to formula (2.39)
He—He	1.4614	14.2	24.580	1.3838	1.30
Ne—Ne	6.88	73.9	21.559	2.668	4.23
Ar—Ar	66.9	1176	15.755	11.09	53.25
Kr—Kr	135.1	2581	13.996	16.72	108
Xe—Xe	281.15	7033	12.127	27.34	250

D. Resonance interaction

Consider two molecules, one of which is in the ground and the other in an excited state. Resonance interactions are said to occur between the molecules if the energy associated with a transition to an excited state is the same in the two molecules (the molecules are in resonance). This situation will always occur in the case of interaction between identical molecules.

Suppose molecule D is initially in an excited state and molecule A in the ground state. The state of this system in the absence of interaction is described by the wave function $\psi_n^D \psi_0^A$. The resonance condition demands that the state described by the function $\psi_0^D \psi_n^A$ must correspond to the same energy. It follows that we have degeneracy. In first-order perturbation theory, this results in an energy matrix of the second rank. This can be diagonalized by constructing symmetric and antisymmetric linear combinations of the original zero-order functions:

$$\psi_{g,u} = \frac{1}{\sqrt{2}} (\psi_n^D \psi_0^A \pm \psi_0^D \psi_n^A). \tag{2.44}$$

The interaction energy in first-order perturbation theory is

$$E_{g,u}^{(1)} = \langle \psi_{g,u} | U | \psi_{g,u} \rangle = \langle \psi_n^D \psi_0^A | U | \psi_n^D \psi_0^A | \rangle \pm \langle \psi_0^D \psi_n^A | U | \psi_n^D \psi_0^A \rangle. \tag{2.45}$$

The first term in this expression represents the electrostatic energy of interaction between molecule D in the n-th excited state and molecule A in the ground state, which was considered in Sec. B. The second term represents the interaction between the transient electron densities in molecules A and D

$$U_{0n,n0} = \int \rho_{0n}^D (i)\, \rho_{n0}^A (j) \frac{1}{r_{ij}} dv_i\, dv_j, \tag{2.46}$$

and is due to the transfer of excitation from molecule D to molecule A. This is usually called the excitation-transfer matrix element or the resonance integral.

When the distance between the interacting molecules is large enough, the interaction energy can be expanded into a multipole series. For neutral molecules, the first nonvanishing term of this series is the dipole-dipole term. The result is that, even in the case of nonpolar molecules, there is a resonance dipole-dipole interaction, which falls off with distance as $\sim 1/R^3$. This resonance interaction has a greater range than the polarization interaction which falls off as $1/R^6$ and, depending on the parity of the stationary state, the energy given by (2.45) may be either positive or negative. The contribution of resonance interactions can also be important in second-order perturbation theory.[59] The interaction of a molecule in an excited electronic state and a molecule in the ground state leads to the formation of the so-called excimers and appears through the shift of the absorption and luminescence frequencies.

The form of the functions given by (2.44), which describe the states of the interacting system, suggests that the excitation can be found in molecule D with the same probability as in molecule A. If we suppose that, at time t, only one molecule is excited, the corresponding state will be nonstationary and the resonance interaction between the molecules will ensure that they will exchange excitation with frequency proportional to the resonance integral (2.46). This type of energy transfer resulting from resonance interaction is responsible for energy migration in crystals[60,61] and along a polymer chain[62] in the case of localized excitation of one of its fragments.

Resonance interaction is the reason for the appearance of delocalized exciton states in molecular crystals.[60,63] The width of the exciton band is then determined by the magnitude of the resonance integral and may reach quite large values. Thus, the resonance splitting of the lowest excited state in anthracene and naphthacene crystals is 220 cm^{-1} and 575 cm^{-1}, respectively.[63]

When the excitation transferred from the donor molecule to the acceptor molecule is rapidly dissipated so that the reverse transport cannot occur because of the departure from resonance condition, we have the unidirectional energy transfer process

$$D^* + A \rightarrow D + A^*, \tag{2.47}$$

which is at the basis of sensitized luminescence, resonance quenching, and certain other phenomena. The transport probability is then proportional to the square of the resonance integral, and falls off as $1/R^6$ for the dipole-dipole interactions. The theory of this radiationless energy transfer has been developed by Forster,[64] Dexter,[65] and Galanin.[66]

E. Inclusion of retardation in long-range interactions. Interaction between macroscopic bodies

It was assumed in the foregoing discussion that the charges interacted instantaneously. The retardation connected with the finite speed of light was not taken into account. However, when the separation between the molecules is large, such retarded effects may become important. In the case of dispersion forces taking retardation into account qualitatively alters their dependence on distance. Retarded effects are important when the separation R between the molecules becomes comparable with the wavelength λ of molecular transitions from the ground to the excited state.

It is interesting to note that the problem of retarded effects in the calculation of dispersion forces was encountered for the first time in connection with the theory of coagulation of colloids. Colloidal particles usually carry a charge which attracts ions of opposite sign in solution. The result is that each particle is surrounded by an electric double layer. These double layers repel one another as the particles get closer, and the forces of repulsion compete with the van der Waals attractive forces. The potential curve then exhibits a minimum which ensures the stability of the colloidal solution. A reduction in the thickness of the double layer leads to the predominance of attractive forces, the particles stick together, and are precipitated out (gel formation). Experimental studies[67] have shown that the observed minimum can only be explained if the dispersion interaction becomes weaker, as compared with the prediction based on the London formula, for distances $R > 400a_0$. Overbeek[67] has suggested that this weakening is due to the retardation associated with the finite time of propagation of the interaction. The dipole-dipole dispersion interaction corrected for retarded effects was first calculated by Casimir and Polder.[68] The calculation involved four orders of perturbation theory in the interaction between the molecule and the electromagnetic field.5) The resulting expression is

$$E_{retard}\,(d-d) = -\frac{4}{\pi}\sum_{n,\,m} |d_{n0}^{A}|^2\,|d_{m0}^{B}|^2\,\omega_{n0}^{A}\omega_{m0}^{B}$$

$$\times \int_0^\infty \frac{du\,u^4 e^{-2uR}}{R^2(\omega_{n0}^{A}+u^2)(\omega_{m0}^{B}+u^2)}\left(1+\frac{2}{uR}+\frac{5}{u^2R^2}+\frac{6}{u^3R^3}+\frac{3}{u^4R^4}\right) \tag{2.48}$$

and can be written in closed form in terms of sine and cosine integrals [see formula (33) in Ref. 72]. When R is much greater than the reduced average excitation wavelength $\bar{ƛ} = ƛ/2\pi$, we obtain the asymptotic Casimir-Polder formula

$$E_{retard\ as}(d-d) = -\frac{23}{4\pi}\frac{1}{\alpha R^7}\alpha_0^A\alpha_0^B, \quad R \gg \bar{ƛ} = \frac{\hbar c}{\overline{\Delta E}}, \tag{2.49}$$

where α_0^A is the static polarizability of molecule A and α is the fine structure constant. We emphasize that the Casimir-Polder formula is in no way a correction to the London formula. For $R > \bar{ƛ}$, the contribution due to transverse photons leads to the suppression of the term $\sim R^{-6}$. In terms of the atomic system of units, we have $\bar{ƛ} = (\Delta\bar{E}\alpha)^{-1}$. For He, $\Delta\bar{E} = 1.14$ atomic units and $\bar{ƛ} = 120a_0$. For the Lyman transitions in hydrogen, H$\bar{ƛ} \sim 245a_0$, and for characteristic transitions in organic molecules, $\bar{ƛ}$ is much greater and is of the order of $1000a_0$.

The physical reasons for the reduction in the strength of the dispersion interaction in the case of retardation can be readily understood. The field due to the instantaneous dipole moment $\mathbf{d}^A$ of molecule A reaches molecule B in a time R/c and induces in it a dipole moment $\mathbf{d}^B$ which interacts with $\mathbf{d}^A$ after a time $2R/c$. The dipole moment $\mathbf{d}^A$ may change its direction during this time and, in particular, it may rotate through 90°, resulting in zero interaction. Naturally, the retarded interaction will be weaker than the instantaneous interaction.

The Casimir-Polder potential is the first term of an asymptotic expansion in powers of $\bar{ƛ}$. For He-He, the first few terms of the asymptotic expansion are[74,75]

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5) Clearer derivations of the Casimir-Polder formula were given later.[59,70] Dzyaloshinskii[71] has derived the Casimir-Polder formula by the methods of quantum field theory. See also the review by Power.[72,73]

$$E^{\mathrm{He-He}}_{\mathrm{retard\ as}} = -3.48\alpha^{-1}R^{-7} + 21{,}51\alpha^{-3}R^{-9} - 395.36\alpha^{-5}R^{-11} + \ldots$$

Attractive forces analogous to the van der Waals forces between molecules are also found to arise when macroscopic bodies are brought together. The general theory of interaction between macroscopic bodies was developed by E. M. Lifshitz.[76] It is based on the idea that the interaction is due to fluctuations in the electromagnetic field within the body and outside its limits. Such fluctuations are always present and, like the thermal fluctuations, are of quantum-mechanical origin. The interacting bodies are looked upon as continuous media. The validity of this approach relies on the fact that the separation between the surfaces of the bodies, although small, is nevertheless much greater than the interatomic distances within them. The only macroscopic characteristic of bodies that determines the interaction forces between them is the imaginary part of their dielectric permittivity, $\varepsilon''(\omega)$. The theory developed in this way is valid for all bodies whatever their molecular structure. Since it starts with the exact equations for the electromagnetic field, it automatically takes into account the retardation effects. The Lifshitz theory has been generalized by the methods of quantum field theory to an arbitrary inhomogeneous medium by Dzyaloshinskiĭ and Pitaevskiĭ.[77] A detailed review of this theory can be found in the literature.[78] A relatively simple method of deriving the Lifshitz formula for the interaction energy between two plates is given by Pack.[84]

If it is assumed that the bodies are of sufficiently low density, the general formulas for the interaction between macroscopic bodies will eventually reduce to formulas for the interaction between individual atoms or molecules. This can be achieved by using the well-known relation between the imaginary part $\varepsilon''(\omega)$ of the dielectric permittivity and the spectral density of the oscillator strength $f(\omega)$. The final result for distances $R \ll \hbar c/\Delta E$ is the London formula with the coefficient C_6 given by (2.39). For $R \gg \hbar c/\Delta E$, the final result is the Casimir-Polder formula given by (2.49).

