where H--H--C and H--D--C are weak bonds and make a negligible contribution, leads to a value of -2 kcal. Therefore, $E_5-E_2=1$ kcal compared with the experimental value of 1.0 kcal.

The preexponential factor for this pair of isotopic reactions can be calculated from the difference in the entropies of activation. Using the same loose complex as above and applying the expression derived by Bigeleisen[8] for the calculation of entropy differences between isotopic molecules, a value of 0.8 is obtained for A_2/A_5, 1.1 being obtained experimentally. The

[8] J. Bigeleisen, J. Chem. Phys. 21, 1333 (1953).

assumption of a weak H--H bond in the activated complex for the $H+H_2CO$ reaction is in reasonable accord with the experimental data. This leads to $E_5=E_7$ and $E_6=E_2$. The activation energies E_2, E_5, E_6 have thus been evaluated relative to E_7. The latter has been determined relative to E_8 and E_9,[2] where

$$(8) \qquad D+H_2 \rightarrow HD+H$$

$$(9) \qquad D+CH_4 \rightarrow HD+CH_3$$
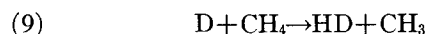
A summary of the activation energies thus far obtained is presented in Table I.

Transport in Dilute Gases and Chemical Forces

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(Received February 4, 1960)

It is shown that the theory of transport phenomena in gases may be so formulated that the potentials characterizing the cross sections, which account for intractions between molecules in the binary collision limit, are the same as those conventionally employed in investigations of molecular structure. Thus it is indicated that at least some of the essential features of chemical forces may be conveniently introduced into the description of such phenomena.

IN recent investigations Dahler[1] and von Roos[2] have formulated descriptions of transport phenomena for systems of polyatomic molecules taking explicit account of internal degrees of freedom. However, in both instances the effective potentials appearing in the Liouville equations for the statistical description of the center-of-mass motion of the molecules were formulated in slowly convergent terms with respect to the actual potentials expected to characterize the interactions between such systems. Specifically, these analyses have been so developed that, when employed in the context of the binary collision approximation for the description of dilute gases, the cross sections for collisions will be defined in terms of first-order perturbation approximations to the actual chemical potentials.

It is the purpose of this note to suggest that in terms of a suitably modified representation for the internal degrees of freedom of the system, some of the essential features of chemical forces can be retained in the statistical description of the systems presently under consideration. In order to develop this suggestion, we recall the structure of the Hamiltonian for such a system,

$$H = \sum_{j=1}^{N} [T(\xi^j) + V(\xi^j) + T(R^j)]$$
$$+ \sum_{i<j} V(\xi^i, \xi^j, R^{ij}), \qquad (1)$$

[1] J. S. Dahler, J. Chem. Phys. 30, 1447 (1959).
[2] Oldwig von Roos, J. Chem. Phys. 31, 1415 (1959).

where $T(\xi^j)$ is the kinetic energy of the internal degrees of freedom of the jth molecule; $V(\xi^j)$ the potential energy of same; $T(R^j)$ the kinetic energy of the center-of-mass motion of the jth molecule, and $V(\xi^i, \xi^j, R^{ij})$ is the potential energy of interaction between particles comprising the ith molecule and those of the jth molecule. We have here introduced the notation, $R^{ij} = R^i - R^j$, where R^j is the position of the center-of-mass of the jth molecule. We now introduce two-molecule wave functions in the conventional manner appropriate to the description of the two molecules in strong interaction. On defining

$$H^{ij} = T(\xi^i) + T(\xi^j) + V(\xi^i) + V(\xi^j)$$
$$+ V(\xi^i, \xi^j, R^{ij}), \qquad (2)$$

we develop the set of eigenfunctions for our present purposes according to

$$H^{ij}\Phi_{a_{ij}}(\xi^i, \xi^j, R^{ij}) = \mathcal{E}_{a_{ij}}(R^{ij})\Phi_{a_{ij}}(\xi^i, \xi^j, R^{ij}). \qquad (3)$$

