

probability of resonance multiphoton ionization.

In conclusion the author thanks N. B. Delone and A. M. Dykhne for a discussion of the work and for valuable advice.

## APPENDIX

Let us discuss the question of the validity of the method presented in this article. Let us consider the complex time plane (see the figure). Let us denote the point

$$s_i = \text{Im} \int E_i dt,$$

where  $t = t_{12}$  by A, the corresponding point where  $t = t_{23}$  by B, and the point where  $t = t_{13}$  by C. The notation 1-2 on the figure means that in the region where the numeral 2 is placed we have  $s_2 > s_1$ , but in the region where the numeral 1 is placed, we have  $s_1 > s_2$ . These regions are separated by the Stokes line AO on which  $s_1 = s_2$ . The notation 2-3 and 3-1 is defined in analogous fashion.

Multiplication of two matrices was utilized for the determination of the resonance transition matrices (7). In this connection, in the time plane one should move from the point A along the curve AO.<sup>[3]</sup> At the point O, where  $s_1 = s_2 = s_3$ , the direction of motion should change to OB, where  $s_2 = s_3$ . It is necessary for the validity of

the method that one should have  $s_3 < s_1 = s_2$  on the Stokes line AO, and  $s_1 < s_2 = s_3$  on the Stokes line OB. This will be true in the case when the numerals 1, 2, and 3 are arranged in cyclic fashion. Precisely such a case is shown in the figure. In the case of an anticyclic arrangement of the indices, the method becomes incorrect. The question of what numerical values of the problem's parameters will cause the arrangement of indices to be cyclic or anticyclic is solved separately in each specific case by numerical methods, and this question is not investigated in the present article.

<sup>1)</sup>The possibility of using such a technique for a three-level system was suggested by A. M. Dykhne.

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# An approximate method for calculating intermolecular interaction

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A method is discussed which allows the determination for arbitrary molecules of the angular dependence of the intermolecular potential from the experimentally-determined averaged (over the angles) potential. The method is based on the effective pair interaction approximation. As an illustration, the potential curves for different relative orientations of the molecules H<sub>2</sub>-H<sub>2</sub> are computed. The curves are found to be in good agreement with the results obtained by other methods.

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## 1. INTRODUCTION

To solve a number of concrete problems (thermal diffusion, the cooling of interstellar gas, relaxation in a shock wave, line broadening, etc.), it is necessary to

know the total and the differential cross sections for elastic and inelastic interactions of molecules.<sup>[1]</sup> However, partial transition cross sections and angular distributions have been measured directly in experiments only for a very limited number of molecular pairs:

$H_2-H_2$ ,  $^{[2]} H_2-CO$ .<sup>[3]</sup> Therefore, usually, these quantities have to be computed theoretically. There exist at present standard methods of computing cross sections from a given interaction potential.<sup>[4]</sup> However, the interaction potentials of the overwhelming majority of molecular pairs are virtually unknown, and they also have to be found theoretically.<sup>[5, 6]</sup>

Usually, the intermolecular potential is represented in the form of a sum of several terms<sup>[1, 7, 8]</sup>:

$$V = V_{\text{mul}} + V_{\text{ind}} + V_{\text{dis}} + V_{\text{val}}, \quad (1)$$

where  $V_{\text{mul}}$  characterizes the multipole interaction of the static moments of the molecules,  $V_{\text{ind}}$  reflects the interaction between the static and induced molecular moments,  $V_{\text{dis}}$  describes the dispersion interaction of the induced molecular moments, and, finally,  $V_{\text{val}}$  represents the valence interaction. The first three interaction modes are relatively long-range interactions. Their angular and radial dependences are known,<sup>[1, 7, 8]</sup> and the corresponding constants—the static multipole moments and the polarizabilities—have either been experimentally determined, or can be computed by standard methods. As to the valence interaction, its functional dependence is, strictly speaking, unknown. Meanwhile, it is precisely this interaction that makes the dominant contribution at small distances, determining the repulsive part of the potential.