Thus, macroscopic analysis leads to the formula for the "microscopic" forces. This indicates that the macroscopic interaction is determined by the London (Casimir-Polder) dispersion forces. Although the interaction between the molecules making up the macroscopic body falls off with distance as R^{-6} (R^{-7}), the interaction between the bodies themselves falls off with distance much more slowly. In fact, the interaction energy per unit area of two flat plates separated by a gap l is obtained by integrating over all the interacting pairs and is given by[76]

$$\bar{E} = -\frac{C_6 \pi n_1 n_2}{12 l^2}, \qquad (2.50)$$

if each pair interacts according to the law C_6/R^6, and n_i is the concentration of the molecules in the i-th plate. When the interaction energy is $\sim 1/R^7$, the attractive energy between the plates decreases as l^{-3}.

Direct measurements of the interaction force between macroscopic bodies and of their dependence on distance have resulted in complete agreement with the theoretical predictions.[79,80] The greatest difficulty in these experiments is to produce pure and smooth surfaces, with protrusions not exceeding 10^{-5}–10^{-7} cm, and to achieve accurate measurement of distance. The latter is performed with the aid of multiple-beam interferometry.[81] The most accurate experiments[80] have resulted in successful measurements of the interaction when the distance between the surfaces was only $20a_0$.

F. Magnetic interactions

Corrections for retardation in the case of large separations between molecules, which were connected with the finite magnitude of the speed of light, i.e., corrections of relativistic origin, were discussed in the last section. Relativistic effects may also be appreciable at shorter distances, namely, for $R < \bar{\lambda}$. They are connected, above all, with magnetic interactions because the magnetic moment is of relativistic origin.

The exact relativistic Hamiltonian for $R < \bar{\lambda}$ can be replaced, to within terms of order α^2 by the Breit-Pauli Hamiltonian

$$\mathscr{H} = H_e + \alpha^2 H_{\mathrm{rel}}, \qquad (2.51)$$

where α is the fine-structure constant, H_e is the nonrelativistic Hamiltonian given by (2.13), and $\alpha^2 H_{\mathrm{rel}}$ represents the interaction between the magnetic moments of the system.[82,83,21]

Meath and Hirschfelder[75] have obtained a multipole expansion for all the terms in H_{rel}. They found that the first few terms of the multipole expansion for H_{rel} can be more slowly varying with R than the first terms in the non-relativistic expansion. Thus, only the dispersion energy remains for the interaction between two atoms in nondegenerate states, since the first-order energies vanish. For $R < \bar{\lambda}$, the result to within α^2 is

$$\mathscr{E} = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \ldots + \alpha^2\left(\frac{W_4}{R^4} + \frac{W_6}{R^6} + \ldots\right). \qquad (2.52)$$

The main relativistic correction to the London energy is provided by the term $\alpha^2 W_4/R^4$, in which the coefficient W_4, like the coefficient C_6 [see formula (2.36)], is expressed in terms of the oscillator strengths and the transition frequencies:

$$W_4 = \frac{1}{2} \sum_{n,\, m \neq 0} \frac{f^A_{n0} f^B_{m0}}{\omega^A_{n0} + \omega^B_{m0}}. \qquad (2.53)$$

Numerical estimates for the interaction between inert-gas atoms[74,75] show that C_6 and W_4 are of roughly the same order of magnitude. It follows that, at large separations, the relativistic contribution to the interaction energy becomes very substantial. The ratio of the leading terms in the relativistic and non-relativistic parts of the interaction energy is $\alpha^2 R^2 W_4/C_6$.

Let us now estimate this ratio for the He-He interaction. It has been reported[74] that, for He-He, the ratio is $W_4/C_6 \approx 0.45$ (see also Refs. 85 and 49). The result is that, for $R \approx 100a_0$, the relativistic repulsion compensates roughly a quarter of the dispersion attraction. It must be remembered, however, that (2.52) is valid in the absence of retardation, i.e., for $R < \bar{\lambda}$ (for He-He, $\bar{\lambda} \sim 120a_0$). Further corrections in α in the far-field zone can be obtained from the exact electrodynamic expression. These corrections are proportional to α^3/R^3

and α^4/R^2. According to the estimates of Meath and Hirschfelder,[75] the Breit-Pauli approximation (2.52) differs from the exact expression by not more than 5% for $R < 0.6\bar{\lambda}$.

For systems in degenerate states, the interaction energy may be nonzero even in first-order perturbation theory. The interaction may then be considered[86] without taking retardation into account for all R. This follows qualitatively from the fact that, in this case, $\bar{\lambda} = \hbar c/\Delta E \sim \infty$. For molecules with nonzero dipole electric and magnetic moments,

$$\mathscr{E} = \frac{C_3}{R^3} + \frac{\alpha^2 W_3}{R^3} + \cdots \tag{2.54}$$

Meath[87] has calculated the interaction energy for two hydrogen atoms in the ground state ($L_a = L_b = 0$) but different spin states:

$$\left.\begin{aligned}
\mathscr{E}(^1\Sigma_0) &= -\frac{6.50}{R^6} + \frac{0.46\alpha^2}{R^4} + \cdots,\\
\mathscr{E}(^3\Sigma_0) &= -\frac{6.50}{R^6} + \frac{0.46\alpha^2}{R^4} + \frac{\alpha^2}{R^3} + \cdots,\\
\mathscr{E}(^3\Sigma_1) = \mathscr{E}(^3\Sigma_{-1}) &= -\frac{6.50}{R^6} + \frac{0.46\alpha^2}{R^4} - \frac{\alpha^2}{2R^3} + \cdots
\end{aligned}\right\} \tag{2.55}$$

The magnetic spin-spin interactions appear only for the triplet states. The resultant relativistic energy for the term $^3\Sigma_0$ is 10% of the London energy already at distances $R \sim 22a_0$, whereas, for the $^3\Sigma_{\pm 1}$ terms, the corresponding distance is $R \sim 30a_0$. The spin-spin interaction becomes dominant for $R > 100a_0$. Since these interactions are static, they retain their form for $R > \bar{\lambda}$. It follows that, at large distances, the dominant term in the interaction energy for systems with zero dipole moment but nonzero spin is $\alpha^2 W_3/R^3$.

Chang[88] has estimated that the contribution of relativistic interactions to the O_g^+ term of the oxygen molecule is about 10–20% of the quadrupole interactions for $R = 30a_0$ and 35–60% for $R = 50a_0$. The inclusion of relativistic interactions is very important in the analysis of the interaction between electronically excited molecules and atoms and, in particular, for resonance interactions.[21,86,87,89-94]

The effect of spin interactions on molecular terms was investigated in detail by Harriman *et al.*[95] (see also Hirschfelder and Meath[21]) by considering the interaction between two hydrogen atoms. The effective Hamiltonian for the spin states of the two electrons with spins $\mathbf{S}_1, \mathbf{S}_2$ and the two protons with spins $\mathbf{I}_a, \mathbf{I}_b$ can be written in the form

$$\mathscr{H} = E_{\text{Coul}} - \left(\frac{1}{2} + 2\mathbf{S}_1\mathbf{S}_2\right) E_{\text{exch}} + (\mathbf{S}_1\mathbf{S}_2 - 3S_{z1}S_{z2})\frac{\alpha^2}{R^3} + A(\mathbf{S}_1\mathbf{I}_a + \mathbf{S}_2\mathbf{I}_b), \tag{2.56}$$

where $A = 0.047\ \text{cm}^{-1}$ is the hyperfine interaction constant. For $R < 9a_0$, terms due to the hyperfine interaction are small and it is sufficient to take into account only the electron spins. For $9a_0 < R < 12a_0$, it is essential to take into account all terms in the Hamiltonian given by (2.56). When $R = 12a_0$ $E_{\text{exch}} = A/12$, the singlet-triplet splitting becomes smaller than the hyperfine splitting. Thus, for $R \geqslant 12a_0$, the H_2 terms can no longer be classified as singlet and triplet on the basis of electron spins and one must start with the atomic states, described by the angular momentum, i.e., the sum of the electron and nuclear spins. Similar results have been reported by Milleur *et al.*[96] for HD and D_2.

Inclusion of the hyperfine interaction is important in scattering involving spin exchange. This influences the intensity of the 21-cm line familiar in rf spectroscopy, the polarization in electron spin resonance, optical pumping, hydrogen masers, and a number of other processes connected with spin interactions.

G. Exchange interactions

For $R \lesssim 15a_0$, it is essential to take into account electron exchange effects that are the consequence of Pauli's principle. According to this principle, the wave function of a system must be antisymmetric under the interachange of electrons not only in each of the molecules but between the molecules as well. In the zero-order approximation in the interaction between the molecules,

$$\Psi_0 = N_{AB}\sum_Q (-1)^q Q\psi_0^A\psi_0^B, \tag{2.57}$$

where Q is a permutation of electron exchange between molecules, q is the parity of the permutation, and N_{AB} is a normalizing factor. The expectation value of the interaction energy for the wave function given by (2.57), normalized for each R, and corresponding to the first-order perturbation theory, can be written in the form:

$$E^{(1)} = N_{AB}^2 N_Q\left(\langle\psi_0^A\psi_0^B|U|\psi_0^A\psi_0^B\rangle + \langle\psi_0^A\psi_0^B|U|\sum_{Q\neq I}(-1)^q Q\psi_0^A\psi_0^B\rangle\right), \tag{2.58}$$

where the first term represents the electrostatic energy (2.16) and the second the exchange energy $E_{\text{exch}}^{(1)}$. To determine this energy, we must include the overlap integrals in the normalizing factor. $N_Q = (N_A + N_B)!/(N_A!N_B!)$ is the number of permutations Q of the molecules, including the unit permutation. We emphasize that the sum over Q includes all the possible permutations of electron exchange between the molecules and not simply single transpositions of pairs. The exchange energy falls off exponentially to zero as the separation between the molecules increases.