Clearly the Φ's have been assumed to be a diagonalizing representation in ξ space, and hence they—as well as their eigenvalues $\mathcal{E}$—depend parametrically upon the components of the center-of-mass displacements R^{ij}. Noting that the potential $V(\xi^i, \xi^j, R^{ij})$ vanishes when the ith and jth molecules are infinitely far apart, and defining molecular wave functions according to

$$H^i\phi_{\alpha_i}(\xi^i) = E_{\alpha_i}\phi_{\alpha_i}(\xi^i), \qquad (4)$$

where

$$H^i = T(\xi^i) + V(\xi^i); \qquad (5)$$

we observe that

$$\underset{|\,\mathbf{R}^{ij}\,|\to\infty}{\mathrm{Lim}} \Phi_{a_{ij}}(\xi^i, \xi_j, \mathbf{R}^{ij})$$

$$\to \phi_{a_i}(\xi^i)\phi_{a_j}(\xi^j), \qquad (6)$$

if one chooses an unsymmetrized representation for the bimolecular states, or

$$\underset{|\,\mathbf{R}^{ij}\,|\to\infty}{\mathrm{Lim}} \Phi_{a_{ij}}(\xi^i, \xi^j, \mathbf{R}^{ij}) \to [\phi_{a_i}(\xi^i)\phi_{a_j}(\xi^j)$$

$$\pm \phi_{a_i}(\xi^j)\phi_{a_j}(\xi^i)]/\sqrt{2} \quad (7)$$

for a symmetrized representation. Symmetrization is here implied with respect to the simultaneous interchange of all of the coordinates of corresponding particles in the ith and jth molecules. Accordingly, one further expects that

$$\underset{|\,\mathbf{R}^{ij}\,|\to\infty}{\mathrm{Lim}} \mathcal{E}_{a_{ij}}(\mathbf{R}^{ij}) \to E_{a_i} + E_{a_j}. \qquad (8)$$

Both the bimolecular functions $\Phi_{a_{ij}}$ and the unimolecular functions ϕ_{a_i} are presumed to be unit vectors in their respective spaces.

The eigenvalues $\mathcal{E}_a$, considered as functions of the relative displacement of two interacting molecules, are the potentials which presumably characterize these interactions. It is part of our present purpose to indicate that transport theory in dilute gases may be so formulated that, in the binary collision approximation, the cross sections describing these collisions are to be computed (at least in part) within the context of a dynamical scheme characterized by these potentials.

We may now construct a complete orthonormal set of states in the space of the internal degrees of freedom of the system of N molecules, i.e.,

$$\{\Phi_{a_{12}}\Phi_{a_{34}}\cdots\Phi_{a_{N-1N}}\}, \qquad (9)$$

and in terms of them exhibit the wave function for the totality of the degrees of freedom of the system as

$$\Psi(\mathbf{R}, \xi, t) = \sum_{a_{12}\cdots a_{N-1-N}} \chi_{a_{12}\cdots a_{N-1N}}(\mathbf{R}, t)\Phi_{a_{12}}\cdots\Phi_{a_{N-1N}}.$$

$$(10)$$

A distribution function for the external degrees of freedom may now be defined by[2]

$$\tilde{F}_{a|a'} = (2\pi)^{-3N/2}\chi_a C_{a'}{}^* e(-i\mathbf{K}\cdot\mathbf{R}). \qquad (11)$$

In this expression the label a stands for the set of labels $\{a_{12}a_{34}\cdots a_{N-1N}\}$; the function $C_{a'}{}^*$ is the complex conjugate of the Fourier transform of $\chi_{a'}$, i.e.,

$$C_{a'}(\mathbf{K}^1\cdots\mathbf{K}^N, t)$$

$$= (2\pi)^{-3N/2}\int d^{3N}R \exp(-i\mathbf{K}\cdot\mathbf{R})\chi_{a'}(\mathbf{R}^1\cdots\mathbf{R}^N, t), \quad (12)$$

and $\mathbf{K}\cdot\mathbf{R}$ is the $3N$ dimensional scalar product

$$\mathbf{K}\cdot\mathbf{R} = \sum_{j=1}^{N}\mathbf{K}^j\cdot\mathbf{R}^j. \qquad (13)$$

Since the time derivatives of χ and C^* are directly deducible from the wave equation for Ψ, it is a straightforward matter to show that

$$D\tilde{F}_{a|a'} = (i/\hbar)\sum_b [\tilde{F}_{a|b}\Omega\{\mathcal{E}_b\delta_{ba'} + U_{ba'} + T_{ba'} + \mathbf{V}\cdot\mathbf{B}_{ba'}$$

$$- i\mathbf{K}\cdot\mathbf{B}_{ba'}\}^\dagger - \{\delta_{ab}\mathcal{E}_b + U_{ab} + T_{ab} - \mathbf{B}_{ab}\cdot\mathbf{V}$$

$$- i\mathbf{K}\cdot\mathbf{B}_{ab}\}\tilde{F}_{b|a}], \quad (14)$$

where all vectors are to be interpreted as $3N$-dimensional and we have introduced the symbols

