Quasiclassical kinetic equation for gases with rotational degrees of freedom

V. D. Borman, A. S. Bruev, and L. A. Maksimov

Moscow Engineering Physics Institute

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The transition from the quantum kinetic equation to the classical Boltzmann equation via the quasiclassical approximation is considered. A quasiclassical representation for describing molecules with rotational degrees of freedom is proposed, in which the expectation values of operators representing physical quantities are equal to the corresponding classical values. For translational degrees of freedom, the states for such a representation are the well-known coherent states. The form of the kinematic part of the quasiclassical kinetic equation is considered for a gas in a magnetic or electric field that may affect the rotational degrees of freedom by interacting with the magnetic or electric dipole moments of the molecules. It is shown that when the rotational quantum numbers are large, the density matrix should be averaged over the rapid rotation. After such averaging, the density matrix should depend only on integrals of the rotational motion. The possible dependence of the collision probability for molecules with rotational degrees of freedom on the orientations of the relative velocity and rotational angular momenta of the colliding molecules resulting from the nonspherical character of the scattering is investigated. The symmetry properties of the collision probability are considered and the point groups are listed that describe the symmetries of molecules for which the probabilities for the direct and inverse collisions are equal.

It is well known that information concerning the interactions of molecules can be derived from studies of phenomena that are described with the aid of the kinetic equation, and the inverse problem of calculating the kinetic coefficients from the known interaction potential is of no less interest. It is clear that for the solution of such problems there must be a connection between the characteristics of the interaction and the kinetic coefficients. At present such a connection can be found with the aid of Boltzmann's equation only for the case of monatomic gas. As regards molecules having internal degrees of freedom, for them the problem is much more complicated owing to the larger number of parameters required to describe the interaction. The interaction between molecules having internal degrees of freedom lacks spherical symmetry, and as a result there appears a whole class of phenomena that are not observed in the case of monatomic gases. Such phenomena may include, for example, changes in the transport coefficients in magnetic and electric fields, birefringence of a gas undergoing viscous flow, the thermomagnetic rotation effect, depolarized Rayleigh scattering, nuclear spin relaxation, and others. To describe these phenomena one must use the kinetic equation for molecules having internal degrees of freedom.

Before 1961, authors of papers on kinetic phenomena attempted formally to extend the Chapman-Enskog method to the case of gases whose molecules have internal degrees of freedom, using various solid-body models (rough spheres, sphero-cylinders, etc.) to describe the molecular collisions. These studies suffered from a common fundamental defect: the solution was sought in a form that involves only a single vector—the velocity vector **v**. Such a solution is not suitable for describing the phenomena listed above, since for these phenomena the dependence of the distribution function on the rotational angular momentum vector **J**[1], which is responsible for the lack of spherical symmetry in the scattering, is important. A kinetic equation for the J-dependent distribution function was first obtained by Kagan and one of us[2] in a discussion of transport phenomena in a diatomic paramagnetic gas in a magnetic field.

Not only is a classical description possible, but also a quantum approach. A quantum equation for gases with rotational degrees of freedom was first obtained by Waldmann[3], and independently by Snider[4]. We note that at room temperatures, when rotational levels with large quantum numbers are excited, the two approaches (classical and quantum) lead to the same results. At the same time, the classical kinetic equation for the J-dependent distribution function is considerably simpler than the corresponding quantum equation, since the density matrix that satisfies the quantum equation, being a function of the coordinate **r** and momentum **p** of the molecule, is still a matrix with respect to the quantum numbers characterizing the orientation of the **J** vector.

The use of the Kagan-Maksimov classical equation or the Waldmann-Snider quantum equation to describe the phenomena listed above made it possible to construct a semiphenomenological theory in which the transport coefficients were related to the matrix $\mathscr{T}$ describing the scattering via the collision integrals. It was difficult to calculate the collision integrals directly because until recently there was no expression available for $\mathscr{T}$ in which the lack of spherical symmetry in the molecular scattering appeared explicitly. The most correct description of nonspherical scattering making use of the quantum theory of scattering was proposed by Hess, Köhler, and Waldmann[5] for treating the collisions of diatomic molecules, and in[6] for collisions of molecules with arbitrary symmetry. Thanks to the nonspherical scattering model proposed in[6] it became possible to take the deviations from spherical symmetry explicitly into account in the kinetic collision integrals. We must note, however, that great mathematical difficulties are encountered in using the quantum collision integral, even in the case of diatomic molecules.[7] But the classical collision integral contains an expression for the collision probability whose calculation in the classical treatment also appears to be impossible. It is therefore desirable to devise a quasiclassical representation in which the quantum kinetic equation would assume a simple classical form in the first order in the expansion parameter $\hbar$ (Planck's constant).