In this paper we discuss an approximate method of computing the angular dependence of the valence part of potential acting between two arbitrary molecules. We consider the collisions of molecules moving with thermal velocities, in which only the rotational degrees of freedom are excited

$$E_{\text{kin}} \ll E_{\text{col}} \ll E_{\text{el}}. \quad (2)$$

In the general case, this potential depends on the relative disposition of the molecules, as characterized by the vector  $\mathbf{r}(r, \mathbf{n})$  joining their centers of gravity, and on the orientation of the molecules, which can be characterized by two sets of Euler angles,  $\Omega_a$  and  $\Omega_b$ . It is convenient to write the potential  $V_{\text{val}}$  in the form of an expansion in terms of products of the spherical function

$$C_m^l(\mathbf{n}) = \sqrt{\frac{4\pi}{2l+1}} Y_{lm}(\mathbf{n}) = D_{m0}^{l*}(\mathbf{n})$$

and the Wigner  $D$  functions  $D^l(\Omega_a)D^l(\Omega_b)$ :

$$V_{\text{val}}(\mathbf{r}, \Omega_a, \Omega_b) = \sum_{\substack{l_a l_b \\ m_a m_b}} R_{0\mu_a\mu_b}^{l_a l_b}(r) A_{0\mu_a\mu_b}^{l_a l_b}(\Omega_a, \Omega_b), \quad (3)$$

where  $A_{0\mu_a\mu_b}^{l_a l_b}$  is an invariant—under rotation of the laboratory system—function of the angular variables  $\Omega_0$ ,  $\Omega_1$ , and  $\Omega_2$ , defined by the relation:

$$A_{\mu_a\mu_b}^{l_a l_b}(\Omega_0, \Omega_1, \Omega_2) = \sum_{m_0 m_1 m_2} \begin{pmatrix} l_a & l_1 & l_2 \\ m_0 & m_1 & m_2 \end{pmatrix} D_{m_0\Omega_0}^{l_a}(\Omega_0) D_{m_1\Omega_1}^{l_1}(\Omega_1) D_{m_2\Omega_2}^{l_2}(\Omega_2). \quad (4)$$

Here

$$\begin{pmatrix} l_0 & l_1 & l_2 \\ m_0 & m_1 & m_2 \end{pmatrix}$$

is the Wigner  $3j$  symbol. The properties of  $A_{\mu_0\mu_1\mu_2}^{l_0 l_1 l_2}(\Omega_0, \Omega_1, \Omega_2)$  are well known, whereas the expansion coefficients  $R_{0\mu_a\mu_b}^{l_a l_b}(r)$  are unknown scalar functions of the distance  $r$ . Thus, the problem of the determination of the angular dependence of  $V_{\text{val}}$  reduces to that of finding these coefficients.

The sum (3) can, in principle, be extended to all integral values of  $l$ ,  $l_a$ , and  $l_b$  from zero to  $\infty$  and all integral  $\mu_a$  and  $\mu_b$  lying in the interval from  $-l_i$  to  $l_i$ . The coefficients  $R_{0\mu_a\mu_b}^{l_a l_b}$  with large values of  $l$ ,  $l_a$ , and  $l_b$  at great distances  $r$  (beyond the minimum of the potential well) decrease very rapidly, since  $R_{0\mu_a\mu_b}^{l_a l_b}(r) \propto R_{000}^{000}(r)/r^{l_a+l_b}$ . At small distances, however, the contribution made to the potential by the higher-order expansion terms corresponding to large values of  $l$ ,  $l_a$ , and  $l_b$  can be quite substantial, especially in the case of nonlinear molecules (see, for example, the interaction potential of  $H_2CO-He$ <sup>[5]</sup>).

It is important that many terms of the expansion (3) drop out as a result of some general requirements imposed on the potential.

First, the interaction energy should be a scalar with respect to rotations of the laboratory system of coordinates. The fulfillment of this requirement is guaranteed by the fact that the potential (3) expands in terms of the functions (4), which are scalar products of three  $D$  functions. This leads to the requirement that the summation indices  $l$ ,  $l_a$ , and  $l_b$  should satisfy the triangle condition:

$$l \leq l_a + l_b, \quad l_a \leq l_b + l, \quad l_b \leq l_a + l. \quad (5)$$

Second, the interaction potential should be invariant under inversion of the coordinate system. In consequence, the indices  $l$ ,  $l_a$ , and  $l_b$  should, in addition, satisfy the condition

$$l + l_a + l_b \text{ is even}. \quad (6)$$

Third, the interaction energy operator should be Hermitian, i. e., the potential  $V$  should be real in the diagonal representation, whence

$$[R_{0\mu_a\mu_b}^{l_a l_b}(r)]^* = (-1)^{\mu_a + \mu_b} R_{0\mu_a\mu_b}^{l_a l_b}(r). \quad (7)$$

This condition also takes account of the invariance of  $V$  under time reversal.