$$D = [(\partial/\partial t) + (\hbar/M)\mathbf{K}\cdot\mathbf{V} - (i\hbar/2M)\nabla^2],$$

$$\Omega = \exp(-i'\nabla_K\cdot\nabla_R'), \qquad (15)$$

where the nablas with primes at the upper left or right are to be interpreted as acting to the left or right, respectively. The matrix elements of T, U, and $\mathbf{B}$ are,

$$T_{ab}$$

$$= (\Phi_{a_{12}}\cdots\Phi_{a_{N-1N}}, \sum_{j=1}^{N}[-(\hbar^2/2M)\nabla_R^{j2}]\Phi_{b_{12}}\cdots\Phi_{b_{N-1N}}),$$

$$U_{ab} = (\Phi_{a_{12}}\cdots\Phi_{a_{N-1N}},$$

$$\times \{(\sum_{\mathrm{Odd}\, i}\sum_{j>i+1} + \sum_{\mathrm{Even}\, i}\sum_{j>i})V(\xi^i, \xi^j, \mathbf{R}^{ij})\}\Phi_{b_{12}}\cdots\Phi_{b_{N-1N}})$$

and

$$\mathbf{B}_{ab} = (\Phi_{a_{12}}\cdots\Phi_{a_{N-1N}}, (\hbar^2/M)\nabla\Phi_{b_{12}}\cdots\Phi_{b_{N-1N}}), \quad (16)$$

and the eigenvalues $\mathcal{E}_a$ are explicitly

$$\mathcal{E}_a = \sum_{\mathrm{Odd}\, i} \mathcal{E}_{a_{i\,i+1}}. \qquad (17)$$

The distribution function defined by Eq. (11) and described by Eq. (14) is related to the conventional Wigner distribution function by

$$F_{a|a'} = \exp(\tfrac{1}{2}\nabla_K\cdot\nabla_R)\tilde{F}_{a|a'}. \qquad (18)$$

This latter function satisfies the Liouville equation

$$[(\partial/\partial t) + (\hbar/M)\mathbf{K}\cdot\mathbf{V}]F_{a|a'}$$

$$- (i/2\hbar)\sum_b [\mathbf{B}_{ab}\exp(\tfrac{1}{2}i'\nabla_R\cdot\nabla_K')\cdot\mathbf{V}F_{b|a'}$$

$$+ \mathbf{V}F_{a|b}e(-\tfrac{1}{2}i'\nabla_K\cdot\nabla_R')\cdot\mathbf{B}_{ba'}]$$

$$= (i/\hbar)\sum_b [F_{a|b}e(-\tfrac{1}{2}i'\nabla_K\cdot\nabla_R')$$

$$\times \{\delta_{ba'}\mathcal{E}_b + U_{ba'} - i\mathbf{K}\cdot\mathbf{B}_{ba'}\}$$

$$- \{\delta_{ab}\mathcal{E}_b + U_{ab} - i\mathbf{K}\cdot\mathbf{B}_{ab}\}e(\tfrac{1}{2}i'\nabla_R\cdot\nabla_K')F_{b|a'}]. \quad (19)$$

At least one aspect of this relation is amusing. It is noted that the transport terms (left-hand side) are modified in a fashion peculiar to systems characterized

by velocity dependent potentials. That indeed the effective potentials in the present representation have this property is supported by the observation that the eigenfunctions χ_a satisfy an equation of the form

$$i\hbar(\partial\chi_a/\partial t) = \sum_b \mathfrak{IC}_{ab}\chi_b, \qquad (20)$$

and

$$\partial\mathfrak{IC}_{ab}/\partial P_j = \delta_{ab}(P_j/M) - (i/\hbar)B_{jab}. \qquad (21)$$

The issue of symmetrization of the total wave function is somewhat more complicated here than in the instance that the internal degrees of freedom are dealt with in the context of the representation, $\{\phi_{\alpha_1}\cdots\phi_{\alpha_N}\}$. However, this difficulty is not inconveniencing here. The implications of the present derivation are such that one would expect the resulting equations to be useful only in the limiting instance that the binary collision assumption is applicable. Under such circumstances, it is sufficient to be able to define a distribution function corresponding to an arbitrary ordering into pairs-appropriate symmetrization *within* a given bimolecular function being presumed.

