MOLECULAR PHYSICS
AND
INTERMOLECULAR FORCES

BY

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THE ANATOMY OF MOLECULAR PHYSICS *

Joseph O. Hirschfelder

I want to develop the thesis that there is more and more need for molecular physics as our range of interests widens to encompass phenomena which occur under extreme conditions of time, temperature, and pressure and as our experimental techniques become more precise so as to give significance to small effects. The development of aviation might serve as an example. Up to the last few years, aeronautical engineers have considered air as an ideal gas with constant specific heat and with the flow characteristics of a continuous media. On such a basis it was possible to explain the flight characteristics of planes flying up to three hundred miles an hour. However, at higher speeds shock waves develop on the surface of the propellers and parts of the airfoil and the characteristics of these shock waves depend on the molecular nature of air. For example, the high speed flow of air through an orifice depends upon the relaxation time (or the collision cross-section) for the transfer of the translational into the vibrational energy of the molecules. At speeds high compared to the speed of sound, the airfoil is surrounded by very hot air and the heat transfer to the airfoil depends upon the mole fractions of each of the various excited molecular, atomic, and ionic species in the hot air, as well as the cross-sections for various types of collisions with and without the emission or absorbtion of radiation. Thus the practical aeronautical engineer has come to seek the help of molecular physicists. In the future this pattern will occur frequently. The chemical and physical phenomena which occur in electrical discharges, detonations, flames, etc. require interpretations on the molecular level. On this account, molecular physicists will have a new task—to serve as the middleman between the engineer or the practical experimentalist on the one hand and the pure fundamental physicist on the other hand. During the next microcentury (John Von Neumann's favorite unit of time for a lecture, 52 minutes and 34 seconds), I would like for you to consider the overall realm of molecular physics and the sorts of development which will be required before we can adequately answer these practical questions. I think you will agree with my conclusion that the gaps in our knowledge are appalling. The following analysis is intended to be schematic rather than encyclopaedic.

The work of physicists may be divided into four different categories :

I. The Fundamental Laws of Physics.

II. The properties and behavior of molecules.

III. The macroscopic properties of materials.

IV. Experiments designed to either test or to apply our knowledge of the laws of physics, the behavior of molecules, or the properties of macroscopic matter.

I. *The Fundamental Laws.*

Pure physicists seek to improve our knowledge of the fundamental laws of physics and the elementary particles with which they deal. As is shown in Table I, most of the laws of physics are summarized by Field Theory which consists of Quantum Mechanics, Relativity, and the Electromagnetic equations in a vacuum. Statistical mechanics might be thought of as a separate law of physics but any good statistician could derive or make logical the statistical mechanical postulates from a knowledge of quantum mechanical phenomena. The laws of physics deal with the behavior of electrons, photons, nuclei, etc. In the equations there appear the universal constants: e, c, g, N, h, ... Theoretical molecular physicists or theoretical chemists assume that the fundamental laws of physics are correct and seek to use these laws to explain in a rational maner, first, the properties and behavior of molecules ; then, the bulk behavior of matter ; and finally, to predict the results of practical experiments.

Table I.

The Fundamentals of Physics

The Fundamental Laws.

Field Theory	Quantum Mechanics
	Relativity
	Electromagnetic equations (vacuum)

(Statistical Mechanics)

The Fundamental Particles.
Electrons, photons, nuclei, etc.

The Fundamental Constants
e, c, g, N, h, . . .

II. *The Microscopic or Molecular Level.*

The problems on the microscopic or molecular level are shown in Table II. Under the column marked microscopic equations are given both an indication of what we have and what we need.

(1) *The Boltzmann Equation.* The Boltzmann equation determines nes from specified boundary conditions the distribution function, f(v, r, t). The distribution function tells the density of molecules in a unit range of velocity and position at a particular time. The Boltzmann equation itself determines the functional form of the macroscopic flux equations. From a knowledge of the distribution functions we can determine the coefficients of viscosity, heat conductivity, diffusion, etc. However, the Boltzmann equation is severely limited to a moderately low density gas containing molecules with no internal degrees of freedom. We very much need two types of generalizations of the Boltzmann equation—one generalization to include high density gas or liquid phenomena, the other generalization to include the internal degrees of freedom of molecules. The high density generalization requires a consideration of three-body or multiple-body collisions. The polyatomic molecule relations require a consideration of non-adiabatic collisions of non-spherical molecules. Actually there is even some discussion as to the validity of the present Boltzmann equation for phenomena such as shock waves where very rapid changes occur in the distribution function.

Table II.

Microscopic or Molecular Phenomena

The Microscopic Equations.

Have	*Need*
Boltzmann Equation	Generalized Boltzmann Equation to include internal degrees of freedom of molecules and high density.
Method of Distorted Waves for determining scattering cross sections, σ	General method for determining differential scattering cross-sections, $I_{kl}^{k'l'}(\theta, \phi)$.
Electromagnetic Local Field Equations	Improved treatment of interaction of radiation and matter.

The Molecular Parameters.

Quantum numbers, oscillator strength, distribution function, collision cross-sections (σ, I); dipole, quadrupole and multipole electric and magnetic moments.

The Molecular Properties.

Energy levels, spectra, structure, and Internuclear forces

Perturbations of energy levels, structure, intermolecular forces, and transition probabilities resulting from electromagnetic fields and collision processes.

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(2) *Collision Cross-Sections.* The solutions of the Boltzmann equation can be expressed in terms of a set of collision cross-sections which are functions of g, the relative velocity of the colliding molecules, and are defined in terms of the variation of χ, the angle of deflection of the trajectory, with the impact parameter, b. Here b is the distance of closest approach of the molecules if the trajectories are assumed to be straight lines. Thus the collision cross-sections do not depend upon the details of the trajectories, but only upon the $\chi(b, g)$. According to classical mechanics, we can calculate the angle of deflection from a knowledge of the intermolecular forces. According to quantum mechanics we must first distinguish whether the collision is adiabatic or non-adiabatic. If the collision is non-adiabatic, the notions of intermolecular forces are rather meaningless. If the collision is adiabatic, we can use the method of distorted waves to calculate the probability of particular angles of deflection but we cannot investigate the detailed trajectories. In discussing intermolecular forces we assume that the electronic motions are separable from the nuclear motions in the sense of Born and Oppenheimer. In actual collision processes the deviations from this separability lead to both velocity-dependent intermolecular forces and to non-adiabatic transitions between quantum states.

In non-adiabatic collisions, the all-important quantity is the differential scattering cross-section, $I_{kl}^{k'l'}(\chi, \phi, g)$. This gives the probability that two molecules which are initially in the quantum states k and l and collide with the relative velocity g will separate with the quantum numbers k' and l' respectively, that their trajectory will be deflected through an angle χ, and that the new plane of the molecular motion is twisted through an angle ϕ from the original plane. Knowledge of the differential scattering cross-sections will provide the detailed information necessary for a better understanding of chemical kinetics as well as the various transport properties. For collisions between atoms in excited electronic states and collisions between non-spherical molecules, the differential scattering cross-sections are needed. In order to calculate the $I_{kl}^{k'l'}$ it is necessary to generalize the method of distorted waves and to develop new methods which will take advantage of the capabilities of high speed digital computing machines.