Further, the interaction potential of the molecules should be invariant under the transformations of the point-group symmetry of these molecules<sup>[9]</sup> if this symmetry does not change (see the condition (2)). This imposes even more severe limitations on the summation indices  $l_a$ ,  $l_b$  and  $\mu_a$ ,  $\mu_b$ , and connects some of the coefficients  $R_{0\mu_a\mu_b}^{l_a l_b}(r)$ . Thus, for molecules possessing an  $n$ -fold symmetry axis  $C_n$ , the component  $\mu_a$  (or  $\mu_b$ ) of the moment  $l_a$  (or  $l_b$ ) along this axis of symmetry assumes only values that are multiples of  $n$ . For exam-

ple, for the molecules  $H_2O$  (the group  $C_{2v}$ )  $\mu_a = 0, \pm 2, \pm 4, \dots \leq l_a$ , for the molecules  $NH_3$  (group  $C_{3v}$ )  $\mu_a = 0, \pm 3, \pm 6, \dots \leq l_a$ , for the molecules  $CO$  (group  $C_{\infty v}$ )  $\mu_a = 0$ . The coefficients  $R_{0\mu_a\mu_b}^{l_a l_b}$  that do not satisfy these conditions drop out. Similarly, for molecules possessing a center of inversion  $i$  (e.g.,  $H_2$ ,  $CO_2$ ,  $C_6H_6$ ), the moments  $l_a$  (or  $l_b$ ) assume only even values  $0, 2, 4, \dots$ . In the general case for molecules belonging to the groups  $C_{nh}$  and  $D_{nh}$ , the quantity  $l_a + \mu_a$  assumes an even value. The limitations and relations for molecules of different symmetries have been investigated in<sup>[10]</sup>, and are summarized there in the form of Tables.

Notice also that in the case of collisions between identical molecules the expansion coefficients should satisfy the supplementary relation:

$$R_{0\mu_a\mu_b}^{l_a l_b}(r) = R_{0\mu_b\mu_a}^{l_b l_a}(r). \quad (8)$$

Finally, in computing the matrix elements of the potential between states (of the molecules  $a$  and  $b$ ) characterized by definite angular momenta  $j$  and parities,  $\pi = \pm 1$ , of the wave function and by a definite angular momentum,  $L$ , of the relative motion of the molecules,  $j_a \pi_a j_b \pi_b L - j'_a \pi'_a j'_b \pi'_b L'$ , all the  $R_{0\mu_a\mu_b}^{l_a l_b}$  terms of the series (3) that do not satisfy the usual laws of conservation of angular momentum and parity:

$$|j'_a - j_a| \leq l_a \leq j'_a + j_a, \quad |j'_b - j_b| \leq l_b \leq j'_b + j_b, \quad |L' - L| \leq l \leq L' + L, \\ \pi'_a \pi_a = (-1)^{l_a}, \quad \pi'_b \pi_b = (-1)^{l_b}, \quad (-1)^{L' + L + l} = 1$$

drop out. Therefore, allowance for the higher-order terms of the expansion (3) is especially important in the computation of the probabilities of transitions involving large changes in the momenta,  $|j'_a - j_a|$  or  $|j'_b - j_b|$ .

The most rigorous and consistent way of finding the  $R_{0\mu_a\mu_b}^{l_a l_b}$  consists in an exact quantum-chemical computation that takes into account the direct and exchange interactions of all the particles entering into the molecules. However, as is well known,<sup>[8]</sup> such a calculation meets with considerable computational difficulties, even for the simplest molecules  $H_2-H_2$ .<sup>[8, 11]</sup> As to complex, multiatomic molecules, the direct computation of their interaction is virtually impossible.