We emphasize the content of these remarks by turning our attention to an investigation of the implications of Eq. (19) for the reduced distribution functions. To this end we define the densities

$$g^{(i)}(\mathbf{x},\mathbf{k}) = \delta(\mathbf{R}^i - \mathbf{x})\,\delta(\mathbf{K}^i - \mathbf{k}),$$

$$g^{(ij)}(\mathbf{x},\mathbf{k},\mathbf{x}',\mathbf{k}')$$
$$= \delta(\mathbf{R}^i - \mathbf{x})\,\delta(\mathbf{K}^i - \mathbf{k})\,\delta(\mathbf{R}^j - x')\,\delta(\mathbf{K}^j - \mathbf{k}'),$$

$$g^{(ijl)}(\mathbf{x},\mathbf{k},\mathbf{x}',\mathbf{k}',\mathbf{x}'',\mathbf{k}'')$$
$$= \delta(\mathbf{R}^i - \mathbf{x})\,\delta(\mathbf{K}^i - \mathbf{k})\,\delta(\mathbf{R}^j - \mathbf{x}')\,\delta(\mathbf{K}^j - \mathbf{k}')$$
$$\times\delta(\mathbf{R}^l - \mathbf{x}'')\,\delta(\mathbf{K}^l - \mathbf{k}''), \qquad (22)$$

and the reduced distribution functions,

$$F_{a|a'}{}^{(i)} = \int d^{3N}R\,d^{3N}K\,F_{a|a'}g^{(i)}, \quad \text{etc.} \qquad (23)$$

If we concentrate our attention upon $F_{a|a'}{}^{(1)}$, we find that it satisfies the equation (neglecting terms which describe ternary collisions),

$$[(\partial/\partial t) + (\hbar/M)\mathbf{k}\cdot\nabla_x]F_{a|a'}{}^{(1)}$$

$$= (i\hbar/2M)\int d^3x'\,d^3k'\sum_b[(\nabla_x\partial_{a|b}{}^{(12)})e(-\tfrac{1}{2}i\,'\nabla_k\cdot\nabla_x')\cdot\Delta_{ba'}{}^{(1)} + \Delta_{ab}{}^{(1)}e(\tfrac{1}{2}i\,'\nabla_x\cdot\nabla_k')\cdot(\nabla_x F_{b|a'}{}^{(12)})]$$

$$+ (i\hbar/2M)\int d^3x'\,d^3k'\sum_b[F_{a|b}{}^{(12)}e(-\tfrac{1}{2}i\,'\nabla_k\cdot\nabla_x')(\Delta_{ba'}{}^2)^{(1)} + (\Delta_{ab}{}^2)^{(1)}e(\tfrac{1}{2}i\,'\nabla_x\cdot\nabla_k')F_{b|a'}{}^{(12)}]$$

$$+ (\hbar/M)\int d^3x'\,d^3k'\sum_b[\{F_{a|b}{}^{(12)}e(-\tfrac{1}{2}i\,'\nabla_k\cdot\nabla_x')(\mathbf{k}\cdot\Delta_{ba'}{}^{(1)} + \mathbf{k}'\cdot\Delta_{ba'}{}^{(2)})\}$$

$$- \{(\mathbf{k}\cdot\Delta_{ab}{}^{(1)} + \mathbf{k}'\cdot\Delta_{ab}{}^{(2)})e(\tfrac{1}{2}i\,'\nabla_x\cdot\nabla_k')F_{b|a'}{}^{(12)}\}]$$

$$+ (i/\hbar)\int d^3x'\,d^3k'[F_{aa'}{}^{(12)}e(-\tfrac{1}{2}i\,'\nabla_k\cdot\nabla_x')\mathcal{E}_{a'}{}^{(12)} - \mathcal{E}_a{}^{(12)}e(\tfrac{1}{2}i\,'\nabla_x\cdot\nabla_k')F_{a|a'}{}^{(12)}]. \qquad (24)$$

Here we have introduced the notation

$$\Delta_{ab}{}^{(1),(2)} = (\Phi_{a_{12}},\nabla_{1,2}\Phi_{b_{12}}),$$

$$(\Delta_{ab}{}^2)^{(1),(2)} = (\Phi_{a_{12}},\nabla_{1,2}{}^2\Phi_{b_{12}}). \qquad (25)$$

It is to be noted that having discarded terms characterizing three particle interactions (terms proportional to triplet densities) the issue of wave function symmetrization remains only in the ultimate treatment of the details of binary collisions and the reduction of the doublet densities to functionals of appropriate singlet densities.