The most convenient representation for passing from the quantum kinetic equation to the corresponding classical one via the quasiclassical approximation proved to be one in which the expectation values of operators representing physical quantities are equal to the corresponding classical values. For translational degrees of freedom, the coherent states that are well known in quantum optics[8] have the desired properties. It was found that states with analogous properties can also be constructed for rotational degrees of freedom: in this representation the off-diagonal elements of the density matrix are small as compared with the diagonal elements and can be neglected. Thus, the quasiclassical description, unifying the classical and quantum approaches, enjoys all the principal advantages of each, since it enables one to use the thoroughly developed formalism of quantum mechanics fo calculate the density matrix, which is diagonal in the quasiclassical limit. We note that the quasiclassical representation for the rotational degrees of freedom also enables one to take into account in the simplest possible manner the possible dependence of the density matrix on the orientation of the rotational angular momentum vector, which is responsible for the lack of spherical symmetry in the molecular scattering, and to take the point symmetry of the molecules into account in deriving expressions for collision probabilities.

In Sec. 1 of this paper we formulate the general properties of the quasiclassical representation that are used to show how the quantum kinetic equation reduces to the classical Boltzmann equation in the first approximation in the expansion parameter. The coherent states mentioned above are used for a quasiclassical description of the translational degrees of freedom. As regards the analogous states for rotational degrees of freedom, we note that definite difficulties that arise in connection with the description of the angular variables[9] are encountered in constructing them.

In Sec. 2 we construct the corresponding quasiclassical rotational states for the case of large rotational quantum numbers and investigate their basic properties. In this section we also consider the form of the density matrix in the representation afforded by the quasiclassical rotational states (QRS).

In Sec. 3 we derive expressions for the left-hand side of the quasiclassical kinetic equation in the presence of a magnetic or electric field that can affect the rotational degrees of freedom by interacting with the magnetic or electric dipole moment of the molecule and thereby alter the density matrix. In such problems the external field must always be treated as perturbation, and the effect of the field can accordingly be treated in the first nonvanishing order of perturbation theory, while the density matrix is to be averaged over the rapid rotation that takes place in the case of large rotational quantum numbers. As a result of this averaging, the density matrix should depend only on integrals of the rotational motion.

Section 4 is devoted to a study of the collision probabilities for molecules with rotational degrees of freedom. In deriving expressions for the collision probability we were primarily interested in its dependence on the mutual orientations of the two rotational angular momentum vectors and the relative velocity vector of the colliding molecules. To obtain this dependence we used an expansion for the scattering matrix $\mathcal{T}$ that takes into account the deviation of the molecular interaction from spherical symmetry[6]. It will be evident from the resulting formulas that the point symmetry of the molecules imposes definite limitations on the behavior of the collision probability. Here we also consider the relation between the probabilities for the direct (w) and inverse (w′) collisions and indicate molecules (having definite symmetry) for which w = w′.

1. THE QUANTUM KINETIC EQUATION IN THE QUASICLASSICAL REPRESENTATION

As is well known, the time variations of the state of a quantum system are determined by the equation of motion for the density matrix:

$$i\hbar\frac{\partial\hat{\rho}}{\partial t}=[\hat{\mathscr{H}},\hat{\rho}], \tag{1.1}$$

where $\hat{\mathscr{H}}$ is the Hamiltonian operator and $[\hat{\mathscr{H}},\hat{\rho}]\equiv\hat{\mathscr{H}}\hat{\rho}-\hat{\rho}\hat{\mathscr{H}}$ In the case of rarefied gas, when we consider only two-body collisions, we can use Eq. (1.1) to derive the following equation for the single-particle density matrix[4] $\hat{\rho}(1)$:

$$\begin{gathered}i\hbar\partial\hat{\rho}(1)/\partial t=[\hat{\mathscr{H}}(1),\hat{\rho}(1)]+\mathrm{Sp}_2[V,\hat{\Omega}\hat{\rho}(1)\hat{\rho}(2)\hat{\Omega}^+],\\ \hat{\mathscr{H}}(1,2)=\hat{\mathscr{H}}(1)+\hat{\mathscr{H}}(2)+V(1,2),\end{gathered} \tag{1.2}$$