The intermolecular potential can, in principle, be found from an analysis of the data on the differential cross sections for elastic scattering of the molecules and on the partial cross sections for collision-induced transitions. Such a procedure was, for example, recently used to determine the potential of  $H_2-H_2$ .<sup>[2]</sup> However, such detailed information does not exist for the overwhelming majority of molecular pairs. As a rule, only the thermodynamic quantities of the type of the second virial coefficient or of viscosity as functions of temperature are known. From them we can establish only the mean potential  $V_{val}(r)$ , i.e., the potential averaged over the orientations of the colliding molecules<sup>[7, 8]</sup>:

$$\bar{V}_{val}(r) = \iiint V_{val}(r, \Omega_a, \Omega_b) \frac{d\Omega_a}{4\pi} \frac{d\Omega_b}{8\pi^2} \frac{d\Omega_c}{8\pi^2} = R_{000}^{000}(r). \quad (9)$$

It is, in the general case, impossible to establish the angular dependence of  $V_{val}$  from these data. It can, neverthe-

less, be done in the framework of an additional assumption about the nature of the valence forces if, in addition, we take the real geometry of the colliding molecules—the angles and the interatomic distances—into account.

## 2. THE EFFECTIVE PAIR INTERACTION APPROXIMATION

Let us assume that the short-range part of the potential  $V_{val}(r, \Omega_a, \Omega_b)$  can be approximated by an effective pair potential of the type

$$V_{val}(r, \Omega_a, \Omega_b) = \sum_{i=1}^{N_a} \sum_{k=1}^{N_b} v_{ik}(r_{ik}), \quad (10)$$

where  $r_{ik}$  is the modulus of the distance between the  $i$ -th atom of the molecule  $a$  and the  $k$ -th atom of the molecule  $b$ ;  $N_a$  and  $N_b$  are the numbers of atoms in these molecules.

The additive nature of the potential (10) is, to some extent, due to the fact that, because of the large slope of the effective pair potential at small distances (near the classical reversal point), the contribution to  $V_{val}$  of one or another pair of atoms  $ik$  belonging to different molecules can become predominant if for this pair the distance  $r_{ik}$  turns out to be less than the distances for all the other pairs of atoms entering into the various molecules. The representation of the intermolecular potential in the form of a sum of pair biatomic interactions is, of course, an approximation. However, this two-atom potential  $v_{ik}$  describes the interaction of not free atoms, but of atoms entering into the given molecules  $a$  and  $b$ , which are in a quite definite quantum state, which does not change in the collision process, since  $E_{kin} \ll E_{co1} \ll E_{e1}$ . It is the latter circumstance that allows us to introduce the effective potential, which effectively takes into account, when the constants have been properly chosen, the contribution of the many-particle forces. As to the long-range potential, it is non-additive. The contribution of the many-particle forces to it is taken into account by the fact that the values of the multipole moments and of the polarizabilities pertain to the entire molecules.

Notice that in the general case the effective interatomic interaction function  $v_{ik}$  may correspond not only to central, but also to tensor forces that depend on the relative orientation of the spins. However, in the case when the electronic spin of each of the molecules is equal to zero we can restrict ourselves to the forces that depend only on the modulus  $r_{ik}$ .

The distance between the atoms  $i$  and  $k$  is determined by three vectors

$$r_{ik} = r - a_i + b_k, \quad (11)$$

where  $a_i$  ( $b_k$ ) is the radius vector of the  $i$ -th ( $k$ -th) atom, drawn from the center of gravity of the molecule  $a$  ( $b$ ). Strictly speaking, the radius vectors  $a_i$  and  $b_k$  characterize the coordinates of not the atomic nuclei, but the corresponding force centers, which, as a result of the

redistribution of the electrons in the molecule, can be somewhat shifted from the position of the corresponding atomic nucleus ( $\Delta a_i/a_i \leq 0.1$ ).<sup>[12]</sup>

The quantity  $\mathbf{r}_{ik}$  depends on the three angles between the vectors  $\mathbf{r}$ ,  $\mathbf{a}_i$ , and  $\mathbf{b}_k$ . Therefore, the angular dependence of the pair potential  $v_{ik}(r_{ik})$  can be represented in the form of an expansion in terms of products of three Legendre polynomials:

$$v_{ik}(r_{ik}) = \sum_{L_a L_b L_{ab}} c^{L_a L_b L_{ab}}(r, a_i, b_k) P_{L_a}(\mathbf{n}_i) P_{L_b}(\mathbf{n}_k) P_{L_{ab}}(\mathbf{n}, \mathbf{n}_i, \mathbf{n}_k), \quad (12)$$

where  $\mathbf{n}$ ,  $\mathbf{n}_i$  and  $\mathbf{n}_k$  are the unit vectors of the vectors  $\mathbf{r}$ ,  $\mathbf{a}_i$ , and  $\mathbf{b}_k$  defined in the laboratory coordinate system.