Finally, it is recalled that the matrix elements (25) are in general expected to be small[3]; hence, if we ignore them entirely in Eq. (24), we obtain

$$[(\partial/\partial t) + (\hbar/M)\mathbf{k}\cdot\nabla_x]F_{a|a'}{}^{(1)}$$

$$= (i/\hbar)\int d^3x'\,d^3k'[F_{a|a'}{}^{(12)}e(-\tfrac{1}{2}i\,'\nabla_k\cdot\nabla_x')\mathcal{E}_{a'}{}^{(12)}$$

$$- \mathcal{E}_a{}^{(12)}e(\tfrac{1}{2}i\,'\nabla_x\cdot\nabla_k')F_{a|a'}{}^{(12)}]. \qquad (26)$$

[3] M. Born and J. R. Oppenheimer, Am. J. Phys. 84, 457 (1927).

In this approximation, $\hbar\mathbf{k}=M\mathbf{v}$, where $\mathbf{v}$ is the velocity of the particles; and the equation for the diagonal elements of (26) may be written compactly as

$$[(\partial/\partial t) + \mathbf{v}\cdot\nabla_x]F_{a|a}{}^{(1)}$$

$$= (2/\hbar)\int d^3x'\,d^3v'\,F_{a|a}{}^{(12)}\sin[(\hbar/2M)'\nabla_v\cdot\nabla_x']\mathcal{E}_a{}^{(12)}. \qquad (27)$$

In the classical limit, (27) becomes

$$[(\partial/\partial t) + \mathbf{v}\cdot\nabla_x]F_{a|a}{}^{(1)}$$

$$= M^{-1}\int d^3x'\,d^3v'\,(\nabla_x\mathcal{E}_a{}^{(12)})\cdot(\nabla_v F_{a|a}{}^{(12)}), \qquad (28)$$

which is simply the familiar Liouville relation between a singlet density $F_{a|a}{}^{(1)}$ and a doublet density $F_{a|a}{}^{(12)}$ for a system of particles interacting according to the potentials, $\mathcal{E}_a{}^{(12)}$.

Approximate Analytical Wave Functions for the 1sns ¹S States of He and He-Like Ions*

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Calculations have been made for the $1s2s$, $1s3s$, and $1s4s$ ¹S states of He and He-like ions, assuming wave functions of the symmetrized product form, $u(1) v(2) + u(2) v(1)$. The results are the best obtained till now using such a functional form, and are even better than some recent calculations which, in addition, use angular correlations.

The energy values obtained for He are: 2.1430_7, 2.0603_6, and 2.0332_0 for the $1s2s$, $1s3s$, and $1s4s$ ¹S states, respectively. The wave functions obtained were checked by other criteria besides the energy criterion.

1. INTRODUCTION

THE ground state of helium and He-like ions has been the subject of several investigations, but relatively little work has been done on the excited states of the same systems since the pioneer work of Hylleraas and Undheim,[1] Hylleraas,[2,3] and Coolidge and James.[4]

Recently, however, there seems to have been a renewed interest in this subject.[5-9] Our aim is to investigate the $1sns$ ¹S states which present the greatest difficulties in a general treatment of the excited states of He.[1] We are looking for a relatively simple functional form for these wave functions which can be physically visualized and the use of which can be extended to more complex systems.

The most powerful method for obtaining approximate wave functions is the variation method. Its use for the excited states is complicated by the additional requirement that the trial function must be kept orthogonal to the *exact* wave functions belonging to the lower states. In the case of two-electron systems, reliable approximations have been obtained only for the ground state, so in practice the condition is replaced by the weaker requirement that the wave function must be orthogonal to the *approximate* trial functions corresponding to the lower states (e.g., Mariott and Seaton[5]) However, this does not ensure that the trial energy value should always be higher than the exact one, and it is very difficult to infer conclusions about the accuracy of the wave function (the trial energy value may coincide with the exact one, but the wave function may be very wrong). Essentially, the same holds for the Hartree-Fock treatment of the excited states (e.g., Vizbarite *et. al*, the energy values for the $1s2s$ ¹S and $1s3s$ ¹S of He lie *below* the experimental value).

There is, however, a variant of the variation method due to Ritz, which is free from this defect. The wave function is approximated by a trial function which is a linear combination of given functions, the coefficients are determined from the condition that $\langle H \rangle_{Av}$ should be stationary and the secular determinant, respectively, give roots I_0, $I_1, \cdots$. Hylleraas and Undheim[1] and MacDonald[10] have shown that these roots are upper limits to the corresponding exact eigenvalues. Shull and Löwdin[11,12] obtained a criterion for the accuracy of the trial wave function and they have shown that the

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