(3) *Electromagnetic Local Field Equations.* The detailed interaction between radiation and molecules can be summarized by the electromagnetic local field equations. Perhaps this is the branch of molecular quantum mechanics which most needs research. It encompasses the polarization of matter and all sorts of spectroscopy. The development of photon counters, microwave techniques and nuclear magnetic and other types of resonance

devices places the experimental measurements far ahead of the theory. Studies of the detailed natural line shape and breadth also provide another type of opportunity for comparing experiment with theory.

There are a wide variety of molecular properties and parameters which are studied both theoretically and experimentally. Some of them are indicated in Table II. The scope of the molecular phenomena is indeed tremendously broad when one considers the large number of types of atoms, molecules, and ions to which these studies apply. Then, too, one must not forget that each electronic state of each molecule possesses its own characteristic properties.

III. *The Macroscopic Phenomena.*

The properties of macroscopic phenomena have a much closer relationship to the molecular or microscopic properties than we usually realize. This relationship is generally established through statistical mechanics. Statistical mechanics has the dual function of determining the macroscopic equations from the microscopic relations and also determining the phenomenological coefficients in terms of the molecular properties. The equations of thermodynamics are unique insofar as they may be established directly from the laws of physics without requiring the microscopic relations as an intermediate step. Thermodynamics of irreversible processes has established general relationships between a number of the phenomenological coefficients which are independent of the molecular model. It is hoped that, eventually, the functional forms for all of the macroscopic equations will also be determined without reference to any form of molecular model, leaving only the phenomenological coefficients to be determined from the detailed properties of the molecules. Table III shows the macroscopic equations, the phenomenological coefficients, and the macroscopic properties which are considered. In the case of dilute gases, where the Boltzmann equation applies on the microscopic level, the flux equations have been derived on a rigorous basis. Because of the lack of a generalized Boltzmann equation, the flux equations for dense media are on a semi-empirical basis. The equation of state for liquids and crystals is also on a semi-empirical basis and very serious efforts are being made by theoreticians to remedy this situation.

The present theory of absolute reaction rates is largely due to Henry Eyring. It is based on the notion of complete separation between the electronic and the nuclear motions, so that for each electronic state of the system at each configuration of the nuclei there is a well defined electronic energy which serves as the potential energy for the nuclear motions. The theory of absolute reaction rates then represents the application of statistical mechanics to the nuclear motions on these potential energy surfaces. Up to the present time molecular quantum mechanicians have not succeeded in calculating such potential energy surfaces and it is difficult to assess the

magnitude of the errors involved in the theory. Eventually the theory of absolute reaction rates will be reformulated in terms of statistical averaging of the differential scattering cross-sections. Such a formulation would no longer depend upon the separation of nuclear and electronic motions and would certainly seem more suited to those chemical reactions which involve "tunneling" through a potential energy barrier. The cis-trans isomerizations of the substituted dichlorethanes are examples of such tunneling reactions. Also a theory based on differential scattering cross-sections would be more suited to consideration of chemical reactions under conditions where the collision velocities differ from the Maxwell-Boltzmann distribution characteristic of a particular temperature. The reaction rate constants serve as the phenomenological coefficients in the general equations of reaction kinetics.

Table III.

The Macroscopic Phenomena

The Macroscopic Equations.

Thermodynamic Relations
Equation of State : $P(V, T)$
Calorific Equation : $H(P, T)$ and $S(P, T)$
Thermodynamics of Irreversible Processes
Equations of Flux :
    Equations of Continuity
    Equation of Motion
    Equation of Energy Balance
    Equations of Diffusion
Equations of Chemical Kinetics
Maxwell Equations for Electromagnetic Phenomena in Dense Media

The Phenomenological Coefficients.

Virial Coefficients : B, C, . . .
Transport Coefficients : $\eta, \lambda, D, \ldots$
Reaction Rate Constants : k
Electric and Magnetic Susceptibility : ε, μ
Specific Heats and Energies of Formation

The Properties of Bulk Material.

$P, V, T, E, H, S, \ldots$
Compressibility, Heat Capacity, . . .
Sound Propagation
Electrical Conductivity
Flame Propagation and Detonations

Under usual conditions, the bulk properties behave in a manner which can be predicted on the basis of empirical experience. However, when the temperature is one million degrees or the pressure is one million atmospheres, i.e. extreme conditions under which experimental data is meager, the theoreticians are required to make the predictions. Under such extreme conditions the statistical mechanical connections between the microscopic and the macroscopic equations often lead to hitherto unexpected behavior.

IV. *Experimental Physics.*

There are two kinds of experiments : useful and informative. Useful experiments are those which apply the various relationships of fundamental physics, molecular physics, and macroscopic physics to obtain some sort of product like a television set or a new type of plastic which is desired on purely utilitarian grounds. Such useful applications are of special interest to the engineers. Physicists, on the other hand, are primarily interested in informative experiments which are designed to test the various relationships which are assumed in the fundamental, microscopic, and macroscopic physics. It is the dream of the theoretician to be able to synthesize all of these relationships on a purely logical basis starting from a few basic postulates. However, nature is so very complex that mathematics is taxed to the utmost in attempting to describe it. For example, think of the difficulty of predicting the shapes and behavior of the clouds in the sky on the basis of a knowledge of the chemical composition of the earth's atmosphere and the equations of aerodynamics. Thus theoreticians are bound to make simplifying assumptions in obtaining workable relationships. Often it is difficult to estimate the magnitude of the errors which are introduced by the approximations. Thus, informative experiments are needed to test the validity of each supposition. More generally, experiment and theory work hand in hand in the development of semi-empirical relations in which the functional forms of the relations are provided by the theory and the numerical constants are provided by the experiment.

Mathematical experiments are a brand new development made possible by high speed computing machines. For example, William Wood[1] assumes that molecules interact with each other in accordance with the hypothetical Lennard-Jones type of intermolecular potential. With the use of a high speed digital computing machine, he follows the positions of a set of these molecules as they move about under thermal agitation and determines their average properties as a statistical equilibrium is approached. Thus he can determine the equation of state of a dense gas, liquid, or crystal composed

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[1] W. W. Wood and F. R. Parker, J. Chem. Phys. *27*, 720 (1957). Actually the method described here is more closely akin to that which is used by Berni J. Alder. However, the results are the same.

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of Lennard-Jones molecules. By comparing the equation of state of an actual substance with that of this hypothetical substance, one can learn a great deal about the forces between the molecules. Thus one can perform a great many interesting experiments with the use of high speed computations.