In order to explicitly separate out the dependence of  $v_{ik}(r_{ik})$  on the direction of each of the three vectors, let us use the addition theorem for three rotations<sup>[13]</sup>:

$$P_{L_a}(\mathbf{n}_i) P_{L_b}(\mathbf{n}_k) P_{L_{ab}}(\mathbf{n}, \mathbf{n}_i, \mathbf{n}_k) = (-1)^{L_a + L_b + L_{ab}} \sum_{l_a l_b l_{ab}} (2l_a + 1)(2l_b + 1)(2l_{ab} + 1) \times \begin{pmatrix} L_a & l_a & L_{ab} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_b & l_b & L_{ab} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_b & l & L_a \\ 0 & 0 & 0 \end{pmatrix} \left\{ \begin{matrix} l & l_a & l_b \\ L_{ab} & L_b & L_a \end{matrix} \right\} A_{000}^{l_a l_b}(n, n_i, n_k). \quad (13)$$

In order to explicitly separate out the dependence of  $v_{ik}$  on the structure of the molecules and their orientation, let us shift the vectors  $\mathbf{n}_i$  and  $\mathbf{n}_k$  from the laboratory coordinate system into the systems connected with the centers of gravity of the molecules  $a$  and  $b$  and oriented in such a way that the  $z'$  axes coincide with the highest-order symmetry axes of the molecules. The function  $A_{000}^{l_a l_b}(n, n_i, n_k)$  can then be represented in the form

$$A_{000}^{l_a l_b}(n, n_i, n_k) = \sum_{\mu_a \mu_b} A_{0\mu_a \mu_b}^{l_a l_b}(n, \Omega_a, \Omega_b) C_{\mu_a}^{l_a}(\mathbf{n}_i') C_{\mu_b}^{l_b}(\mathbf{n}_k'). \quad (14)$$

As a result, the valence potential can be written as follows:

$$V_{\text{val}} = \sum_{\substack{L_a L_b L_{ab} \\ l_a l_b l \\ \mu_a \mu_b}} (2l_a + 1)(2l_b + 1)(2l + 1) \begin{pmatrix} L_a & l_a & L_{ab} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_b & l_b & L_b \\ 0 & 0 & 0 \end{pmatrix} \times \begin{pmatrix} L_b & l & L_a \\ 0 & 0 & 0 \end{pmatrix} \left\{ \begin{matrix} l & l_a & l_b \\ L_{ab} & L_b & L_a \end{matrix} \right\} A_{0\mu_a \mu_b}^{l_a l_b}(n, \Omega_a, \Omega_b) B_{l_a l_b l_{ab}}^{L_a L_b L_{ab}}(r), \quad (15)$$

where

$$B_{l_a l_b l_{ab}}^{L_a L_b L_{ab}}(r) = \sum_{i, k=1}^{N_a, N_b} c^{L_a L_b L_{ab}}(r, a_i, b_k) C_{\mu_a}^{l_a}(\mathbf{n}_i') C_{\mu_b}^{l_b}(\mathbf{n}_k'). \quad (16)$$

It can be seen from the formula (15) that the entire dependence of  $V_{\text{val}}$  on the structure of the molecules  $a$  and  $b$  is contained in the factor  $B_{l_a l_b l_{ab}}^{L_a L_b L_{ab}}$ . Further, it follows from (16) that, contrary to the assertion made in<sup>[10]</sup>, the quantity  $B_{l_a l_b l_{ab}}^{L_a L_b L_{ab}}$  cannot be represented in the form of a product of a  $\mu_a$ - and  $\mu_b$ -independent radial function and two numerical factors that depend on  $l_a \mu_a$  and  $l_b \mu_b$  and that respectively characterize the internal structures of the molecules  $a$  and  $b$ . Therefore, in the general case the use of the potential proposed in<sup>[10]</sup> seems to us to be incorrect.