When electron exchange is taken into account, the standard Rayleigh-Schrödinger perturbation theory cannot be used because the zero-order function (2.57) is not an eigenfunction of the zero-order Hamiltonian $H_0 = H_A + H_B$. Many different variants of the theory[97-119] have been constructed since the original paper by Eisenschitz and London.[13] They will be reviewed in Sec. 3B. Here, we merely mention that, in second- and higher-order perturbation theory, the exchange and polarization contributions to the energy cannot be separated and form the combined exchange-polarization energy. The omission of exchange in the second-order for $R \lesssim 6a_0$ leads to a substantial change in the polarization energy. This was clearly illustrated by Murrell and Shaw,[120] who calculated the dispersion energy for two hydrogen atoms in the ground state, with and without exchange. The contribution of exchange forces to the dispersion energy was calculated by Kochanski and Gauget[121] for the H_2-H_2 system.

The total contribution of exchange forces to the interaction energy increases rapidly as the molecules approach one another. For small distances, the interacting molecules can no longer be regarded as separate systems, and perturbation theory is no longer valid.

Figure 3 shows the variation in electron-density distribution in lithium atoms, calculated by a precision method involving the multi-configurational self-consistent field.[122] The electron distribution exhibits an analogous behavior in the case of interaction moelcules. In this region of separations, the interacting subsystems must be regarded as forming a single quantum-mechanical system—the quasimolecule—and the same methods must be used as in the case of calculations involving the electron shells of molecules. The variational approach and, in particular, the self-consistent field approximation with its various improved variants in which electron correlation is taken into account, has been found to be very acceptable. The variational method yields the total energy E of the system. The interaction energy is defined as the difference

$$E_{\text{int}} = E - (E_A + E_B). \tag{2.59}$$

If we neglect all terms containing the exchange electron density, we obtain the Coulomb interaction energy E_{Coul}, which includes all the multipole interactions. The exchange energy is then given by the difference

$$E_{\text{exch}} = E_{\text{int}} - E_{\text{Coul}}. \tag{2.60}$$

The most accurate calculations of the interaction energy have been carried out by Kolos and Vol'nevich[29,30,123,124] for the system of two hydrogen atoms, and recently by Kolos.[125-128] These calculations involve the use of 60-80-term variational functions of the James-Coolidge type. For the $^3\Sigma_u$ term, the van der Waals minimum with a depth of 4.3 cm^{-1} ($\sim 5 \times 10^{-4}$ eV) was obtained for $R = 7.85a_0$. The energy of zero-point oscillations is greater than this figure for H_2 but, in the case of D_2, it is found to be smaller. For the $^1\Pi_u$ terms, the van der Waals minimum turns out to be deeper, namely, $\sim$105.5 cm^{-1} ($\sim 1.3 \times 10^{-2}$ eV), and occurs at $R = 9a_0$.

For diatomic molecules with two valence electrons, the Coulomb and exchange energies are often[21,129] defined in terms of the energies of the lowest singlet and triplet terms:

$$E_{\text{Coul}} = \frac{1}{2}[E(^1\Sigma_g^+) + E(^3\Sigma_u^+)], \tag{2.61}$$

$$E_{\text{exch}} \equiv \Delta E^{ST} = \frac{1}{2}[E(^1\Sigma_g^+) - E(^3\Sigma_u^+)]. \tag{2.62}$$

Whilst, in first-order perturbation theory, the energies defined by (2.61) and (2.62) for atoms are identical with the atomic Coulomb and exchange energies, in the case of molecules, there is a discrepancy even in the first approximation because of the presence of the overlap integrals in the normalizing factor [see (2.58)], although the main contribution to (2.61) and (2.62) is, as before, provided by the Coulomb and exchange energies, respectively.

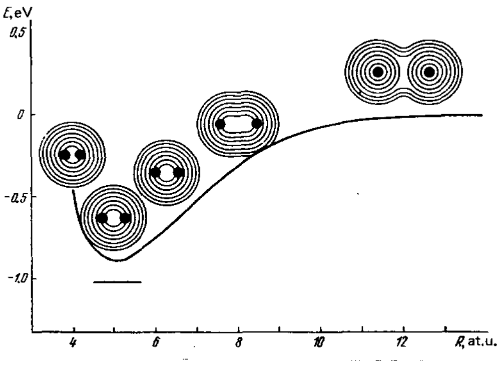

FIG. 3. Behavior of the charge density distribution as Li atoms approach one another:[122] solid curve—calculated binding energy; horizontal line—experimental binding energy.

Since the Heitler-London function yields the correct limiting expression for the energy as $R \to \infty$, one would expect that it would provide a better approximation to ΔE^{ST} as R increases. However, Herring[130] and Gor'kov and Pitaevskiĭ[131] have shown that the Heitler-London function leads to an incorrect asymptotic behavior of ΔE^{ST}. The correct asymptotic expression is[132]

$$\Delta E_{\text{as}} = -0.82\, R^{5/2} e^{-2R} + O\,(R^2 e^{-2R}), \tag{2.63}$$

whereas the Heitler-London approximation gives

$$(\Delta E_{as}^{ST})_{HL} = \left[-\frac{28}{45} + \frac{2}{15}(\gamma + \ln R)\right] R^3 e^{-2R} + O\,(R^2 e^{-2R}), \tag{2.64}$$

where $\gamma = 0.5772$ is the Euler constant. When $R \geqslant 60a_0$, the Heitler-London energy for $^3\Sigma_u^+$ becomes less than the energy of the ground state $^1\Sigma_g^+$. The reason for this is that electron correlation has not been adequately taken into account. Even the simplest variational function involving the 1s orbitals and taking into account electron correlation, i.e., the so-called Weinbaum function, gives nonintersecting singlet and triplet terms. Calculations performed[133] for $R = 8a_0$ in the case of the singlet-triplet splitting in a hydrogen molecule, taking into account the superposition of excited and ionic configurations, have resulted in an improved agreement with the exact Kolos-Vol'nevich variational calculation.

Table VII lists the values of ΔE^{ST}, calculated from the asymptotically correct formula (2.63) and the Heitler-London formula (2.64). The values of the dipole-dipole term in the dispersion energy are also given for comparison. It is clear from the table that, in the range $R = 7a_0$–$12a_0$, in which ΔE^{ST} is still small, the departure from the Heitler-London approximation is small. Substantial departures appear only for $R \geqslant 20a_0$, for which values of ΔE^{ST} become much smaller than the dispersion energy. For $R \gtrsim 30a_0$, magnetic spin-spin interactions provide an appreciable contribution (see Sec. F).

Moreover, for $R \geqslant 12a_0$, hyperfine interactions within the hydrogen atoms become greater than the exchange

TABLE VII. Singlet-triplet splitting ΔE^{ST} for two hydrogen atoms, calculated in different approximations (atomic units).

R, in units of a_0	$\Delta E_{\text{var}}^{ST}$ 124	$(\Delta E_{\text{as}}^{ST})_{HL}$	$\Delta E_{\text{as}}^{ST}$	$65R^{-6}$	ΔE^{ST} 133
7	0.0^4968	0.0^482	0.0^488	0.0^455	
8	0.0^41765	0.0^415	0.0^417	0.0^425	0.0^417
9	0.0^53117	0.0^528	0.0^530	0.0^412	
10	0.0^6537	0.0^649	0.0^654	0.0^565	
11	0.0^791	0.0^784	0.0^792	0.0^537	
12	0.0^716	0.0^714	0.0^715	0.0^522	
15		$0.0^{10}58$	$0.0^{10}67$	0.0^657	
20		$0.0^{14}50$	$0.0^{14}62$	0.0^610	
50		$0.0^{39}11$	$0.0^{39}54$	0.0^912	
60		$-0.0^{49}11$	$0.0^{47}18$	0.0^914	

energy. The molecular terms of H_2 can then no longer be classified by the total electron spin because there is a change in the nature of the coupling (see Sec. F). In this region of distances, ΔE^{ST} does not determine the actual splitting of the terms. Nevertheless, accurate values of ΔE^{ST} are of considerable interest because the cross sections for collisions with electron exchange are governed by this difference.[134,38]

The asymptotic behavior of the exchange term splitting in the case of many-electron atoms has been investigated in the literature[135-137] and is reviewed in detail in Smirnov's monograph.[38]

Charge transfer in which a valence electron is transferred from a neutral atom to an ion has a large cross section[134,38] in the case of collisions between ions and atoms (molecules). The charge-transfer cross section is determined by the exchange splitting of the symmetric and antisymmetric terms. In the case of H_2^+, the exchange splitting is given by

$$\Delta E_{\text{exch}} = \frac{1}{2}\,[E\,(^2\Sigma_g^+) - E\,(^2\Sigma_u^+)]. \tag{2.65}$$

It was first noted by Landau[39] and Herring[130] that the use of linear combinations of atomic orbitals leads to incorrect asymptotic expressions for (2.65). The asymptotic series for the energy of exchange interaction between a proton and a hydrogen atom in the ground state has been examined in the literature.[138-141] The first five terms of this series are

$$E_{\text{exch}}\,(H_2^+) = 2Re^{-R-1}\left(1 + \frac{1}{2R} - \frac{25}{8R^2} - \frac{131}{48R^3} - \frac{3923}{384R^4} - \dots\right). \tag{2.66}$$

In evaluating the asymptotic expansion for each value of R, only those terms are retained that are not greater than the preceding terms. Beginning with $R = 10a_0$, calculations based on (2.66) agree with those obtained from the exact solution of the problem.[142]

Electron transfer can also occur in the case of interaction between neutral molecules.[143-144] This happens when the potential energy curves that correspond at infinity to neutral molecules A, B and ions A^+, B^- approach one another very closely in a certain range of distances (in the absence of interaction, the curves will cross). Electron-transfer effects have been found in the case of collisions between alkali-metal atoms and halogen and other molecules with high electron affinities. The necessary energy can be drawn not only from the initial kinetic energy of the partners but also from the dissociative chemiionization.[144]

Allowance for energy transfer may lead to the stabilization of the system. In the zero-order approximation in the interaction, degeneracy is found to set in in the region of the AB and A^+B^- term crossing. The wave function for the system can be written as a superposition of the antisymmetric functions

$$\Psi_0 = \Psi_0\,(AB) + \alpha\Psi_0\,(A^+B^-), \tag{2.67}$$

where the coefficient α governs the contribution of the ionic states. If the molecule A has a low ionization potential and the molecule B^a high electron affinity, the contribution of states with energy transfer may substantially reduce the total energy of the system. This should lead to stable donor-acceptor complexes, as was first demonstrated by Mulliken.[145] Examples of such complexes are quinone-hydroquinone and I_2-benzene.