The comparison between experiments and theory used to be easy. Experiments were designed to test a single relationship or measure the value of a single phenomenological coefficient. The experimental conditions were set up to minimize the effects of boundaries and variations in all of the variables except the one under investigation. However, as greater accuracy was required, this was no longer feasible. Nowadays great accuracy is achieved at the expense of simple interpretations. The physicist measures the velocity of light by studying the characteristics of a complicated micro-wave resonance circuit. The chemist learns about reaction rates from a study of phenomena which takes place in a shock tube when a strong shock wave is passed through a mixture of various substances. Thus the physicist must unravel the theory of wave guides before he can reach a conclusion as to the velocity of light ; and the chemist must unravel the aerodynamics of shock waves before he can obtain his chemical information.

As the experiments become more complex, the effect of boundary conditions has become more important. In order to obtain solutions to the equations of theoretical physics it is always necessary to postulate the boundary conditions. I have the feeling that these boundary conditions and their effects have not been sufficiently stressed. The engineers are far ahead of the physicists in this respect. The engineers have studied the rapid changes which take place in boundary layers, and the discontinuities which often result from the boundary conditions as applied to the non-linear equations of natural phenomena. New mathematical techniques are required to cope with such behavior.

V. Conclusion.

In thinking about the four levels of research of molecular physicists, one is impressed by the wide variety of problems which remain to be solved in all of the different branches. Also, one is impressed by the dependence of the macroscopic phenomena on the molecular properties and the dependence of the molecular properties on the fundamental laws of physics. However, very often, one can learn a great deal about the properties of molecules from a study of the macroscopic behavior. Indeed, one has learned a great deal about the forces between molecules from using statistical mechanical notions to interpret the equation of state and the transport properties of dilute gases. Thus the various branches of molecular physics are completely interdependent.

With the advent of sharper experimental tools on the one hand and of high speed computing devices and better mathematical methods on the other,

one can predict that the physics of the future will continue to open up exciting new vistas of knowledge.

INTERATOMIC FORCES—THE FOOTSTEPS OF LENNARD-JONES*

I am thrilled to have the honor of following in the footsteps of Sir J. E. Lennard-Jones who in 1938 gave the first Cooch-Behar lectures on the subject of "Interatomic Forces". Lennard-Jones was a great scientist whose interests encompassed the whole spectrum of natural phenomena. His enthusiasm and clear thinking were a source of inspiration to everyone with whom he came in contact. The Cooch-Behar lectures which Lennard-Jones presented have served as a blue print for many of us to follow. In them, he discussed all of the different types of interatomic forces and showed how they might be determined by combining experiments and theory. During the past nineteen years, many of the developments which he suggested have been carried out. And now we are ready to take the next big step and study the forces between atoms, molecules, and free radicals in excited electronic states. In this paper I want to discuss how far we have progressed in carrying out Lennard-Jones' program and explain what sorts of problems we are going to face in the future.

Let me quote the first two paragraphs of Lennard-Jones' speech which seem as appropriate to my speech in 1957 as they were in 1938:[1]

"The object of theoretical chemistry is to coordinate existing experimental data, to effect a correlation of phenomena apparently unconnected, and to suggest, stimulate, and direct further experimental research. Since chemistry is concerned primarily with the interaction of atoms and molecules, it would appear that the most fundamental problem of theoretical chemistry is to elucidate, classify, and determine the forces which atoms and molecules exert on each other. This information must provide the key as to which atoms will react chemically with each other, what energies will be involved, what will be the effect of temperature, pressure and other imposed conditions, and what consequential changes are likely to occur as a result of a chemical reaction. It must further provide the connecting link between the properties of matter in the different states of aggregation, interpret the nature of the solid and the liquid state, and explain the processes of fusion and evaporation.

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[1] J. E. Lennard-Jones, "Interatomic Forces", Indian Assoc. for Cultivation of Sci., Special Publication 8 (Calcutta, 1939).

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"In order to understand the nature of interatomic forces it is necessary to make a detailed study of the electronic structure of atoms and molecules, so that these forces can be interpreted in terms of the fundamental concepts of physical theory. The ultimate object must be to predict chemical phenomena in terms only of the electrons and nuclei in the reacting systems, and so to bridge the gap between physics and chemistry. In view of the central role played by interatomic forces in physics and chemistry, it seemed to me fitting that I should devote my attention in the Cooch-Behar lectures to a consideration of some of the recent advances in the subject and to indicate the progress which has been made in their determination and interpretation."

Lennard-Jones developed a multiple-pronged attack on intermolecular forces. In essence it amounted to:

(1) Make strictly quantum mechanical calculations of intermolecular forces by trying to solve the Schrödinger equation for a wide variety of problems. Since it is impossible at the present time to obtain accurate solutions to most molecular quantum mechanics problems, we try to obtain the best approximations which are currently feasible.

(2) Use the quantum mechanical calculations to predict the proper functional forms for the different types of intermolecular forces as functions of the internuclear separation. These functional forms are obtained by curve-fitting the quantum mechanical results. Most of the constants which occur in these theoretically determined expressions are then discarded, later to be replaced by empirical values.

(3) Use statistical mechanics to calculate the bulk properties of matter assuming that the intermolecular forces are given by the above functional forms. The constants which occur in the functional forms are then adjusted to make the calculated and experimental values of the bulk physical properties agree as well as possible.

We shall be following this procedure for a long time. In principle one might suppose that it would be possible to make calculations of the intermolecular forces directly by obtaining sufficiently accurate approximations to the solutions of the appropriate Schrödinger equations. However, up to the present time this has not been feasible. The principal difficulty is that the variational procedure (which is generally followed) leads to an estimation of the total energy of the system. Unfortunately the intermolecular potential is generally only a very small fraction of the total energy of the system. For example, consider the interaction between two helium atoms in their ground states. The total energy of the two atom system is 157.2 e. V. whereas the maximum energy of attraction between the two atoms is 0.00088 e.V. Thus in order to detect the maximum energy of attraction to within fifteen percent,

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the total energy of the system must be calculated to an accuracy of one part in one million. In order to obtain this degree of accuracy, entirely new types of quantum mechanical procedures are required.

Many quantum mechanics experts use approximate wave functions to calculate the energy of the system when two atoms are close together and then make the calculation on the same basis when the atoms are far apart. The difference between these energies is then assumed to be the energy of interaction. If the errors in the two calculations were the same, this would provide a good method for determining intermolecular forces. Unfortunately the relative magnitude of the errors in the two cases depends rather sensitively on the assumed functional form of the approximate wave-functions. Thus the semi-empirical intermolecular forces calculated by the Lennard-Jones procedure are much more accurate than any purely theoretical calculations obtained up to the present time.