Comparison of the formulas (3) and (15) allows us to

express the sought functions  $R_{0\mu_a \mu_b}^{l_a l_b}$  in terms of the coefficients  $c^{L_a L_b L_{ab}}$ , which are determined by the effective pair interaction  $v_{ik}(r_{ik})$ :

$$R_{0\mu_a \mu_b}^{l_a l_b}(r) = (2l_a + 1)(2l_b + 1)(2l + 1) \sum_{L_a L_b L_{ab}} \left\{ \begin{matrix} l & l_a & l_b \\ L_{ab} & L_b & L_a \end{matrix} \right\} \begin{pmatrix} L_a & l_a & L_{ab} \\ 0 & 0 & 0 \end{pmatrix} \times \begin{pmatrix} L_b & l_b & L_b \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_b & l & L_a \\ 0 & 0 & 0 \end{pmatrix} \sum_{i, k=1}^{N_a, N_b} c^{L_a L_b L_{ab}}(r, a_i, b_k) C_{\mu_a}^{l_a}(\mathbf{n}_i') C_{\mu_b}^{l_b}(\mathbf{n}_k'). \quad (17)$$

Usually, as the function  $v_{ik}(r_{ik})$ , potentials of the Lennard-Jones, Buckingham, or Morse type, or exponential functions with shifted interaction centers are taken.<sup>[7, 8, 12]</sup> However, for all these functions the coefficients  $c^{L_a L_b L_{ab}}$  and, consequently, the  $R_{0\mu_a \mu_b}^{l_a l_b}$  cannot be computed analytically. Furthermore, the number of variable parameters in them sometimes turns out to be insufficient for the description of the experimental data in a wide range of energies (temperatures) to be possible. Therefore, it seems to us to be more convenient to use for the description of the effective pair interaction in the general case the following approximating polynomial:

$$v_{ik}(r_{ik}) = \sum_{n=0}^N e^{-\alpha_n(i, k) r_{ik}} \sum_{m=0}^M \beta_{mn}(i, k) r_{ik}^{2m}, \quad (18)$$

where the parameters  $\alpha_n(i, k)$  and  $\beta_{mn}(i, k)$  characterize the interaction between the pair of atoms  $i$  and  $k$ , and are determined with the aid of the procedure described below. Practical calculations have shown that, for a good approximation of the function  $v_{ik}$ , it is sufficient in many cases to restrict ourselves to one or two terms in the formula (18).

The fact that the approximating polynomial depends only on even positive powers of  $r_{ik}$  allows us to express  $c^{L_a L_b L_{ab}}$  in terms of derivatives of modified Bessel functions, and to write the expressions for  $c^{L_a L_b L_{ab}}$  and  $R_{0\mu_a \mu_b}^{l_a l_b}$  in analytic forms. In this case the functions  $R_{0\mu_a \mu_b}^{l_a l_b}$  and, in particular,  $R_{000}^{000}$  will depend on all the parameters of the effective pair interaction. This allows us to determine  $\alpha_n(i, k)$  and  $\beta_{mn}(i, k)$  from the condition

$$R_{000}^{000}(r) = \bar{V}_{\text{val}}(r), \quad (19)$$

where

$$\bar{V}_{\text{val}}(r) = \bar{V}_{\text{emp}}(r) - [\bar{V}_{\text{mul}}(r) + \bar{V}_{\text{ind}}(r) + \bar{V}_{\text{dis}}(r)]. \quad (20)$$

Here  $\bar{V}_{\text{emp}}(r)$  is the averaged empirical potential determined from thermodynamic or kinetic quantities. The expression in the brackets in (20) represent the contributions of the multipole, the induction, and the dispersion potentials averaged over the orientation of the molecules.

As a specific method for calculating the parameters  $\alpha_n(i, k)$ ,  $\beta_{mn}(i, k)$ , it is convenient to use, for example, the minimization of the following functional:

$$\Phi\{\alpha_n(i, k), \beta_{mn}(i, k)\} = \sum_{r=0}^g \{R_{000}^{000}(r_i) - \bar{V}_{\text{val}}(r_i)\}^2, \quad (21)$$

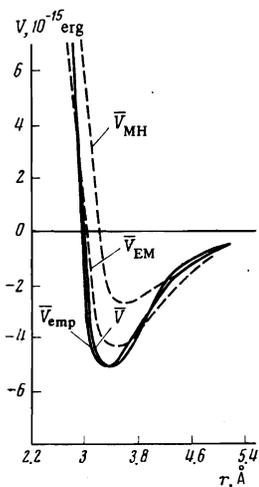


FIG. 1. Comparison of the averaged—over the orientations—interaction energy,  $\bar{V}$ , obtained in the present paper for two hydrogen molecules with the empirical potential  $\bar{V}_{\text{emp}}$  and with the mean potentials,  $\bar{V}_{\text{EM}}$  and  $\bar{V}_{\text{MH}}$ , obtained in<sup>[8,11]</sup> from quantum-chemical calculations.

where the  $r_s$  are the points where the functions are joined and  $S$  is the total number of connection points, i. e., of the  $r_s$ .