The inclusion of ionic terms leads to a reduction in the energy of the system in the case of identical molecules as well. Instead of (2.67), we then take

$$\Psi_0 = \Psi_0\,(AB) + \alpha\,[\Psi_0\,(A^+B^-) + \Psi_0\,(A^-B^+)]. \tag{2.68}$$

The use of the functions given by (2.67)–(2.68) in second-order perturbation theory results in corrections to the induction and dispersion energies, known as charge-transfer corrections.[146,147]

Transfers of charge and polarization are also additional stabilizing factors in the case of complexes with hydrogen bonding,[148-150] which is characterized by a relatively large stabilization energy (5–30 kcal) and forms in many hydrogen-containing compounds in the presence of an unshared electron pair. Characteristic complexes with hydrogen bonding are, for example, dimers of water, dimers of organic acids, and many protein structures. The hydrogen atom forms a kind of bridge between the interacting molecules in such complexes. The idea of charge transfer in compounds with hydrogen bonding (the donor-acceptor model) was put forward by Sokolov.[151-153] Several qualitative models were later suggested and analyzed.[148-150,154-156] It has become clear in the course of the last few years that a quantitative description of the hydrogen bond can be achieved only as a result of a complete quantum-mechanical calculation, including all the electrons in the complex and not merely the triatomic fragment containing the hydrogen atom. Such calculations rely on the variational method or the exchange perturbation theory (see below). A number of reviews have examined this question.[157-159]

H. Contribution of different kinds of interaction to the energy of the system of two hydrogen atoms

The analysis of different types of interaction given above in Secs. B–G enables us to represent the total interaction energy at large and intermediate distances as the sum of terms whose relative weight varies with the intermolecular distance. In the simplest case of two hydrogen atoms, the expression for the total energy for $8a_0 < R < 200a_0$ can be written in the form of the following asymptotically convergent series:[21] 6)

$$\begin{aligned} E_{\text{H-H}} = {} & \mp 0.82R^{5/2}\exp(-2R) + (W_3\alpha^2 - 0.3714\alpha^3)\,R^{-3} - 0.4628\alpha^2R^{-4} \\ & - 6.49927\,(1 + 0.00723)\,R^{-6} - 124.4\,(1 + 0.0038)\,R^{-8} \\ & -(1135 + 2150)\,(1 + 0.0049)\,R^{-10} - 3986\,(1 + 0.0054)\,R^{-11} + \dots \end{aligned} \tag{2.69}$$

In this expression, the exponential terms provide an asymptotically correct exchange energy [see (2.63)] and the negative and positive signs refer to the singlet and triplet electronic states, respectively. The term $W_3\alpha^2R^{-3}$ describes the spin-spin interactions. For R

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6) Bukta and Meath[236] have given an improved value for the coefficient of R^{-11} which appears in third-order perturbation theory. They have also calculated the coefficient of R^{-12}, which contains contributions of second- and fourth-order perturbation theory. These terms are: $3475R^{-11} - 122728R^{-12}$.

$<9a_0$, electron spin is a good quantum number and, at the same time, $W_3=0$ for $S=0$, $W_3=1$ for $S=1$, $M_S=0$, and $W_3=1/2$ for $S=1, M_S=\pm 1$ [see (2.55)]. For $R>9a_0$, electron spin is no longer a good quantum number since the interaction between the electron spin and the spin of the corresponding nucleus becomes greater than the interaction between the spins of the two electrons. The values of W_3 in this case were calculated by Harriman *et al.*[95] (see also Hirschfelder and Meath[21]). The terms proportional to α^3R^{-3} and α^2R^{-4} are the relativistic corrections obtained from the exact electrodynamic expression for $R<ƛ$ (see Sec. F). The terms $-6.499\ 027R^{-6}$, $-124.4R^{-8}$, $1135R^{-10}$, and $2150R^{-10}$ correspond to the dipole-dipole ($E^{(2)}_{dd}$), dipole-quadrupole ($E^{(2)}_{dq}$), quadrupole-quadrupole ($E^{(2)}_{qq}$), and dipole-octupole ($E^{(2)}_{d\text{-oct}}$) contribution to the second-order dispersion energy. The term $3989R^{-11}$ represents the third-order dipole-quadrupole-dipole dispersion energy ($E^{(3)}_{dqd}$). Finally, the small corrections to unity in parentheses are the nonadiabatic corrections to the Born-Oppenheimer approximation.

Table VIII lists the values of the different contributions to $E_{\text{H-H}}$. It follows from these data that, for $R>30a_0$, all the terms are smaller than the dispersion dipole-dipole term by at least two orders of magnitude, and only the contributions of the spin-spin interaction are comparable with the latter and even exceed it for $R>50a_0$.

We also note that, if we take into account the terms proportional to R^{-8}, R^{-10} in second-order dispersion theory, we must also take the term $\sim R^{-11}$ in third order. For $R>20a_0$, the contribution of the terms $\sim\alpha^2R^{-4}$ and α^3R^{-3}, which are due to relativistic corrections, are comparable in magnitude with $\sim R^{-10}$ and, for $R>40a_0$, with $\sim R^{-8}$.

3. METHOD OF CALCULATING THE POTENTIAL ENERGY CURVES AND THE CRITERIA FOR THEIR VALIDITY

In this section of our review, we shall briefly discuss the main methods for calculating different parts of the potential-energy curve. We shall devote particular attention to the criteria for the validity of the methods and to the analysis of the attendant uncertainties. We shall begin by considering the most commonly employed multipole expansion for the interaction energy, which can be used to calculate the tail of the potential energy curve. We shall follow this by a discussion of the recently developed numerous perturbation-theory formalisms which take into account electron exchange between subsystems. Finally, in the last section, we shall examine variational methods which can be used to calculate the entire potential curve rather than just its individual segments, as in the case of perturbation theory.

TABLE VIII. Contributions to the interaction energy between two hydrogen atoms (atomic units).

R, a_0	$E^{(1)}_{\text{exch}}$	$E^{(2)}_{dd}\sim R^{-6}$	$E^{(2)}_{dq}\sim R^{-8}$	$E^{(2)}_{qq}\sim R^{-10}$	$E^{(2)}_{d\text{-oct}}\sim R^{-10}$	$E^{(3)}_{dqd}\sim R^{-11}$	E_{rel}	$\alpha^2R^{-3}\sim E_{\text{spin}}$
7	$0.0^{4}88$	$0.0^{4}55$	$0.0^{4}22$	$0.0^{5}40$	$0.0^{5}76$	$0.0^{5}20$	$0.0^{8}98$	$0.0^{6}16$
9	$0.0^{5}30$	$0.0^{4}12$	$0.0^{5}29$	$0.0^{6}32$	$0.0^{6}62$	$0.0^{6}13$	$0.0^{8}36$	$0.0^{7}73$
11	$0.0^{7}92$	$0.0^{5}37$	$0.0^{6}58$	$0.0^{7}44$	$0.0^{7}83$	$0.0^{7}14$	$0.0^{8}16$	$0.0^{7}40$
15	$0.0^{10}67$	$0.0^{6}37$	$0.0^{7}48$	$0.0^{8}20$	$0.0^{8}37$	$0.0^{9}46$	$0.0^{9}44$	$0.0^{7}16$
18	$0.0^{12}26$	$0.0^{6}19$	$0.0^{7}11$	$0.0^{9}32$	$0.0^{9}60$	$0.0^{10}62$	$0.0^{9}21$	$0.0^{8}91$
20	$0.0^{14}62$	$0.0^{6}10$	$0.0^{8}48$	$0.0^{9}11$	$0.0^{9}21$	$0.0^{10}19$	$0.0^{9}14$	$0.0^{8}66$
35	$0.0^{26}24$	$0.0^{8}35$	$0.0^{10}55$	$0.0^{12}41$	$0.0^{12}78$	$0.0^{13}41$	$0.0^{10}13$	$0.0^{8}12$
50	$0.0^{39}54$	$0.0^{9}42$	$0.0^{11}32$	$0.0^{13}12$	$0.0^{13}22$	$0.0^{15}82$	$0.0^{11}28$	$0.0^{9}42$
60	$0.0^{47}18$	$0.0^{9}14$	$0.0^{12}74$	$0.0^{14}19$	$0.0^{14}36$	$0.0^{15}11$	$0.0^{11}12$	$0.0^{9}25$

A. Perturbation theory for long-range forces and the multipole expansion

For separations $R\gtrsim 10a_0-15a_0$ between the molecules exchange effects are negligible and the interaction energy can be calculated by standard Rayleigh-Schrödinger perturbation theory. The Hamiltonian for the system

$$H_e=H_A+H_B+U(R)\equiv H_0+U(R) \tag{3.1}$$

then contains the intermolecular interaction potential $U(R)$ which is regarded as a small perturbation to the zero-order Hamiltonian H_0. The zero-order wave function is taken to be the simple product of the wave functions of the isolated molecules. The interaction energy is then obtained in the form of the perturbation-theory series

$$E_{\text{Coul}}(R)=-E^{(1)}_L(R)+\sum_{n=2}^{\infty}E^{(n)}_{\text{pol}}(R), \tag{3.2}$$

whose terms can be calculated from standard formulas of quantum mechanics.[24,39] We emphasize that electron exchange is not taken into account in (3.2), i.e., the latter is the purely Coulomb energy.

At large distances, the Coulomb energy is usually written as a series in inverse powers of the intermolecular distance:

$$E_{\text{Coul as}}(R)=-\sum_{m=k}^{\infty}\frac{C_m}{R^m}. \tag{3.3}$$

The value of k depends on the number of the first nonzero multipole moment of the molecules (see Sec. 2B).