Lennard-Jones first considered the energy of interaction of two spherical non-polar molecules in their ground states. The noble gas atoms are the only truly spherical non-polar molecules. However, molecules like N_2, O_2, CO, NO, and CO_2 are sufficiently close to being spherical that they satisfied his criterion. At large separations, Lennard-Jones knew that there must be an energy of attraction of the London dispersion type which varies inversely as the sixth power of the separation. At small separations, the quantum mechanical calculations indicate an energy of repulsion which varies exponentially with the separation. Thus the total energy of interaction should be of the form:

$$\phi(r) = b \exp(-ar) - cr^{-6} \qquad \qquad (1)$$

Here the three constants a, b, and c are to be determined empirically. In discussing intermolecular forces, it is important to introduce the concept of the low velocity collision diameter, σ, defined as the separation at which $\phi(\sigma) = 0$. For most of the bulk physical properties with which Lennard-Jones was concerned, only gentle thermal collisions are important and in such collisions the separation seldom gets much smaller than σ. Thus the exponential repulsive potential was of interest only in a very small range of separations centering on $r = \sigma$. In this small range of separations the exponential could be approximated by a constant times an inverse power of the separation. Thus was born the Lennard-Jones $(n-6)$ potential:

$$\phi(r) = sr^{-n} - cr^{-6} \qquad \qquad (2)$$

It is most conveniently written in terms of the low velocity collision diameter and the maximum energy of attraction, ε:

$$\phi(r) = \frac{\varepsilon n (n/6)^{6/(n-6)}}{(n-6)} \left[\left(\frac{\sigma}{r} \right)^n - \left(\frac{\sigma}{r} \right)^6 \right] \qquad \qquad (3)$$

The maximum energy of attraction occurs when the separation is

$$r_m = [n/6]^{1/(n-6)} \sigma = [ns/6c]^{1/(n-6)} \qquad (4)$$

Lennard-Jones was primarily a physicist but at the same time he was an excellent mathematician. He knew from the early statistical mechanical work of Clausius, Keesom, Jeans, etc., that the equation of state of a dilute gas can be expressed in terms of the virial expansion,

$$PV/RT = 1 + B(T)/V + C(T)/V^2 + \dots \qquad (5)$$

where $B(T)$, $C(T)$,............... are the second virial coefficient, third virial coefficient,............... and the second virial coefficient is related to the intermolecular potential by the definite integral,

$$B(T) = 2\pi N \int_0^{\infty} r^2 [1 - \exp(-\phi(r)/kT)] \, dr \qquad (6)$$

But none had evaluated this integral using a physically realistic form for the intermolecular energy. Jeans[2] had evaluated this integral for molecules which repel each other with an energy which varies inversely with a power of the separation. And Keesom[3] had evaluated it for a rigid sphere surrounded by an attractive field whose energy varies as an inverse power of the separation. Lennard-Jones[4] evaluated the second virial coefficient for his $(n-6)$ potential, Eq. (6). In order to do this with sufficient accuracy and without a prohibitive amount of work it was necessary to resort to mathematical trickery. He expanded $\exp(-\phi/kT)$ in the form

$$\exp\left[-\left(\frac{s}{kTr^n}\right) + \left(\frac{c}{kTr^6}\right)\right] = \exp\left(-\frac{s}{kTr^n}\right)\left[\sum_{j=0}^{\infty} \frac{1}{j!}\left(\frac{c}{kT}\right)^j r^{-6j}\right] \qquad (7)$$

Substituting this expansion into Eq. (6), the resulting integral corresponding to each term of the expansion can be evaluated in terms of closed analytical expressions. Thus he found that

$$B(T) = b_0(\sigma) F_n(T^*) \qquad (8)$$

Here $b_0(\sigma)$ is the van der Waals' constant which would be characteristic of the low velocity collision diameter,

$$b_0(\sigma) = \left(\frac{2\pi N}{3}\right)\sigma^3 \qquad (9)$$

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[2] J. Jeans, "Dynamical Theory of Gases" (Cambridge University Press (1925)), p. 134.

[3] W. H. Keesom, Comm. Phys. Lab. Leiden, Suppl. 24 B, p. 32 (1912).

[4] J. E. Lennard-Jones writing in Chapt. X, R. H. Fowler, "Statistical Mechanics" (Cambridge University Press, (1929)), p. 221; see also J. E. Lennard-Jones, Proc. Roy. Soc. A 106, 463 (1924).

and the $F_n(T^*)$ are functions of the reduced temperature, $T^* = kT/\varepsilon$:

$$F_n(T^*) = y^{3/(n-6)}\left[\prod\left(\frac{n-3}{n}\right) - \sum_{j=1}^{\infty} c_j(n)y^j\right] \tag{10}$$

where

$$c_j(n) = \frac{3}{j!\,n}\prod\left(\frac{6j-3}{n}\right) \tag{11}$$

and

$$y = n[6^{6/n}(n-6)^{(n-6)/n}]^{-1}(T^*)^{-(n-6)/n} \tag{12}$$

The infinite series in Eq. (10) converges rapidly, especially at high temperatures. Lennard-Jones calculated $F_n(T^*)$ for $n=8$, 9, 12, and 14 and for a large number of values of T^*. Thus the second virial coefficient as a function of temperature is expressed in terms of the three parameters: n, σ, and ε. These constants can be adjusted so as to make the theoretical second virial coefficient, Eq. (8), agree with the experimentally determined values over a wide range of temperature. One way of evaluating these constants is to plot $\log_{10}F_n(T^*)$ versus $\log_{10}T^*$ as shown in Fig. 1. Now plot on transparent paper to the same scale the experimentally obtained values of $\log_{10}B(T)$ versus $\log_{10}T$. Slide this transparent paper graph horizontally and vertically on top of Fig. 1 until the best fit is obtained with a curve for
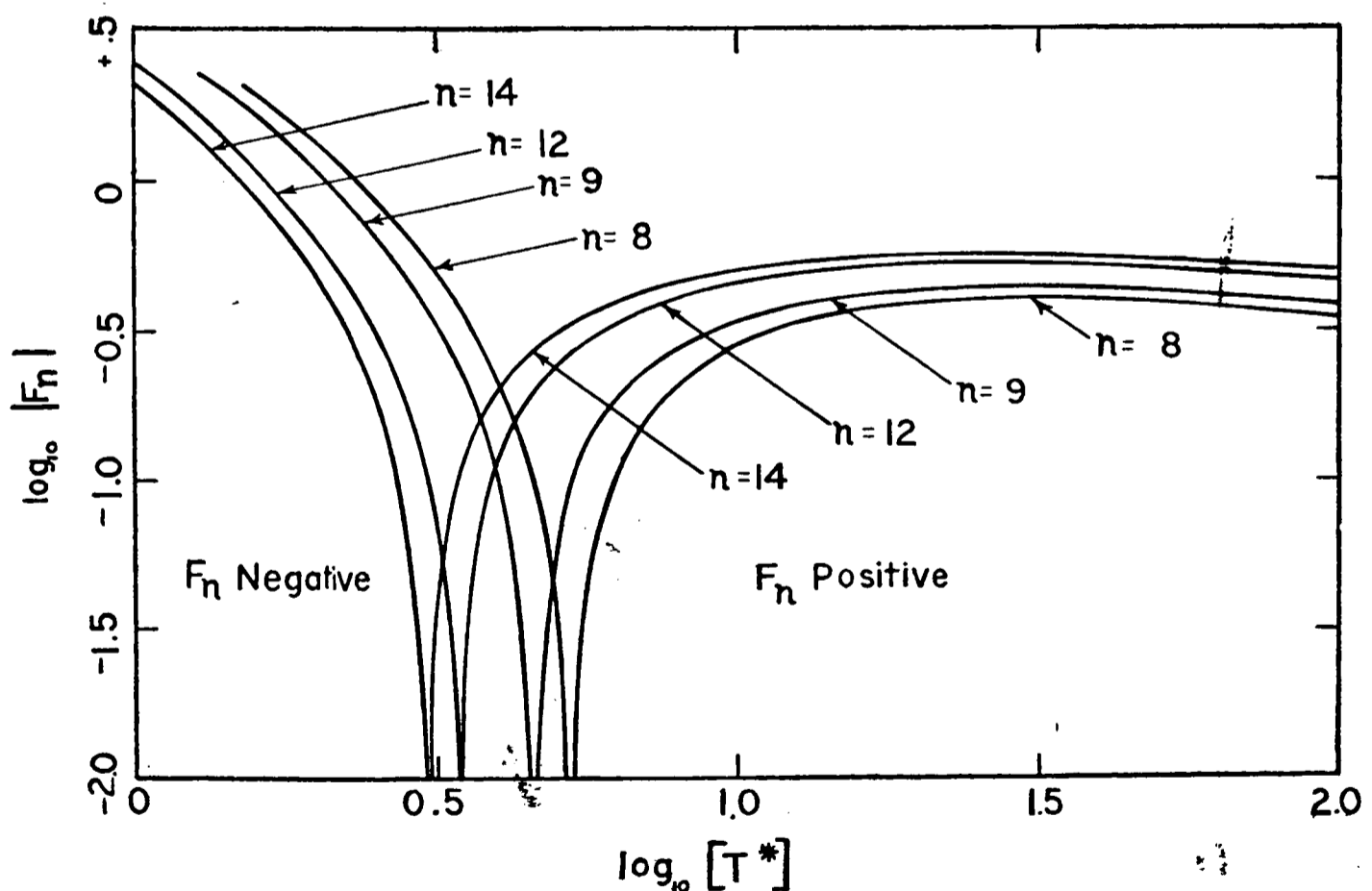