The pair-interaction parameters thus found allow us to compute the coefficients  $R_{000}^{l_a l_b}$  with  $l, l_a, l_b \neq 0$  and thereby re-establish the complete angular dependence of the potential from the averaged potential  $\bar{V}_{\text{emp}}(r)$ .

### 3. THE INTERACTION ENERGY OF $\text{H}_2\text{-H}_2$

As an illustration of the considered method, let us compute the angular dependence of the intermolecular potential of  $\text{H}_2\text{-H}_2$ . The choice of the molecules  $\text{H}_2\text{-H}_2$  is due to the fact that it is only for this pair that the obtained orientational dependences can be compared with both the results of quantum-chemical calculations and experimental data on the differential cross sections for scattering. The valence part of the interaction potential  $V_{\text{val}}$  in this case assumes the form

$$V_{\text{val}}(r, \Omega_a, \Omega_b) = \sum_{l_a l_b} R_{000}^{l_a l_b}(r) A_{000}^{l_a l_b}(\mathbf{n}, \Omega_a, \Omega_b), \quad (22)$$

where  $l, l_a,$  and  $l_b$  run through only even values.

For the computations of the pair-interaction parameters from the formula (21), as  $\bar{V}_{\text{emp}}$  in (20), we chose the Lennard-Jones potential<sup>[7]</sup>:

$$\bar{V}_{\text{emp}}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad (23)$$

with  $\epsilon = 5.11 \times 10^{-14}$  erg and  $\sigma = 2.93 \times 10^{-8}$  cm. This empirical potential describes the temperature dependence of the second virial coefficient for the  $\text{H}_2$  molecules with a relative error not exceeding  $\sim 10\%$ .

As to  $\bar{V}_{\text{mul}}$  and  $\bar{V}_{\text{ind}}$ , they are, in the case under consideration, equal to zero, while  $V_{\text{dis}} = -k/r^6$ , where

$$k = 1.05 \times 10^{-59} \text{ erg-cm}^6.$$

As the approximating pair-interaction function, we used the polynomial (18) with five independent parameters. These parameters were varied until the functional  $\Phi$  being minimized became, for  $S=8$ , less than  $0.04 \epsilon^2$ . It turned out in this case that the pair interaction is, to within an error of 5%, well described by the function

$$v_{\text{HH}}(r_{\text{HH}}) = \beta e^{-\alpha r_{\text{HH}}}, \quad \alpha = 0.72 \cdot 10^{16} \text{ cm}^{-2}, \quad \beta = 1.34 \cdot 10^{-12} \text{ erg}. \quad (24)$$

The corresponding  $R_{000}^{l_a l_b}$  coefficients for this case have the form

$$R_{000}^{l_a l_b}(r) = [1 + (-1)^{l_a}] [1 + (-1)^{l_b}] (2l_a + 1)(2l_a + 1)(2l_b + 1) \sum_{l_a l_b} \begin{pmatrix} L_a & l_a & L_{ab} \\ 0 & 0 & 0 \end{pmatrix} \times \begin{pmatrix} L_{ab} & l_b & L_b \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_b & l & L_a \\ 0 & 0 & 0 \end{pmatrix} \left\{ \begin{matrix} l & l_a & l_b \\ L_{ab} & L_b & L_a \end{matrix} \right\} c^{l_a l_b l_{ab}}(r, a), \quad (25)$$

where

$$c^{l_a l_b l_{ab}}(r, a) = (-1)^{l_a + l_b + l_{ab}} (2L_a + 1)(2L_b + 1) \times (2L_{ab} + 1) \beta e^{-\alpha(r^{2+2a})} i_{L_a}(2\alpha ar) i_{L_b}(2\alpha ar) i_{L_{ab}}(2\alpha a^2). \quad (26)$$

In particular,

$$R_{000}^{00}(r) = 4\beta e^{-\alpha(r^{2+2a})} \sum_{L=0}^{\infty} (2L+1) i_L(2\alpha a^2) [i_L(2\alpha ar)]^2. \quad (27)$$

For the molecules  $\text{H}_2$  the distance  $a = 3.72 \times 10^{-9}$  cm.