Theoretically there exist two equivalent methods for obtaining the expansion (3.3). The first method consists of the exact evaluation of the terms in the perturbation-theory series (3.2), followed by the expansion of each expression in powers of R^{-1}. This method is realistic only for simple systems, for example, H_2^+. In practice the second method is used, namely, the interaction operator in the matrix elements of the perturbation-theory formulas is expanded into a multipole series.

When the energy is written in the form of a series in powers of R^{-1}, this means in relation to (3.2) that exponentially decreasing terms have been neglected. The presence of the exponentially decreasing terms in the Coulomb energy is connected with the exponential decrease in the density of the charge cloud. We emphasize that, although these terms do have the distance dependence characteristic of exchange terms, they have, in fact, a different origin. It is therefore surprising to see the attempt[160] to obtain an asymptotic expansion of the singlet-triplet splitting with the aid of the perturbation-theory series (3.2).

Dalgarno and Lynn[161] have demonstrated the equivalence of the above two methods of deriving (3.3) by considering the energy of interaction between the ground-state of the hydrogen atom and H^+ in second-order perturbation theory. After neglecting the exponentially decreasing terms in the exact expression for the energy $E^{(2)}_{\text{pol}}$ and then expanding in powers of $1/R$, these workers obtained the following expression:[162]

$$E^{(2)}_{\text{pol.as}} = -2\sum_{l=1}^{\infty} \frac{(2l+2)!\,(l+2)}{(2R)^{2l+2}\,l\,(l+1)}. \tag{3.4}$$

This is identical with the expression obtained by expanding the interaction operator into a multipole series.[163] In the case of the excited states of H_2^+, the error introduced by expanding the energy in powers of $1/R$ may be quite large.[164]

Summation of the expansions in terms of powers of R^{-1} for each order of perturbation theory leads to (3.3). We note that if, in this procedure, we retain only the first two orders of perturbation theory, there is the danger that the neglected terms will be of the same order as those retained. Thus, in the case of H_2^+, expansion of the interaction potential into a multipole series has been used[165] to obtain the following expressions for the first few corrections to the energy:

$$\left.\begin{aligned} E^{(2)}(R) &= -\frac{9}{2R^4}-\frac{15}{R^6}-\frac{525}{4R^8}-\frac{2835}{4R^{10}}-O\left(\frac{1}{R^{11}}\right),\\ E^{(3)}(R) &= -\frac{213}{2R^7}-\frac{1773}{R^9}-O\left(\frac{1}{R^{11}}\right),\\ E^{(4)}(R) &= -\frac{3555}{32R^8}-\frac{80379}{8R^{10}}-O\left(\frac{1}{R^{11}}\right). \end{aligned}\right\} \tag{3.5}$$

It is clear from this that the retention of terms up to R^{-10} *inclusive in second-order perturbation theory is* sensible only if one also calculates the corrections to the interaction energy in the third and fourth orders.

It must, however, be remembered that the tendency to retain a large number of terms in the expansion in powers of R^{-1} may lead to a deterioration rather than an improvement in the results because the series in (3.3) converges only asymptotically, i.e., for $R\to\infty$. Thus, it is readily verified that the series (3.4) diverges for any finite R. To do this we determine the ratio of the $(n+1)$-th term to the n-th term:

$$\frac{a_{n+1}}{a_n} = \frac{1}{(2R)^2}\,\frac{2n\,(2n+3)\,(n+3)}{(n+2)}. \tag{3.6}$$

This ratio tends to infinity with increasing n for any finite R.

One of the first papers devoted to the convergence of the expansion in powers of $1/R$ was that due to Brooks,[166] who considered the interaction between two three-dimensional isotropic harmonic oscillators in second-order perturbation theory by writing the interaction potential in the form of the multipole series. Having evaluated the terms of these series analytically, he showed[7)] that the expansion of the interaction potential in powers of $1/R$ represented the exact value of $E^{(2)}_{\text{pol}}$ only asymptotically. At this point, it is obviously useful to introduce the definition of an asymptotic series.[168]

A series $\sum_k C_k/R^k$ is called asymptotic to the function $E(R)$ in the sense of Poincaré if for any positive integer N

$$\lim_{R\to\infty} R^N\left[E(R)-\sum_{k=0}^{N}\frac{C_k}{R^k}\right]=0 \ \text{for given } N, \tag{3.7}$$

even if

$$\lim_{N\to\infty} R^N\left[E(R)-\sum_{k=0}^{N}\frac{C_k}{R^k}\right]=\infty \ \text{for given } R. \tag{3.8}$$

Although the asymptotic series diverges for each given R, there is an optimum N for which the representation of the function by the series is the best. For a given N, the asymptotic series will represent the function with any given precision for sufficiently large R.

A rigorous proof that the multipole expansion is asymptotic has been given only for the ground states of simple systems such as H_2^+[161,163,169] and H_2.[167] For complicated systems, the divergence of the expansion is indicated by the behavior of the terms with decreasing R: successive terms in the series become comparable in magnitude.[164,170-172,42] Convergence of multipole expansions is worse in the excited than in the ground states because of the greater smearing out of the electron cloud in the former. Kolos[126] has calculated the interaction energy of H_2 in the $B^1\Sigma_u^+$ state dissociating into hydrogen atoms in 1*s* and 2*pσ* states, and has shown that the multipole series for E_{pol} as is, is a poor approximation to E_{pol} up to $R\sim 10a_0$ (Table IX).

For sufficiently large distances, the multipole expansion provides a satisfactory description of the interaction energy. In practice, the asymptotic series is truncated at the term after which an increase begins. One then takes the sum of all the terms up to the smallest plus half the smallest term.[165] For qualitative estimates at large R, it is sufficient to calculate the first term in the expansion. In the case of neutral systems, this term is C_6/R^6 (the methods for calculating C_6 are described in Sec. 2C.)

Direct evaluation of the perturbation-theory series (3.2) is a much more difficult problem than evaluation by expansion into powers of $1/R$. Nevertheless, this complication can be justified because, as a rule, the approximation (3.2) remains valid down to smaller distances than the expansion in powers of $1/R$. The connection between (3.2) and (3.3) has been investigated by Kreek *et al.*[169,173-177] In each order, the energy is written as the sum of terms, the so-called "unexpanded en-

TABLE IX. Estimated accuracy of the multipole expansion for the $B^1\Sigma_u^+$ state of H_2 (cm^{-1})[126].

R, a_0	$E^{(1)}_{\text{el}}$	$E^{(1)}_{\text{el.as}}$	$100\,\dfrac{E^{(1)}_{\text{el}}-E^{(1)}_{\text{el.as}}}{E^{(1)}_{\text{Coul}}}$	$E^{(2)}_{\text{pol}}$	$E^{(2)}_{\text{pol.as}}$	$100\,\dfrac{E^{(2)}_{\text{pol}}-E^{(2)}_{\text{pol.as}}}{E^{(2)}_{\text{pol}}}$
12	−155.41	−140.96	9.3%	−44.8	—	—
15	−73.37	−72.17	1.6%	−7.4	−5.6	24%
18	−41.86	−41.77	0.2%	−1.9	−1.6	15.8%
20	−30.46	−30.45	0.03%	−0.88	−0.71	19.3%

[7)] A critique of Brooks' proof has been given by Young.[167]

ergies," each of which (or their combination) tends with increasing R to zero or to one of the terms of the expansion in powers of $1/R$ in (3.3). The unexpanded energies contain exponentially decreasing terms due, as already noted, to the overlap of the charge distributions. Kreek and Meath[169] assert that the convergence problem does not arise in the case of the "unexpanded energy" series because each term is smaller than the preceding one. The sum of unexpanded energies converges smoothly to $E_{\text{pol}}^{(2)}$ at all distances. Calculations have been performed[169,173-176] for H_2^+, H_2, He_2, He, and H. The validity of the multipole expansion for the Coulomb energy in the first order has been discussed by Kin-Chue Ng *et al.*[177] in the case of the H_2-H_2 system.

B. Exchange perturbation theories

In the intermediate range of distances, $4a_0 \lesssim R \lesssim 15a_0$, the interaction between the molecules can still be looked upon as a perturbation but exchange effects must be taken into account in this region. The zero-order wave function must be antisymmetrized by introducing the wave functions of the isolated molecules:

$$\psi^{(0)} = A\psi_k \equiv A\psi_n^A\psi_m^B. \tag{3.9}$$

Since the functions ψ_n^A and ψ_m^B are antisymmetric, the operator A contains only the exchange permutations Q:

$$A = \sqrt{\frac{N_A!\,N_B!}{(N_A+N_B)!}} \sum_Q (-1)^q Q. \tag{3.10}$$

However, the function (3.9) is not an eigenfunction of the zero-order Hamiltonian H_0 since the latter is not invariant under the interchange of electrons between molecules.[8] The symmetry group of the total Hamiltonian turns out to be broader than the symmetry group of the zero-order Hamiltonian. In other words, the total Hamiltonian H_e [see (3.1)] commutes with the antisymmetrization operator:

$$[H_e, A] = 0, \tag{3.11}$$

while the zero-order Hamiltonian and the perturbation operator do not commute with A:

$$[H_0, A] \neq 0, \quad [U, A] \neq 0. \tag{3.12}$$

Consequently, the use of the antisymmetrized functions (3.9) as the zero-order functions will not allow us to employ the standard formulas of the Rayleigh-Schrödinger perturbation theory or the Brillouin-Wigner theory. On the other hand, if the zero-order eigenfunctions of the operator H_0 are taken to be $\{\psi_n^A\psi_m^B\}$, this leads to nonphysical solutions.[178]

The set of antisymmetric functions $\{A\psi_k\}$, where ψ_k is the product of the eigenfunctions of the isolated molecules, has a number of undesirable properties. The functions $A\psi_k$ are not orthogonal to one another which, apart from computational difficulties, means that the functions $A\psi_k$ cannot be the eigenfunctions of a Hermitian Hamiltonian. Moreover, the set of functions $\{A\psi_k\}$ is not complete because the $A\psi_k$ are not linearly independent. The proof of the last assertion can be given in a more general case.