Figure 1.

Logarithm of Second Virial Coefficient Plotted Against Logarithum of Temperature. The different values of n corresponds to different inverse powers of the repulsive term in the Lennard-Jones (n-6) potential.

one of the $\log_{10}F_n(T^*)$; the value of n for which the best fit is obtained is then the proper value. Also, from the distance that the transparent paper is displaced horizontally and vertically with respect to Fig. 1, determine the contants σ and ε. From such studies, Lennard-Jones found that the interaction between two helium atoms is best fitted by $n=9$ but that for most other substances n is usually less than 14 and averages close to $n=12$. Thus for the remainder of our discussion, we shall consider just the case of $n=12$.

The best method of determining the Lennard-Jones constants is another graphical procedure developed by Buckingham[5]. In the Buckingham method, each experimental value of the second virial coefficient at a particular temperature is represented by a curve. If all of these curves cross at a single point, then the Lennard-Jones potential leads to good agreement between the calculated and the experimental second virial coefficients over the observed temperature range. Furthermore, the manner in which the curves fail to cross at a single point can be used to interpret the experimental deviations from the Lennard-Jones potential. Thus MacCormack and Schneider[6] have found that for CF_4 interactions, the Lennard-Jones $(12-6)$ potential provides an excellent fit; for SF_6 the agreements are fair; and for CO_2 the agreement is poor.

If all substances obeyed the Lennard-Jones $(12-6)$ potential law of interactions, then, except for quantum effects, all substances would obey the law of corresponding states.[7] That is if T_c, V_c, and P_c are the critical temperature, volume, and pressure respectively, then

$$P/P_c = f(V/V_c, \ T/T_c) \qquad .... \qquad .... \qquad (13)$$

where f is a universal function. It also follows that T_c should be proportional to ε/k; that V_c should be proportional to $N\sigma^3$; and that P_c should be proportional to ε/σ^3. Thus for those noble gases and other spherical nonpolar gases whose molecules obey the Lennard-Jones (12-6) potential rather well, it is found that

$$T_c = 1.28 \ \varepsilon/k$$
$$V_c = 3.00 \ N\sigma^3$$
$$P_c = 0.125 \ \varepsilon/\sigma^3 \qquad .... \qquad .... \qquad (14)$$
$$\frac{P_c V_c}{RT_c} = 0.293$$

However, it is clear that there are a great many substances which do not obey the Lennard-Jones (12-6) type of potential. It is easiest to spot these substances by examining their critical compressibility factor. Thus the

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[5] R. A. Buckingham, Proc. Roy. Soc. (London) *A 168*, 264 (1938) ; see also A. Münster, "Statistische Thermodynamik" (Springer, 1956), 390.

[6] K. E. MacCormack and W. G. Schneider, J. Chem. Phys. *19*, 849 (1951).

[7] J. S. Rowlinson, Trans. Faraday Soc. *51*, 1317 (1955).

hydrocarbons have $P_c V_c/RT_c = 0.27$ and water has $P_c V_c/RT_c = 0.23$. The corresponding states equation of state can only apply to classes of substances which have the same value of the critical compressibility factor and for such a class it is reasonable to suppose that a single type of two constant potential energy function would provide a representation of their energy of inter-action. Many people at the present time are proposing generalized corres-ponding states equations of state in which the critical compressibility factor[8,9] (or the slope of the vapor pressure with respect to temperature at the critical point[10]) plays the role of a third constant. Such equations of state provide a very accurate representation of gases up to the critical density. At densities higher than the critical for either liquids or gases the corresponding states notions do not lead to a very accurate representa-tion because of additional properties of the molecules which determine their packing, etc. For example, it is evident that the various liquids should be classified in the same manner as crystals on the basis of the lattice symmetry of the unit cells and on the basis of coordination numbers.

Many people have adopted and carried on the Lennard-Jones program. For example, in 1937, after completing my work as a graduate student, I found that Prof. J. R. Roebuck at the University of Wisconsin had made some very excellent measurements of the Joule-Thomson coefficients. On the basis of thermodynamics, one can calculate these coefficients from a knowledge of the equation of state, $P(V, T)$, but it is not possible to calculate the equation of state from a knowledge of the Joule-Thomson coefficients, as this introduces an unknown constant of integration. The beauty of statistical mechanics is that it permits the evaluation of all of these constants of integration. Thus, I assumed that the molecules of Roebuck's gases obeyed the Lennard-Jones $(n-6)$ potential; extended Lennard-Jones' analysis of the second virial coefficient so as to apply to the low pressure limit of the Joule-Thomson coefficients; and used Roebuck's data to determine the constants in the potential law. Using these constants together with the Lennard-Jones formulae, I could calculate the corresponding second

[8] A. L. Lydersen, R. A. Greenkorn, and O. A. Hougen, "Generalized Thermo-dynamic Properties of Pure Fluids", Univ. Wis. Engineering Experiment Station Report No. 4 (Madison, Wis., Oct. 1955) ; see also A. L. Lydersen, University of Wisconsin Engineering Experiment Station Report No. 3 (Madison, Wisconsin, April 1955), "Estimation of Critical Properties of Organic Compounds by the Method of Group Contributions."