in which $\hat{\Omega}$ is the Møller wave operator[10], which is well known from scattering theory and satisfies the equation

$$\hat{\Omega}|a\rangle=\{1+\hat{G}_aV\hat{\Omega}\}|a\rangle=\{1+\hat{\Omega}\hat{G}_aV\}|a\rangle, \tag{1.3}$$

in which

$$\hat{G}_a=(E_a-\hat{K}+i\varepsilon)^{-1},\quad \hat{K}|a\rangle=\{\hat{\mathscr{H}}(1)+\hat{\mathscr{H}}(2)\}|a\rangle=E_a|a\rangle,\quad \varepsilon\to+0. \tag{1.4}$$

Equation (1.2) is written in operator form and therefore is independent of the representation, which is always to be chosen from considerations of convenience. A representation in which the expectation values of operators representing physical quantities agree with the corresponding classical values has been found to be the most convenient for passing from the quantum kinetic equation to the classical one. Operators representing physical quantities are diagonal to terms of the order of $\hbar$ in the quasiclassical limit, so the passage from the quantum equations to the corresponding classical equations is very clear in such a representation, since it reduces simply to the passage to the limit $\hbar\to 0$. Moreover, the plane-wave representation $|p\rangle$ usually used in the quantum theory of scattering has definite disadvantages from the point of view of a quasiclassical treatment since the quantity $\langle p|x|p\rangle$ is not defined at all in this representation. For translational degrees of freedom (TDF) the so called coherent states[8], which are well known in quantum optics, have the required properties. The analogous states for the rotational degrees of freedom (RDF) have not been so thoroughly studied, although attempts have been made to construct them[11]. We also note that the quasiclassical case of large rotational quantum numbers was not considered in those studies.

Now let us formulate the fundamental properties of the quasiclassical states and show in general form how the quantum kinetic equation (1.2) in the quasiclassical representation passes over into the classical kinetic equation.

In the traditional quantum mechanical approach one usually seeks a complete set of commuting operators representing physical quantities and uses their common eigenfunctions as the required set of basis vectors. In a quasiclassical treatment we include the operators for all the physical quantities that are necessary for a description of the state of the gas molecules in the complete set of operators $\{\hat{\lambda}_i\}$, i = 1, . . . p, even though these operators may not commute. Hence the quasiclassical states $|\lambda\rangle$ are not necessarily orthogonal to one another. However, in the general case the completeness condition is sufficient when choosing a set of basis vectors[8].

In accordance with what was said above, we define the quasiclassical representation $|\lambda\rangle$ by the following formulas:

$$\mathrm{Sp}_\lambda |\lambda\rangle\langle\lambda| = 1, \tag{1.5a}$$

$$\langle\lambda|\hat{\lambda}_i|\lambda\rangle = \lambda_i, \quad i = 1, \ldots, p, \quad \langle\lambda|\lambda\rangle = 1, \tag{1.5b}$$

$$\hat{\lambda}_i = \mathrm{Sp}_\lambda |\lambda\rangle\lambda_i\langle\lambda| + O(\hbar), \tag{1.5c}$$

where

$$|\lambda\rangle \equiv |\lambda_1 \ldots \lambda_p\rangle, \quad \mathrm{Sp}_\lambda \equiv \sum_{\lambda_1 \ldots \lambda_p}.$$

We note that in order for condition (1.5c) for the quasiclassical approximation to be satisfied it is sufficient that

$$\langle\lambda'|\hat{\lambda}_i|\lambda\rangle = \langle\lambda'|\lambda\rangle\lambda_i + O(\hbar) = \lambda_i'\langle\lambda'|\lambda\rangle + O(\hbar), \tag{1.6}$$

as can be easily seen by substituting (1.6) into the expansion

$$\hat{\lambda}_i = \mathrm{Sp}_\lambda\, \mathrm{Sp}_{\lambda'} |\lambda'\rangle\langle\lambda'|\hat{\lambda}_i|\lambda\rangle\langle\lambda|,$$

which is valid for any operator $\hat{\lambda}_i$.