Consider an arbitrary symmetric function φ_g. Let us expand it into a series over a certain complete set $\{\varphi_n\}$. This set can be taken to be, for example, the set $\{\psi_n^A\psi_m^B\}$, if φ_g is defined in the space of the N_A+N_B electrons:

$$\varphi_g = \sum_n C_{gn}\varphi_n. \tag{3.13}$$

If we apply the antisymmetrization operator A to both sides of (3.13), we obtain

$$A\varphi_g = 0 = \sum_n C_{gn} A\varphi_n. \tag{3.14}$$

This shows that the set $\{A\varphi_n\}$ is not linearly independent.

Since an expansion over a set that is not linearly independent is not unique, we have the possibility of constructing different variants of perturbation theory with the aid of the functions given by (3.9). It can be shown[179] that the expansion coefficients of a certain function f based on the antisymmetric set (3.9), i.e.,

$$f = \sum_k C_k A\varphi_k \tag{3.15}$$

have the following form:

$$C_k = N_Q^{-1/2}\langle\varphi_k | f\rangle + \langle\varphi_k | B\xi\rangle, \tag{3.16}$$

where $N_Q = (N_A+N_B)!/(N_A!N_B!)$ is the number of exchange permutations, $B = I - N^{-1/2}A$, and ξ is an arbitrary function of electron coordinates. Eisenschitz and London[13] define the coefficients C_k by demanding that the sum of the squares of the absolute values of the coefficients C_k be a minimum, which corresponds to $\xi = 0$. This choice is, in general, arbitrary and has no advantages as compared with the different choices characteristic of other formalisms.[179]

The Eisenschitz-London perturbation theory (EL)[13] was reformulated in the language of wave operators[180-181] by Van der Avoird.[106] This resulted in compact formulas for the energies and wave functions in arbitrary order of perturbation theory. For the first two orders, the interaction energy is

$$E^{(1)} = \frac{\langle\psi_0 | AU | \psi_0\rangle}{\langle\psi_0 | A\psi_0\rangle}, \tag{3.17}$$

$$E^{(2)} = \frac{1}{\langle\psi_0 | A\psi_0\rangle} \sum_{k\neq 0} \frac{\langle A(U-E^{(1)})\psi_0 | A\psi_k\rangle \langle\psi_k | A(U-E^{(1)})\psi_0\rangle}{E_0 - E_k}. \tag{3.18}$$

Expressions identical with these have also been obtained by Hirschfelder.[108] We shall refer to this particular variant of perturbation theory as EL-HAV (Eisenschitz-London-Hirschfelder-Van der Avoird).

The fact that the expansion in terms of the antisymmetric functions is not unambiguous has led to the appearance of a large number of different exchange perturbation theories. They can be divided into two groups, depending on the zero-order Hamiltonian em-

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[8] For example, for the simple case of two hydrogen atoms,
$$H_0 = H_A + H_B = -\tfrac{1}{2}\nabla_1^2 - \frac{1}{R_{a1}} - \tfrac{1}{2}\nabla_2^2 - \frac{1}{R_{b2}}.$$
It is clear that H_0 is not symmetric under the interchange of the numbers labeling the electrons. The symmetric Hamiltonian is obtained only by adding to H_0 the interaction operator U
$$U = -\frac{1}{R_{a2}} - \frac{1}{R_{b1}} + \frac{1}{r_{12}} + \frac{1}{R_{ab}}.$$

ployed. "Nonsymmetric" theories[106-119] use $H_0 = H_A + H_B$ as the zero-order Hamiltonian.[9] The theories differ by the different methods used to choose the zero-order functions. In "symmetric" formalisms,[97-105] the procedure is to construct a symmetric zero-order Hamiltonian H_s with antisymmetric eigenfunctions. Once this is done, the usual Rayleigh-Schrödinger perturbation theory is employed.

Symmetric theories encounter considerable difficulties when the number of electrons is greater than two. Moreover, the Hamiltonian H_s is not Hermitian. "Nonsymmetric" theories are much more widely used. Before we review the various non-symmetric approaches, we define the following abbreviations: AM (Amos-Musher[112]), MS-MA (Murrell-Shaw-Musher-Amos[109-110]), HS (Hirschfelder-Silbey[114]), CBH (Chipman-Bowman-Hirschfelder[118]), and MJ (Matsen-Junker[115]).

An analysis of the ambiguities of nonsymmetric formalisms and a discussion of the connection between them can be found in the literature.[182-185,115,118] When the symmetry of a Hamiltonian is examined, it must be remembered that the symmetry of the Hamiltonian H may be different from that of H_0 both with respect to permutations and operations of spatial transformation. In general, one must start with the symmetry group G that is the outer product of the permutation group by the point symmetry group of the system. The basis function corresponding to the representation ${}^{\nu}\Gamma$ of the group G can be constructed from the nonsymmetric function ξ with the aid of the projection operator[41]

$${}^{\nu}A = \frac{{}^{\nu}f}{g} \sum_R {}^{\nu}\chi(R)\, R, \tag{3.19}$$

where ${}^{\nu}f$ is the dimensionality of the representaion ${}^{\nu}\Gamma$, g is the number of elements in the group, and ${}^{\nu}\chi(R)$ is the character of the representation. The operators ${}^{\nu}A$ are idempotent, orthogonal, and complete:

$${}^{\nu}A\,{}^{\mu}A = \delta_{\mu\nu}\,{}^{\nu}A, \quad \sum_{\nu} {}^{\nu}A = 1. \tag{3.20}$$

The function that is the solution of the Schrödinger equation with the total Hamiltonian H_e can be written as follows:

$${}^{\nu}\psi = {}^{\nu}A\,\xi_{\nu}, \tag{3.21}$$

where ξ_ν is a nonsymmetric function. The subscript ν on the function ξ_ν indicates that, for each representation ${}^{\nu}\Gamma$, one can, in general, take its own nonsymmetric function ξ_ν.

When the wave function is taken in the form given by (3.21), the perturbation-theory equations assume the following form:

$${}^{\nu}AH_0\xi^{(0)} = E_0\,{}^{\nu}A\xi^{(0)}, \tag{3.22a}$$

$${}^{\nu}A\,(H_0 - E_0)\,{}^{\nu}\xi^{(1)} = {}^{\nu}A\,({}^{\nu}E^{(1)} - U)\,\xi^{(0)}, \tag{3.22b}$$

$${}^{\nu}A\,(H_0 - E_0)\,{}^{\nu}\xi^{(n)} = {}^{\nu}A\,({}^{\nu}E^{(1)} - U)\,{}^{\nu}\xi^{(n-1)} + \sum_{m=2}^{n} {}^{\nu}A\,{}^{\nu}E^{(m)}\,{}^{\nu}\xi^{(n-m)} \quad (n \geqslant 2). \tag{3.22c}$$

Byers Brown[182] (see also Amos[183]) was the first to note that these equations would not define ${}^{\nu}E^{(m)}$ because there was no function which, when multiplied by the left-hand side and integrated, would yield zero. This means that Eqs. (3.22b)–(3.22c) can be solved for any ${}^{\nu}E^{(m)}$, i.e., ${}^{\nu}\xi^{(m)}$ are not uniquely defined by the set of equations (3.22).[10] This was to be expected in view of the ambiguities mentioned above.

Amos[183] has shown that many of the variants of exchange perturbation theory can be obtained by eliminating the operator ${}^{\nu}A$ from (3.22). This, in fact, means the imposition of additional conditions on ξ_ν and ensures that it is uniquely defined.

Thus, the EL-HAV method[13,106,108] corresponds to the solution of (3.22) without the operator ${}^{\nu}A$ on the left-hand side of the equations. This is equivalent to the assumption that

$$(1 - {}^{\nu}A)(H_0 - E)\,\xi_{\nu}^{(n)} = 0 \text{ for all } n, \tag{3.24}$$

or, on summing the equations over n,

$$(1 - {}^{\nu}A)\;(H_0 - E_0)\xi = 0; \tag{3.25}$$

which, according to Amos,[183] is the additional condition on ξ_ν. When this condition is taken into account, the Schrödinger equation yields

$$(H_0 - E_0)\xi_\nu + {}^{\nu}A\,[U - ({}^{\nu}E - E_0)]\xi_\nu = 0, \tag{3.26}$$

which is, in fact, the basic equation of the EL-HAV method.

The exclusion of ${}^{\nu}A$ from (3.22) everywhere except for the terms in which this operator precedes U leads to the equation of the AM method:[112]

$$(H_0 + {}^{\nu}A\,U)\,\xi_\nu = {}^{\nu}E\xi_\nu, \tag{3.27}$$

with the following condition on ξ_ν:

$$(1 - {}^{\nu}A)\;(H_0 - {}^{\nu}E)\,\xi_\nu = 0. \tag{3.28}$$

The MS-MA method[109-110] is obtained from (3.22) by eliminating ${}^{\nu}A$ from the first term in (3.22b) and from all terms of (3.22c):

$$(H - {}^{\nu}E)\,\xi_\nu = (1 - {}^{\nu}A)\;(H - {}^{\nu}E)\,\xi^{(0)}, \tag{3.29}$$

and this corresponds to the additional condition

$$(1 - {}^{\nu}A)\;(H - {}^{\nu}E)\;(\xi_\nu - \xi^{(0)}) = 0. \tag{3.30}$$

Further conditions are imposed on the wave function in the HS[114] and MJ[115] methods.

The above procedures correspond to the subdivision of the equation

$$(H - E)\,A\xi = 0 \tag{3.31}$$

into the basic equation of the method

$$L_1\xi' = 0, \tag{3.32}$$

and the equation

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[9] A common phrase used in English-language literature is "*symmetry adapted theories*," which reflects the fact that, although the Hamiltonian H_0 is not symmetric, the zero-order functions have the right symmetry.

[10] In traditional Rayleigh-Schrödinger perturbation theory, H_0 commutes with A. If we multiply (3.22b) by $\xi^{(0)}$ from the left and integrate, we obtain

$$E^{(1)} = \frac{\langle \xi^{(0)} | U | \xi^{(0)} \rangle}{\langle \xi^{(0)} | \xi^{(0)} \rangle}, \tag{3.23}$$

and $\xi^{(1)}$ is uniquely determined by (3.22b).

$$L_2\xi' = 0, \tag{3.33}$$

which is referred to[183-184,115] as the additional condition on the function ξ'. The interpretation of (3.33) as the condition that must be satisfied by ξ' means that we must solve (3.32) and (3.33) simultaneously.