[9] J. O. Hirschfelder, R. J. Buehler, H. A. McGee, and J. R. Sutton, "Generalized Equation of State and Thermodynamic Properties for Both Gases and Liquids", J. Ind. and Eng. Chem., Feb. (1958) ; also Univ. Wis. Naval Research Laboratory Reports Wis-OOR-15 and Wis-OOR-16 (Oct. 1956).

[10] K. S. Pitzer, D. Z. Lippmann, R. F. Curl, C. M. Huggins, and D. E. Petersen, J.A.C.S. 77, 3427 (1955) and 77, 3433 (1955).

virial coefficients and compare them with directly measured values. This was one of the first examples where a property of a gas was estimated from a knowledge of another property by calculating the forces between the molecules as an intermediate step.

Just before and just after World War II, many of us got acquainted with the excellent treatise of Chapman and Cowling[11] in which all of the statistical mechanics of transport properties of dilute gases made up of spherical non-polar molecules is developed and reduced to the evaluation of a set of collision integrals. Unfortunately these collision integrals had not been evaluated for any realistic sort of intermolecular interaction. Thus many of us determined that at the very first opportunity we would evaluate the set of collision integrals using the Lennard-Jones (12—6) potential. Although these integrals could not be expressed in closed analytical form, they did yield to numerical two-dimensional quadrature. Thus tables of these collision integrals were prepared independently by workers in four different countries (and may be more).[12,13,14,15] Our tables were the most complete since we had access to an I.B.M 604 automatic digital computing machine. Thus began the use of high speed computing devices in the calculation of properties of gases. The table of collision integrals made it possible to calculate the coefficients of viscosity, diffusion, heat conductivity, and thermal diffusion with the same ease as the second virial coefficient. Intrinsically, the coefficient of viscosity is the most sensitive measurement of gas imperfection since J. A. Bearden[16] developed a method for determining it to a precision of better than one part in ten-thousand. Unfortunately most of the measurements of coefficients of viscosity of gases in the literature have systematic errors which must be corrected.[17] From a knowledge of

[11] S. Chapman, and T. G. Cowling, "The Mathematical Theory of Non-uniform Gases", (Cambridge University Press, 1939).

[12] T. Kihara and M. Kotani, Proc. Phys. Math. Soc. Japan, 24, 76 (1942).

[13] J. de Boer and J. van Kranendonk, Physica, 14, 442 (1938).

[14] J. S. Rowlinson, J. Chem. Phys. 17, 101 (1949).

[15] J. O. Hirschfelder, R. B. Bird, and E. L. Spotz, J. Chem. Phys., 16, 968 (1948) ; see also J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids", (John Wiley, 1955).

[16] J. A. Bearden, Phys. Rev. 56, 1023 (1939).

[17] At a recent meeting of the American Rocket Society, Second Biennial Gas Dynamics Symposium, Northwestern University, Aug. 26, 1957, F. G. Keyes stated that many of the values of coefficients of viscosity quoted by M. Trautz and his coworkers are erroneous since the original measurements were made relative to the viscosity of air and value for the coefficient of viscosity of air has subsequently been changed by one and a half percent. Also, J. Kestin stated that the values given by H. L. Johnston and his coworkers need correcting because they were measured with a rotating disc viscosimeter and no account was taken of the edge corrections. Kestin is developing the proper edge corrections and finds that it is a very complex aerodynamical problem.

the constants in the energy of interaction law as determined from any one property, the values of any other property at any arbitrary temperature can be readily estimated. Another application of the table of collision integrals was to calculate a set of potential constants from a knowledge of a property over a limited temperature range, then use the table of collision integrals to predict the value of this same or other properties at much higher or lower temperatures. The fact that the Lennard-Jones (12-6) potential can be used in this manner is indeed proof that it is very close to being accurate. When one attempts to make such inter-relations between various physical properties using square-well or other less realistic models of intermolecular potential, very poor agreement with experimental values is obtained.

The ability to treat dilute gas mixtures came as a pleasant surprise. For collisions between unlike molecules one takes the collision diameter to be the arithmetic average between the collision diameters for the like molecules,

$$\sigma_{12} = \tfrac{1}{2}(\sigma_{11} + \sigma_{22}) \tag{15}$$

and the maximum energy of interaction to be the geometrical mean,

$$\varepsilon_{12} = \sqrt{\varepsilon_{11}\varepsilon_{22}}. \tag{16}$$

These empirical rules lead to very excellent agreement between experiment and calculations for the coefficient of binary diffusion as a function of temperature. Eqs. (15) and (16) can be derived theoretically on the basis of a number of rather bad assumptions and therefore we have no apriori right to expect them to work as well as they do. Hildebrand[18] has used these same combining rules quite successfully to explain the properties of regular solutions of liquids.

When it became evident that the properties of binary mixtures can be nicely treated using the Lennard-Jones (12-6) potential and the combining rules, there was real need to extend the formal statistical mechanics so as to encompass the transport properties of multi-component mixtures. In Chapman and Cowling's book it is stated that such an extension is obvious and easy to do. Actually it took Charles Curtiss and me[19] one and a half years to develop the multi-component equations and much work remains to be done in the simplification of some of these relations.[20]

A considerable amount of effort has gone into improving the Lennard-Jones (12-6) potential by using the exponential repulsion term, as in Eq. (1),

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[18] J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes", (Reinhold, 1950).

[19] C. F. Curtiss and J. O. Hirschfelder, J. Chem. Phys. *17*, 550 (1949).

[20] B. N. Srivastava and S. C. Saxena, J. Chem. Phys. *27*, 583 (1957).

[21] W. E. Rice and J. O. Hirschfelder, J. Chem. Phys. *22*, 187 (1954).

instead of the inverse power. This (exp-6) function is known as the Buckingham potential. Tables of both the second virial coefficients[21] and the collision integrals[22] have been constructed for it. However, except for helium and for hydrogen, the extent of the improvement is disappointingly small.

In addition to pioneering the theory of real gases, Lennard-Jones played a leading role in opening up the theory of liquids. Lennard-Jones and Devonshire[23] supposed that all of the molecules in a liquid, except the one under consideration, are held fixed at their lattice points. The molecule under consideration can wander in the potential energy field due to all of the neighbouring molecules. Using the Lennard-Jones (12-6) potential to describe the interaction between each pair of molecules, they developed a very satisfactory free-volume type of equation of state. William Wood[24] has recently shown by direct Monte Carlo calculations that the Lennard-Jones Devonshire equation of state is very good for liquids at very high density but very poor for low density liquids near their critical points. Efforts are now being made[25] to improve the Lennard-Jones Devonshire equation of state by integrating the Kirkwood[26] integral equations so as to obtain the optimum free volume equation of state of liquids and dense gases.