Now let us consider the properties of the single-particle density matrix $\hat{\rho}$ in the λ representation. With the aid of Eq. (1.5c) and the formal expansion

$$\hat{\rho}|\lambda\rangle = \rho(\hat{\lambda}_1 \ldots \hat{\lambda}_p)|\lambda\rangle = \left\{\rho(\lambda_1 \ldots \lambda_p) + \sum_{i=1}^{p} \frac{\partial\rho(\lambda_1 \ldots \lambda_p)}{\partial\lambda_i}(\hat{\lambda}_i - \lambda_i) + \ldots\right\}|\lambda\rangle, \tag{1.7}$$

we obtain

$$\hat{\rho} = \mathrm{Sp}_\lambda |\lambda\rangle\rho(\lambda)\langle\lambda| + O(\hbar). \tag{1.8}$$

In writing Eq. (1.8) we have assumed that the density matrix $\hat{\rho}$ becomes a diagonal operator in the quasiclassical limit and have written only the first diagonal term. It is clear that $\rho(\lambda)$, which is real and nonnegative because the density matrix $\hat{\rho}$ is Hermitian and positive definite[8], has the properties necessary for a classical distribution function. The rule for calculating average values in the $|\lambda\rangle$ representation is

$$\bar{\hat{G}} = \lim_{\hbar\to 0} \mathrm{Sp}_\lambda \langle\lambda|\hat{\rho}\hat{G}|\lambda\rangle = \mathrm{Sp}_\lambda\, \rho(\lambda)\langle\lambda|\hat{G}|\lambda\rangle,$$

i.e., it reduces in the limit $\hbar \to 0$ to the rule for calculating average values in classical statistical mechanics.

To obtain an equation for $\rho(\lambda)$ we calculate the diagonal matrix elements in Eq. (1.2) in the limit $h \to 0$. With the aid of Eq. (1.7) we obtain

$$\mathscr{L}\rho = \frac{d}{dt}\rho = \left\{\frac{\partial}{\partial t} + \dot{\lambda}\frac{\partial}{\partial\lambda}\right\}\rho, \quad \dot{\lambda} = \frac{i}{\hbar}\langle\lambda|[\hat{\mathscr{H}}, \hat{\lambda}]|\lambda\rangle \tag{1.9}$$

for the left-hand side of Eq. (1.2). To calculate the right-hand side of Eq. (1.2) we make use of (1.3), (1.4), (1.8), and the well known relations

$$\langle\lambda|\hat{T}^+ - \hat{T}|\lambda\rangle = \langle\lambda|\hat{T}^+(\hat{G}_\lambda^+ - \hat{G}_\lambda)\hat{T}|\lambda\rangle = \langle\lambda|\hat{T}(\hat{G}_\lambda^+ - \hat{G}_\lambda)\hat{T}^+|\lambda\rangle,$$
$$\hat{T} = V\hat{\Omega} \tag{1.10}$$

and after some manipulation we obtain

$$\hat{I}_{\mathrm{col}}[\rho(1), \rho(2)] = \mathrm{Sp}_2\, \mathrm{Sp}_{1'2'}\{\rho(\lambda_1')\rho(\lambda_2')w(\lambda_1'\lambda_2' \to \lambda_1\lambda_2) - \rho(\lambda_1)\rho(\lambda_2)w(\lambda_1\lambda_2 \to \lambda_1'\lambda_2')\}, \tag{1.11}$$

in which $|\lambda\rangle = |\lambda_1\rangle \cdot |\lambda_2\rangle$, the subscripts 1 and 2 refer to the first and second particles, respectively, and

$$w(\lambda_1'\lambda_2' \to \lambda_1\lambda_2) = (2\pi/\hbar)|\langle\lambda|\hat{T}|\lambda'\rangle|^2\delta(E_{\lambda'} - E_\lambda)$$

is the probability density per unit time for the transition from state λ' to state λ. We also note that by using the unitarity condition (1.10) we can easily obtain the following relation between the probabilities w and w′:

$$\mathrm{Sp}_{1'2'} w(\lambda_1\lambda_2 \to \lambda_1'\lambda_2') = \mathrm{Sp}_{1'2'} w(\lambda_1'\lambda_2' \to \lambda_1\lambda_2). \tag{1.12}$$

As is evident from Eqs. (1.9) and (1.11), the equation obtained for $\rho(\lambda)$ is indeed the kinetic equation of classical statistical mechanics.