In actual fact, Eq. (3.32) is the only to be solved in exchange perturbation theories, i.e., the functions obtained by these methods do not necessarily satisfy the additional conditions. Moreover, it has been shown[184] that additional conditions cannot be satisfied in EL-HAV, AM, MS-MA by the functions ξ' used in these methods. On the other hand, Suzuki and I'Haya[184] have concluded that this means that the basic equations of these methods are not physically consistent. This conclusion cannot be regarded as justified. In fact, the complete equation (3.31) is replaced in these methods by the approximate equation (3.32) and the quality of this approximation depends on the size of the neglected terms. Since the neglected terms are determined by the exchange of electrons between the molecules, the corresponding matrix elements will be small for large enough distances, and the approximation may yield good results whether or not the additional conditions are satisfied.

Particular calculations have shown (see, for example, Chipman and Hirschfelder[186] and Certain and Hirschfelder[187]) that the EL-HAV, AM, MS-MA, HS, CBH, and so on formalisms lead, in general, to satisfactory results for real systems. This has been quoted by Chipman[185] as the main argument in favor of the exchange perturbation formalisms criticized by Suzuki.[184]

The question as to which of these methods is the best can be answered only on the basis of numerical calculations.

Such calculations have been performed for H_2[187,188] and H_2^+.[186] (For recent calculations of the triplet state of H_2 by the MS-MA method, see Magnasco *et al.*[189]) The sum of the first and second orders of exchange perturbation theory provides a good representation of the interaction energy for $R \geqslant 8a_0$. The only exception is the EL-HAV method. The best results are obtained by the CBH method whereas other methods are roughly equivalent at intermediate distances. Although the CBH method gives the best results, it is much more complicated in computational respects than the other formalisms and, in this sense, is comparable with the variational method. As the distance increases, the EL-HAV method gives inferior results. Calculations for the ground and first excited state of H_2 have shown[187-188] that $E^{(2)}$ (EL-HAV) is about half $E^{(2)}_{\text{disp}}$ at $R = 8a_0$ although, at distances at which exchange effects are small, exchange perturbation theory should give results that are close to standard perturbation theory. The relation $E^{(2)}\text{(EL-HAV)} = \frac{1}{2}E^{(2)}_{\text{disp}}$ has been obtained for large distances also in the case of H_2^+[190] and for model systems.[191,192] The factor 1/2 initially appeared to be magic. However, calculations[186] in the case of H_2^+, using a broader basis than that employed by Van der Avoird,[190] yielded a factor of ~3/4. A small modification of the δ-function model yielded[193] a factor of 1. The asymptotic behavior of the energy in the EL-HAV method is, therefore, sensitive to the choice of basis. A sufficiently broad basis should lead to correct asymptotic behavior and, therefore, the proof given by Basilevsky and Berenfeld[105] that the asymptotic behavior of energy is independent of the size of the finite basis seems to us to be incorrect.

The formalisms examined above are found to differ in second-order perturbation theory because of the presence of exchange terms. For noble-gas atoms in ground states, Murrell *et al.*[194-196] have found that the interaction energy can be represented, to a good approximation, by the sum of the first-order Coulomb exchange energy, the second-order polarization energy, and the "zero-order" energy connected with the approximate character of the atomic basis functions. The precision of these calculations is comparable with that of the variational calculations, and they satisfactorily reproduce the experimental curves.

Calculations performed by Kolos[125-126] in the case of the $^3\Sigma_u^+$ and $X^1\Sigma_g^+$ states of H_2 have also shown that the predominant contribution to the interaction energy is due to the sum of first-order Coulomb and exchange energies and second-order polarization energy:

$$E \sim E^{(1)}_{\text{el}} + E^{(1)}_{\text{exch}} + E^{(2)}_{\text{pol}}. \tag{3.34}$$

Since the difficulties encountered in finding the exchange terms in the exchange perturbation theory begin with the second order, the formula given by (3.34) enables us to perform calculations in the case of complicated systems. In fact, Jeziorski and Van Hemert[197] have used this approximation in the case of the water dimer $(H_2O)_2$. The wave functions obtained by the self-consistent field method were used as the wave functions for the monomers. These calculations have shown that the dominant terms in the energy are the electrostatic attraction $E^{(1)}_{\text{el}}$ and the exchange repulsion $E^{(1)}_{\text{exch}}$ (Table X). However, in the region of the minimum, these two terms are not sufficient because they lead to bonding that is too weak. Hydrogen bonding is stabilized by the polarization interaction. It is also interesting to note that, whereas at small distances the contribution of induction forces exceeds the contribution of dispersion forces, the picture changes as the distances increase.

However, the three-term expansion (3.34) is not always sufficient to achieve a satisfactory description of the potential curve. Thus, the energy corresponding to the molecular term $B^1\Sigma_u^+$, obtained in the case of the interaction between the H atom in the 1s state and the

TABLE X. Contributions to the $(H_2O)_2$ interaction energy[197] (kcal/mol).

$R_{\text{O-O}}$, in units of a_0	$E^{(1)}_{\text{el}}$	$E^{(1)}_{\text{exch}}$	$E^{(2)}_{\text{ind}}$	$E^{(2)}_{\text{disp}}$
4.0	−43.09	105.49	−49.30	−14.46
4.40	−27.10	51.58	−21.00	−8.41
4.80	−17.07	25.11	−9.30	−4.80
5.20	−11.10	12.03	−4.12	−2.85
5.67	−7.12	4.90	−1.63	−1.54
7.00	−2.79	0.30	−0.18	−0.31
9.00	−1.12	0.00	−0.02	−0.05
15.00	−0.21	0.00	−0.00	−0.00

H atom in the $2p\sigma$ state, is determined by the terms[126]

$$E \sim E^{(1)}_{\rm el} + E^{(2)}_{\rm exch}. \qquad (3.35)$$

In the case of the H^+-He system, the first-order energy turns out to be negligible compared with the second- and higher-order energies:[127]

$$E \sim E^{(2)}_{\rm pol} + E^{(2)}_{\rm exch}. \qquad (3.36)$$

We conclude this section by briefly considering symmetric variants of exchange perturbation theory. It has been shown[97-98] that, for two-electron systems, it is possible to contruct the zero-order Hamiltonian H_s for which the antisymmetric function is an eigenfunction. This is the so-called Sternheimer Hamiltonian. This Hamiltonian has been used[187,188] in calculations of the interaction in the ground state of H_2, and has yielded satisfactory results. The different modifications of the symmetric Hamiltonian can be found in the literature.[99,103-104] They are all valid in the case of systems with not more than two electrons.[198,199] An attempt was made by Epstein and Karl[101] to generalize the definition of the Sternheimer potential to many-electron systems but no specific calculations were reported. The basic difficulty in using the above symmetric variants of the exchange perturbation theory is that the zero-order Hamiltonian is not Hermitian. Basilevsky and Berenfeld[105] have constructed a variant of symmetric exchange perturbation theory using the second quantization formalism and orthogonalization of the basis functions.

An unusual approach in which standard perturbation theory can be used to calculate intermolecular interactions has been developed by Daudey *et al.*[200-202] Here, the Rayleigh-Schrödinger perturbation theory is used to calculate the total energies of dimers and monomers by replacing the perturbation operator by the corresponding Hamiltonian. The interaction energy is obtained as in the variational method in the form of the energy difference between the dimers and the monomers, calculated in the same perturbation-theory orders. A preliminary step is the solution of the self-consistent field equations and the determination of the molecular orbitals of the monomers. To ensure that standard perturbation theory can be used, the molecular orbitals of the different monomers are orthogonalized and then the zero-order wave functions are constructed as antisymmetrized products of determinants for the isolated monomers, including singly and doubly excited monomer configurations. This approach is close to the variational method[203-205] (see Sec. 3C) except that, instead of the exact solution of the secular equation on a restricted basis its solution is sought in successive orders of perturbation theory. The procedure has been applied[201,202] to the computation of the potential energy curve for $(He)_2$ and $(H_2O)_2$.

C. Variational methods

At small distances, the individual molecules cannot be separated in the interacting system. The system must therefore be looked upon as a single quasimolecule and must be treated by the same methods that are used for isolated molecules. Variational methods are at present the most commonly used. The interaction energy is then determined by subtracting the energies of the isolated molecules from the total energy of the system [see (2.59)]. At large distances, the interaction energy is very small and this imposes stringent conditions on the precision of the calculation and restricts R to the region of small and intermediate distances. We have already discussed the H-H calculations of Kolos and Wolniewicz.[29-30,123-128]

In the case of more complicated systems, accurate variational calculations similar to those of Kolos and Wolniewicz in the case of H_2 cannot be carried out. The self-consistent field method in which the molecular orbitals are approximately represented by linear combinations of atomic orbitals (LCAO MO SCF) is widely used in calculations both of electron shells of molecules and of molecular associations. The atomic orbitals are usually taken to be the Slater or Gauss functions. The Hartree-Fock equation for the molecular orbitals is reduced to a set of nonlinear algebraic equations for the coefficients of the expansion of the molecular orbitals in terms of the given atomic orbitals. Detailed accounts of the various approximations used in the SCF method are readily available.[206-212]

Since the work of Clementi[213] and Morokuma and Pedersen,[214] there have been many calculations by the LCAO MO SCF method in which all the electrons of the system were taken into account and a sufficiently broad basis set was employed. Schuster *et al.*[158-159,215-216] have given an analysis and a generalization of papers on ion-molecular complexes and different classes of compounds with hydrogen bonding. Comparisons with the more accurate computed data and with experiments have shown that the *ab initio* calculations performed by the LCAO MO SCF method reproduce the geometry of the complex quite well. The well depths are less satisfactory.