Altogether one may conclude that the physical properties of gases and liquids composed of spherical or almost spherical non-polar molecules in their ground states are well understood from a semi-empirical standpoint. We are now ready to take the big step and consider molecules with dipoles, non-spherical molecules, and molecules in excited electronic states. The equation of state of such molecules offers no conceptual difficulties and indeed, even now, one can calculate the second virial coefficients for such species. However, there are enormous difficulties in calculating their transport properties.

The problem of determining intermolecular forces between non-spherical molecules or molecules in excited electronic states is orders of magnitude more difficult than is the case for spherical non-polar molecules. First of all, it is difficult to use the semi-empirical approach since one must determine the angular dependence of the forces as well as their variation with the separation. Clearly, experiments involving the macroscopic properties of gases or liquids could not provide such details. There is, indeed, the

[22] E. A. Mason, J. Chem. Phys. *22*, 169 (1954).

[23] J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. (London), A *163*, 53 (1937).

[24] W. W. Wood and F. R. Parker, J. Chem. Phys. *27*, 720 (1957).

[25] J. S. Dahler, J. O. Hirschfelder, and H. C. Thacher, J. Chem. Phys. *25*, 249 (1956).

[26] J. G. Kirkwood, J. Chem. Phys. *18*, 380 (1950).

possibility of making use of the structure and properties of crystals. For non-spherical molecules in their ground states, crystal structure data will undoubtedly be very valuable. However, crystal structure data could not be used for molecules in excited electronic states because their forces are not pairwise additive. Thus it appears that we must rely to a large extent on purely quantum mechanical calculations in order to determine the forces between chemically interesting molecules.

This offers a real challenge to theoretical chemists inasmuch as no one has succeeded, up to the present time, in making a satisfactory theoretical calculation of the forces between even the simplest atoms.

Right after World War II and up to the time of his death, Lennard-Jones devoted his attention to trying to develop a new approach to this problem. The present status of this problem seems to be as follows: We understand the nature of long range forces between all types of molecules. At large separations these forces are of the nature of electrostatic or dispersion forces. The electrostatic forces include the two types of resonance: (1) the resonance in which the two molecules are identical, and (2) resonance in which the collision process breaks up a degeneracy in the energy of one of the molecules. Both of these resonance types are well understood and are illustrated by Figures 2a and 2b.

Figure 2a
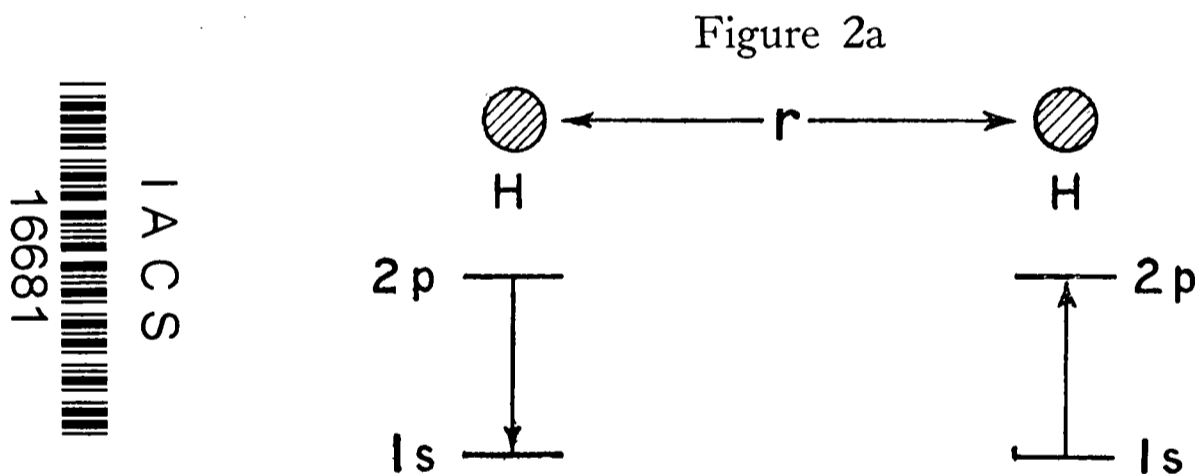
Example of Two Molecule Resonance:

Interaction of Hydrogen Atom in 2p State with a Hydrogen Atom in 1s State. Resonance occurs through the emission of a virtual photon from one atom and its absorption by the other. Four molecular states are possible in such a collision. If $(\mu)_{sp}$ is the transition dipole moment, the four molecular states and their interaction energies are

$$\Sigma_g, \quad \phi = +2(\mu)_{sp}^2/r^3$$
$$\Pi_u, \quad \phi = +(\mu)_{sp}^2/r^3$$
$$\Sigma_g, \quad \phi = -(\mu)_{sp}^2/r^3$$
$$\Pi_u, \quad \phi = -2(\mu)_{sp}^2/r^3$$

If it were not for resonance, the energy of interaction would vary as the inverse sixth instead of the inverse third power of the separation.

Figure 2b
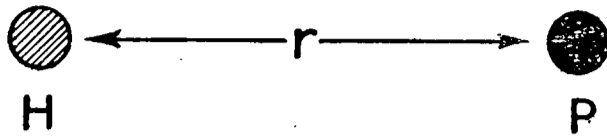
Example of One Molecule Resonance:

Interaction of Hydrogen Atom in Either 2s or 2p State with a Proton. The collision destroys the energy degeneracy of the 2s and 2p states. The resonance energy of interaction is then

$$\phi = \pm 3/(r/a_0)^2 \qquad \text{(in units of } e^2/a_0)$$

Without resonance, the energy of interaction would vary as the inverse fourth power rather than the inverse square of the separation.

Dispersion forces correspond to electron correlation as shown in Figure 3a. The dispersion forces are expressed in terms of the oscillator

Figure 3a

Instantaneous   Induced
Dipole   Dipole

Nature of Electron Correlation Involved in Long
Range Dispersion Forces.

strength and of the positions of the positive and negative elements of the transition charge distributions[27]. The resonance forces, like the dispersion forces, can also be expressed in terms of transition charge distributions[28].

Our real difficulties are concerned with the forces at intermediate and short range. We would like to make use of a truly variational principle, but as was mentioned for the case of helium-helium interaction, this would require such great accuracy that it does not seem feasible with present techniques. With bad wave functions we have the problem of the zeroeth order perturbations[29]. The energy of interaction might be calculated in either of two ways. In the first, we might calculate the energy of a total system in a particular nuclear configuration and subtract from it the energy of the separated molecules a and b.

$$\phi(r) = \int \psi^* \mathscr{H} \psi d\tau - E_a - E_b. \qquad (17)$$

[27] Eugene F. Haugh and J. O. Hirschfelder, J. Chem. Phys. *23*, 1778 (1955).

[28] John S. Dahler and J. O. Hirschfelder, J. Chem. Phys. *25*, 986 (1956).

[29] Edward A. Mason and J. O. Hirschfelder, J. Chem. Phys. *26*, 173 (1957).