As we mentioned above, we shall use the coherent states as the states $|\lambda\rangle$ for the TDF. Equations (1.5a) and (1.5b), which define the quasiclassical representation, are derived in[8]. However, it is not difficult to see that condition (1.6) for the quasiclassical approximation is valid by making use of known properties of the coherent states. Thus, for example, for the coordinate operator $\hat{x}$ we have

$$\langle\lambda'|\hat{x}|\lambda\rangle \equiv \langle Z'|x|Z\rangle = x_0\langle Z'|Z\rangle + \frac{(Z'-Z)^*}{\sqrt{2}}\langle Z'|Z\rangle = x_0\langle Z'|Z\rangle + O(\hbar),$$

where

$$Z = \frac{1}{\sqrt{2}}(x_0 + ip_0), \quad \langle Z'|Z\rangle = \exp\left\{-\frac{1}{2\hbar}[|Z|^2 + |Z'|^2 - 2Z^*Z']\right\}, \tag{1.13}$$

$$\langle x|Z\rangle \equiv \langle x|x_0p_0\rangle = (\pi\hbar)^{-1/4}\exp\left(-\frac{(x-x_0)^2}{2\hbar}\right)\exp\left(\frac{i}{\hbar}p_0x\right)\exp\left(-\frac{i}{\hbar}\frac{x_0p_0}{2}\right).$$

2. QUASICLASSICAL STATES FOR ROTATIONAL DEGREES OF FREEDOM

a) Linear (diatomic) molecules

We shall define the wave functions for the quasiclassical rotational states (QRS) so as to minimize the quantity

$$\left(\frac{\Delta J}{J}\right)^2 = \frac{\langle\hat{J}^2\rangle - \langle\hat{J}\rangle^2}{\langle\hat{J}^2\rangle}$$

The attainable minimum is $(\Delta J/J)^2_{\min} = 1/(J+1)$; in the $|JM\rangle$ representation this value is achieved only for the states $|J \pm J\rangle$. In view of this, we choose

$$\langle\omega|JJ\rangle \equiv \langle\omega|J0J\rangle = i^J\left[\frac{2J+1}{8\pi^2}\right]^{1/2} D_{J0}^J(\omega), \quad J \gg 1. \tag{2.1}$$

as the QRS with $\langle J\rangle$ along the z axis (here the $\langle\omega|JKM\rangle$ are wave functions characterizing the orientation of a dynamical system with definite quantum numbers J, K, and M[12], and $D^J_{MK}(\omega)$ is Wigner's function[12]). We recall that K = 0 for linear molecules (K is the projection of the rotational angular momentum onto the axis of the molecule). The QRS functions for arbitrary orientation of the rotational angular momentum vector are obtained from (2.1) with the aid of the unitary operator $\mathscr{R}(\varphi\theta 0)$ that rotates the coordinate system from one in which J is directed along the z axis to one in which the orientation of J is specified by the angles θ and φ:

$$|\mathbf{J}\rangle \equiv |J\theta\varphi\rangle = \hat{\mathscr{R}}(\varphi\theta 0)|JJ\rangle, \tag{2.2}$$

We easily find the coefficients for expansion of the function $|\mathbf{J}\rangle$ in the complete set of basis functions $|JM\rangle$:

$$\langle J'M'|J\theta\varphi\rangle = \delta_{JJ'}D_{M'J}^{J*}(\varphi\theta 0). \tag{2.3}$$

Making use of the completeness of the states $|JM\rangle$, the orthogonality of the matrices $D^J_{MK}(\omega)$, and Eq. (2.3), we can easily show that the QRS functions form a complete set:

$$(2J+1)\int\frac{do}{4\pi}|J\theta\varphi\rangle\langle J\theta\varphi| = P_J, \quad P_J = \sum_M |JM\rangle\langle JM|, \tag{2.4}$$

$$\sum_J P_J = 1, \quad do = \sin\theta\, d\theta\, d\varphi.$$

We also note that the QRS functions are normalized to unity because of the unitarity of $\mathscr{R}(\varphi\theta 0)$. However, the QRS, like the coherent states, are not orthogonal. Using the theorem on the addition of rotations, we obtain the following expression for the overlap integral for two QRS:

$$\langle J'\theta'\varphi'|J\theta\varphi\rangle = \delta_{J'J}D_{JJ}^{J}(\varphi', \theta'-\theta, -\varphi). \tag{2.5}$$

It can be shown that in order for the condition

$$\langle J'\theta'\varphi'|\hat{G}|J\theta\varphi\rangle = \langle J'\theta'\varphi'|J\theta\varphi\rangle\langle J\theta\varphi|\hat{G}|J\theta\varphi\rangle + O(1/J) \tag{2.6}$$

for the quasiclassical approximation in the QRS representation to be satisfied, the operator $\hat{G}$ must satisfy the following conditions:

1. Only terms for which l is small as compared with J should appear in the expansion of $\hat{G}$ in the spherical tensors G_{lm}; and

2. For all positive p not exceeding l, $\exp(-pJ) \times \langle J \| \hat{G}_l \| J\rangle$ should tend to zero as J tends to infinity ($\langle J \| G_l \| J\rangle$ is the reduced matrix element of the operator $\langle \hat{G}_{lm}\rangle$).