Comparative analysis of calculations based on perturbation theory and SCF shows[197] that the intermolecular interaction energy in the case of the SCF method contains contributions due to the direct electrostatic, exchange, and induction interactions. On the other hand, dispersion interactions are not taken into account[55] in the SCF method. The question therefore arises as to why the resulting potential curves satisfactorily describe the interaction energy despite the fact that dispersion energy has been ignored and is known to be very appreciable in the region of the van der Waals minimum. Analysis of this question[217,158-159] has shown that the reasons must be sought in the mutual cancellation of errors. In particular, such cancellation also occurs in connection with the use, in the case of the complex, of a broader basis (belonging to both molecules) as compared with energy calculations for isolated molecules, which leads to an artificial stabilization of the complex. This artefact has been examined numerically[218-220,201-202] by using the same basis in calculations of the energies of the isolated molecules as in the case of the entire complex. For small bases, the error is quite large.

Ab initio calculations by the SCF method consume a considerable amount of machine time because they involve the evaluation of complicated many-center integrals whose number increases as $\sim n^4$ with increasing basis length n. A number of semiempirical methods have therefore been proposed. They are based on either complete or partial neglect of exchange terms in the SCF equations and the replacement of the remaining integrals by parameters. The semiempirical methods have been reviewed in detail in the linterature.[209-212] The results of calculations on molecular complexes by the semiempirical CNDO/2 and INDO methods have been reviewed by Murphy and Rao.[221] This analysis shows that many of the characteristics of the intermolecular interaction are satisfactorily reproduced by the semiempirical scheme. Stability of the complexes is, on average, slightly overestimated in this way. On the other hand, delocalization of electrons and intermolecular repulsion are highly overestimated. On the whole, it may be concluded that the subdivision of the interaction energy into the individual contributions within the framework of the semiempirical method is not physically significant because it depends on the nature of the approximations and the number of parameters. More or less satisfactory results are due to cancellation of errors.[222,158] We emphasize that calculations of intermolecular forces by the semiempirical method may lead to qualitatively incorrect results, for example, to incorrect geometry. This is so in the case of calculations[205] of the ethylene dimer (see below).

Ab initio calculations are essential if more realistic potential curves are to be obtained. At the same time, although the LCAO MO SCF method does predict the correct geometry, it is nevertheless inadequate if correct values of the interaction energy are desired. The reason for this is that the SCF method does not take into account correlations between the relative motions of the electrons.[206-208,223-224] Electron correlation can be subdivided into intermolecular (this leads to dispersion forces) and intramolecular which leads to a reduction in the dipole moment and an increase in polarizability.[225]

The simplest way of taking into account electron correlation is to write the variational function as a linear combination of functions describing the different one-electron configurations of the interacting molecules. Since the configurational expansion is known to converge, the precision of the calculation increases with increasing number of configurations that are taken into account. A colossal number of configurations can be taken into account when modern computers are employed. For example, Diercksen *et al.*[20] have reported calculations on the water dimer in which variational functions were employed with 56,268 singly and doubly excited configurations. Their results show that the absolute value of the correlation energy increases with decreasing distance between the molecules. At the minimum on the potential energy curve, the correlation correction to the binding energy is 1.03 kcal/mole or about 16% of the total binding energy of the dimer. Apart from the substantial increase in the binding energy produced by electron correlation, it also leads to a small reduction in the equilibrium separation: from $R_{0-0}=3.00$ Å in the case of SCF to $R_{0-0}=2.919$ Å when the configurational interaction is taken into account.

The above calculations on molecular dimers, which take electron correlation into account, start with the excited electronic configurations of the entire complex, which corresponds to the inclusion of electron correlation within the framework of the method of molecular orbitals. Kaplan and Rodimova[203] and, independently, Wormer, Van Berkel and Van der Avoird[204-205] have developed a variational method for calculating the intermolecular interaction energy, which starts with the states of the isolated molecules. In this sense, the method is close to the perturbation-theory method except that the energy is found by solving the secular equation whose order is determined by the number of excited states of isolated molecules taken into account. Each such state is a molecular multiplet ${}^{2S_a+1}\Gamma^{(\alpha_a)}$, characterized by total electron spin S_a and index of the irreducible representation $\Gamma^{(\alpha_a)}$ of the point symmetry group of the molecule. The variational function Ψ is constructed as a linear combination of functions that are antisymmetrized with respect to all the interchanges of electrons between the molecules and corresponding to definite molecular states:

$$\Psi=\sum_{a,b} C_{ab}\Psi\left({}^{2S_a+1}\Gamma^{(\alpha_a)},\ {}^{2S_b+1}\Gamma^{(\alpha_b)}\right). \tag{3.37}$$

The main part of the problem is to evaluate the matrix elements of the Hamiltonian using the antisymmetric functions in (3.37). This is solved by the technique of projection operators and fractional parentage coefficients.[203]

The energy obtained by solving the secular equation corresponds to the inclusion of all perturbation theory orders on a restricted number of molecular states. The diagonal matrix element corresponds to first-order perturbation theory, i.e., the interaction energy is defined in first order as

$$E^{(1)}_{S_a\alpha_a,\,S_b\alpha_b} =\langle\Psi({}^{2S_a+1}\Gamma^{(\alpha_a)},{}^{2S_b+1}\Gamma^{(\alpha_b)})|H|\Psi({}^{2S_a+1}\Gamma^{(\alpha_a)},{}^{2S_b+1}\Gamma^{(\alpha_b)})\rangle-E_{S_a\alpha_a}-E_{S_b\alpha_b}. \tag{3.38}$$

The difference between the total energy obtained by diagonalizing the secular equation and the energy (3.38) provides, after subtraction of the energies of the isolated molecules, the total contribution of the second- and higher-order perturbation theory. Neglect of exchange terms in the matrix elements gives the Coulomb interaction energy, including all the multipole interactions and corresponding to the inclusion of all perturbation-theory orders in the restricted basis. Exchange energy is found as the difference between the total interaction energy and the Coulomb energy [see (2.60)].

The above method has been used to perform calculations on $(H_2)_2$, $(He)_2$, and $(C_2H_4)_2$ (Refs. 203, 204, and 205, respectively). Let us consider the results for the ethylene dimer,[205] which are of considerable methodological interest for estimates of the contributions of different types of interaction. This calculation took into account only the one-electron excitations of the monomers. The wave functions for the isolated molecules were taken to be the LCAO MO SCF functions in the Gaussian basis. Induction energy was obtained in the case of excitation of only one monomer, and the dispersion energy in the case of the simultaneous excitation of both monomers. The energy corresponding to the singlet state of the dimer then also includes the contribution due to the dispersion energy corresponding to the triplet excitations of the monomers. Altogether about 600 configurations were taken into account.

The two conformations shown in Fig. 4 were examined. In the conformation shown in Fig. 4a, the molecular planes are parallel to one another and perpendicular to the plane of the drawing, whereas, in the conformation shown in Fig. 4b, the molecular planes are perpendicular to each other.

Figure 4 shows the calculated potential-energy curves for the two conformations. For purposes of comparison between the contributions due to the second and higher-order perturbation theories, we also reproduce curves obtained in the first approximation in accordance with (3.38). The stable dimer corresponds to the conformation of Fig. 4b, and this is mainly due to the first-order electrostatic interaction. The calculated depth of the minimum is $\varepsilon = 33.5 \times 10^{-5}$ atomic units for $R_0 = 9.4a_0$. The experimental values determined from viscosity are $\varepsilon = 72.0 \times 10^{-5}$ atomic units and $\varepsilon = 65 \times 10^{-5}$ atomic units (Refs. 226 and 1, respectively). The discrepancy between the experimental and theoretical values of ε is explained, on the one hand, by the insufficient precision of the calculations and, on the other, by inaccuracies in the experimental determinations of ε. It is emphasized by Flynn and Thodos[226] that ε is very sensitive to the conditions under which it is determined from viscosity. The experimental data were interpreted in terms of the isotropic (6–12) Lennard-Jones potential which bears very little resemblance to the real potential in the case of this particular dimer.

Although the ethylene molecule does not have a dipole moment in the ground state, direct electrostatic interaction exceeds the contribution due to the polarization forces. Wormer and Van der Avoird[205] have also carried out a multipole expansion in the matrix elements and have found the contributions of the individual terms.[11] The results of these calculations show that, for distances $R \leq 15a_0$, it is essential to take into account such apparently exotic terms as hexadecupole contributions (in the present case this was due to the fact that ethylene has zero dipole and octupole moments). For $R < 6a_0$, the fact that the multipole series diverges affects even the second term. The contribution of exchange forces is important up to $R \leq 10a_0$. All these conclusions must be borne in mind in practical calculations.

We must also note that the calculations performed by Wormer and Van der Avoird[205] in the case of the ethylene dimer by the semiempirical CNDO method have led to results that are qualitatively in conflict with the *ab initio* calculation: conformation I was found to be stable. This indicates that great caution must be exercized when semiempirical methods tested in the case of individual molecules are used in problems involving intermolecular interactions.

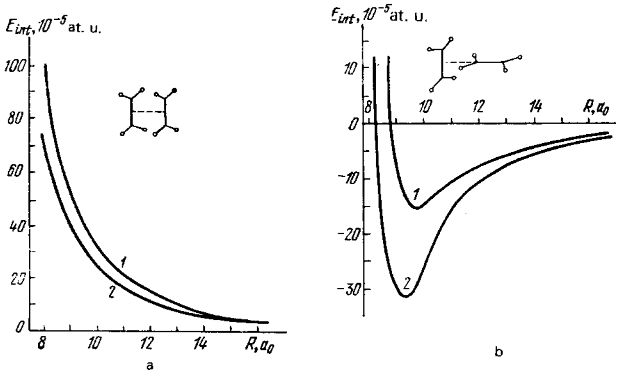

FIG. 4. Interaction potentials for two ethylene molecules:[205] curve 1—$E^{(1)}$; 2—$E = E^{(1)} + E^{(2)}$.

Because of lack of space, we shall not be able to examine statistical methods of *ab initio* calculations of potential curves based on the electron gas model. This approach was first put forward and developed by Nikulin and Gaydaenko[228-229] and was subsequently modified by Gordon and Kim.[230-231] Further improvement,[232-233] which took into account the contribution of dispersion forces, has resulted in good accuracy in calculations of intermolecular potentials for the dimers UF_6–UF_6 and CH_4–CH_4 (Refs. 234 and 235, respectively).

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