Here, $\mathscr{H}$ is the Hamiltonian for the total system, and E_a and E_b are the energies of separated molecules calculated on exactly the same basis as the energy of the total system in a state of collision.

Figure 3b

Nature of Electron Correlation involved in Short Range Polarization.

The second method of calculating the energy of interaction is to evaluate the expectation value of the extra terms in the total Hamiltonian which arise due to the interaction between the two molecules. This is called the atoms in molecules approximation. The two approximations give quite different results, sometimes even differing as to orders of magnitude. Let me illustrate the two methods for the case of the interaction between two hydrogen molecules. Here the Hamiltonian for the total system may be written in the form

$$\mathscr{H}(1234) = \mathscr{H}_a(12) + \mathscr{H}_b(34) + V(1234) \tag{18}$$

and the wave functions for the separated hydrogen molecules are $\psi_a(12)$ and $\psi_b(34)$ respectively. The antisymmetrized wave function for the system in its lowest electronic state is

$$\psi = \psi_a(12)\psi_b(34) - \psi_a(14)\psi_b(23) - \psi_a(23)\psi_b(14) + \psi_a(34)\psi_b(12). \tag{19}$$

The energies of the separated molecules calculated on this basis are

$$E_a = \int \psi_a^*(12)\mathscr{H}_a(12)\psi_a(12)d\tau \tag{20}$$

$$E_b = \int \psi_b^*(34)\mathscr{H}_b(34)\psi_b(34)d\tau. \tag{21}$$

Here we assume that the wave functions for the isolated molecules are normalized. Then, using the first method, which involves the variational principle, we obtain for the energy of interaction

$$\phi(r) = -E_a - E_b + [\int \psi^* \mathscr{H}\psi_a(12)\psi_b(34)d\tau / \int \psi^*\psi_a(12)\psi_b(34)d\tau] \tag{22}$$

whereas for the atoms in molecules approximation we obtain

$$\phi(r) = \int \psi^* V\psi_a(12)\psi_b(34)d\tau / \int \psi^*\psi_a(12)\psi_b(34)d\tau. \tag{23}$$

Margenau and his coworkers[30] believe that the first method gives the

[30] A. A. Evett and H. Margenau, Phys. Rev. *90*, 1021 (1953); J. Chem. Phys., *21*, 958 (1953).

best results, whereas de Boer[31] emphatically defends the atoms in molecules approximation. If the wave functions were perfect, then both methods would give the same results. But we have no way of getting the perfect wave functions so this is not an important consideration. Instead, we find that Margenau's calculations differ qualitatively from those of de Boer with respect to the angular dependence which they obtain for the intermolecular forces. If indeed we are going to make purely quantum mechanical calculations of intermolecular forces, we should reach a definite decision as to which of these procedures should be followed.

Perhaps our greatest difficulty in making quantum mechanical calculations is the difficulty in evaluating all of the necessary integrals. One of the first requirements on the functional form which we use for the wave functions is that it must be capable of producing good dispersion forces at large separations and be sufficiently flexible to change from the dispersion type of electron correlation shown in Figure 3a to the close separations type of electron correlation shown in Figure 3b (see p. 22). A further requirement on the functional form is that it must be capable of reducing to a good wave function for the proper states of the united atom at very close separations. The importance of this last requirement is demonstrated by some recent work of Buckingham[32] in which he showed that the functional forms that various quantum mechanicians have assumed for the helium-helium interaction approach, for zero separation, a wave function for an excited state of the beryllium atom rather than a wave function for the ground state. It is on this account that the theoretical calculations for the interaction between two helium atoms do not agree with the experimental molecular beam scattering measurements of Amdur and his coworkers.

It is not reasonable to suppose that a second order perturbation calculation is necessary for very large separations while only a first order perturbation is necessary for small separations. The second order treatment involves electron correlation. The first order treatment does not. Some people simply add the results of first and second order perturbation calculations. In some cases this might work if the second order perturbations were calculated correctly. However, instead of calculating the second order with the true Hamiltonian with the correct perturbation potential, they use only the first one or two terms of the long range power series expansion of the perturbation potential. Thus they get repulsive short range terms varying

[31] J. de Boer, Physica, 9, 645 (1942).

[32] R. A. Buckingham, "The Repulsive Interactions of Atoms in S. States", University of Wisconsin Naval Research Laboratory Report WIS-AEC-9, (December, 1956).

exponentially with the separation, and long range energies of attraction or repulsion varying as an inverse power of the separations. For intermediate separations these long range dispersion forces become very large and there arises the question of how they should be truncated. In addition to the first and second order perturbation energies there are the second order exchange forces which become very important at intermediate separations.

More and more, we are becoming impressed with the importance of ionic terms and electron exchange forces at intermediate separations. For example, Aono[33] has recently shown that the important directional forces between conjugate double bond molecules is principally due to electron exchange forces. Mulliken and Platt and their coworkers are finding spectroscopic evidence for many different types of charge exchange complexes. Thus any good functional form for a wave function must include ionic terms.

Frankly, we require new tools for calculating intermolecular forces. We must seek to find an alternative to the Ritz variational procedure for calculating the total energy of the system. We need a better understanding of the inherent significance of the quantum mechanical forces. Löwdin is providing excellent insight into this problem,[34] but a great deal more work is required. One possibility is to extend the Fermi-Thomas method for use in connection with intermolecular force problems. The Fermi-Thomas approach essentially eliminates the wavelike nature of the electron from consideration and reduces the calculations to a purely electrostatic problem. Gombas[35] has been very successful in modifying the Fermi-Thomas method so as to take into account the Pauli exclusion principle and he has been very successful in calculating the energies of atoms.

When one considers the simplicity of chemistry, the great uniformity of both distances and angles in molecules, uniformity of both energies, etc., it seems that the quantum mechanics required for both chemistry and intermolecular forces must itself be simple, if only we had the proper clue. The purpose of my trip to India and to the other distant countries which we are visiting is to discuss with you the formidable nature of these problems and to get your advice as to how we can best arrive at a solution. Indeed

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[33] Shigeyuki Aono, "Charge Transfer Forces Between Long Chain Molecules" speech presented at Molecular Quantum Mechanics Symposium at the Yukawa Institute, Kyoto, Japan, March 30, 1957. Probably submitted for publication to the J. Phys. Soc. Japan.

[34] Per-Olov Löwdin. Phil. Mag. Supplement, 5, No. 17, p. 1 (January, 1956).

[35] P. Gombas, "Theorie und Losungsmethoden des Mehrteilchenprobleme der Wellenmechanik", (Birkhauser, Basel, 1950) ; also "Statistische Behandlug des Atoms", Handbuch der Physik (S. Flügge, Marburg, 1936), volume 36.

it seems that we shall continue to grope in our efforts to calculate intermolecular forces between chemically interesting molecules until some new great leader like Lennard-Jones shall arise and present us with a broad program to follow in attacking this problem, just as Lennard-Jones pointed the way in his Cooch-Behar Lectures of 1938.