A numerical analysis of the individual terms in the sum (22) showed that, for  $E_{\text{kin}} < 10^{-13}$  erg, at virtually all the distances under consideration the maximum contribution to this sum is made by the terms with the indices  $l, l_a, l_b = 0, 2$ , so that

$$V_{\text{val}}(r) \approx R_{000}^{00}(r) \{1 + \varphi(r) [P_2(\mathbf{n}_a) + P_2(\mathbf{n}_b)]\}. \quad (28)$$

The contribution of the polynomial  $P_2(\mathbf{n}_a, \mathbf{n}_b)$  is considerably smaller ( $(a/r)^2$  times smaller); the coefficient attached to it almost does not depend on  $r$  and is approximately equal to  $4(\alpha a^2)^2/3$ . The contribution of the next polynomials,  $P_4(\mathbf{n}_a), P_4(\mathbf{n}_b)$ , and  $P_2(\mathbf{n}_a)P_2(\mathbf{n}_b)$  is also very small. For  $\alpha ar < 1$ , the function  $\varphi(r) \equiv R_{000}^{20}/R_{000}^{00}$  is approximately equal to  $\frac{2}{3}(\alpha ar)^2$  in the region of the minimum of the potential. At large distances, however, it decreases like  $(a/r)^2$ . The contribution of the  $R_{000}^{l_a l_b}$  terms with  $l, l_a, l_b > 2$  is negligibly small, since in the molecules  $\text{H}_2$  the transitions involving angular-momentum changes greater than two units are connected with large energy changes  $\Delta E > E_{\text{kin}}$ .

The averaged—over all the orientations of the molecules—potential  $\bar{V}(r)$  with the parameters  $\alpha$  and  $\beta$  given above and the empirical potential  $V_{\text{emp}}(r)$  are shown in Fig. 1.

The orientational dependences of the interaction energy, including, besides the above-computed  $V_{\text{val}}$ , the quadrupole and dispersion interactions, are shown in Fig. 2. Also shown there for comparison are the Evett-Margenau (EM) curves,<sup>[8]</sup> which were computed by quantum-chemical methods, and which are at present appar-

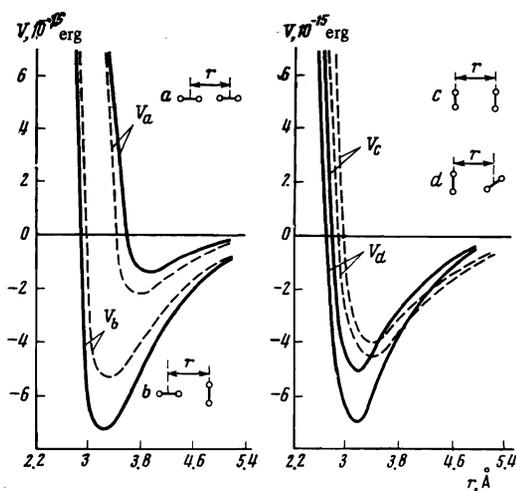


FIG. 2. The energy of interaction between two hydrogen molecules for four molecular orientations. The solid curves are the curves obtained in the present paper; the dashed curves are the results of Eveit and Margenau's quantum-chemical calculations.<sup>[8]</sup>

ently the most exact. The more recent results obtained by Mason and Hirschfelder (MH)<sup>[11]</sup> are, in the opinion of the authors themselves, less exact. As can be seen from the figures, the angular dependence of the obtained curves is more critical than that of the EM curves. A similar trend was revealed in<sup>[11]</sup>. This is partly due to the fact that Eveit and Margenau did not take the angular dependence of the dispersion interaction into account. Another reason for this may be the difference between  $\bar{V}_{EM}$  and  $\bar{V}_{emp}$ , to which difference the present calculation (Fig. 1) is tied. Considering all the foregoing, the agreement between the curves shown can be considered to be quite satisfactory. This indicates that the pair-interaction approximation for the valence potential is a good one in the low-energy region. The errors of the calculation are due mainly to the errors in  $V_{emp}(r)$ , and can be reduced by determining the latter more accurately.

On the whole, it should be said that the method under consideration allows us to fairly simply compute the interaction energy of the molecules, and, what is especially important, this method enables us to determine the interaction of complex molecules, for which the exact quantum-chemical calculation is not possible and there are no data on the differential cross sections for elastic and inelastic scattering.

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