It is clear that the operators $\hat{J}_i$ for the components of the rotational angular momentum satisfy this condition. It now remains to show that, in accordance with (1.5b),

$$\langle J|\hat{J}_i|J\rangle = J_i. \tag{2.7}$$

One can see that Eq. (2.7) holds for the QRS functions by making use of the definition of the functions $|J\rangle$ and the formula

$$\exp(-i\Phi\hat{J}_i)\hat{J}_k\exp(i\Phi\hat{J}_i) = \cos\Phi\hat{J}_k + \sin\Phi\varepsilon_{ikl}\hat{J}_l, \quad i\neq k.$$

In concluding, we also give the equation satisfied by the functions $|J\rangle$:

$$\{(\cos\theta\cos\varphi + i\sin\varphi)\hat{J}_x + (-\cos\theta\sin\varphi + i\cos\varphi)\hat{J}_y + \sin\theta\hat{J}_z\}|J\rangle = 0.$$

b) Symmetric top molecules

The QRS functions for a symmetric top can be constructed in a manner similar to that described above for linear molecules. First we select a quasiclassical state for which

$$\langle\hat{J}_z\rangle = \langle\hat{J}_{z'}\rangle = J, \quad \langle\hat{J}_x\rangle = \langle\hat{J}_y\rangle = \langle\hat{J}_{x'}\rangle = \langle\hat{J}_{y'}\rangle = 0.$$

We have

$$\langle\omega|JJJ\rangle = i^J\left[\frac{2J+1}{8\pi^2}\right]^{1/2} D_{JJ}^{J}(\omega).$$

Here the $\hat{J}_{i'}$ are the operators for the components of the rotational angular momentum in the coordinate system $\{x', y', z'\}$ fixed rigidly to the molecule. The remaining QRS with arbitrary orientations of J can be written as follows:

$$|J\rangle \equiv |J\theta\varphi\sigma\psi\rangle = \hat{\mathscr{R}}(\varphi\theta 0)\hat{\mathscr{R}}(-\psi - \sigma 0)|JJJ\rangle. \tag{2.8}$$

Here σ and ψ define the orientation of J in the coordinate system fixed to the molecule. The minus signs in front of σ and ψ appear because the operators $\hat{J}_{i'}$ on which $\mathscr{R}(-\psi, -\sigma, 0)$ depends are generators of the inverse rotations of the coordinate system fixed to the molecule about the principal axes[12]. On expanding $|J\rangle$ in the complete set of basis states $|JKM\rangle$, we obtain the following expression for the expansion coefficients:

$$\langle J'K'M'|J\theta\varphi\sigma\psi\rangle = \delta_{JJ'}D_{M'J}^{J*}(\varphi\theta 0)D_{K'J}^{J*}(-\psi, \sigma, 0).$$

It is evident from (2.8) that all the properties of the QRS for symmetric top molecules are similar to those of the QRS for linear molecules and so need not be discussed in detail. Here we give only the completeness relation:

$$(2J+1)^2\iint\frac{do\, d\Omega}{(4\pi)^2}|J\theta\varphi\sigma\psi\rangle\langle J\theta\varphi\sigma\psi| = P_J,$$

$$P_J = \sum_{M,K}|JKM\rangle\langle JKM|, \quad \sum_J P_J = 1, \quad d\Omega = \sin\sigma\, d\sigma\, d\psi.$$

c) The density matrix in the QRS representation.

In the general case the density matrix $\hat{\rho}$ for the rotational degrees of freedom can depend both on the angular variables, for which we choose the Euler angles $\omega = \{\alpha, \beta, \gamma\}$, and on the operators $\hat{J}_i$ for the components of the rotational angular momentum. In view of this, we expand the density matrix as follows:

$$\hat{\rho} = \sum_{lm}\hat{\rho}_m^l(\hat{n}, \hat{J}_i)B_m^l(\omega), \tag{2.9}$$

where $\hat{n}$ is a set of operators describing the translational degrees of freedom and

$$B_m^l(\omega) = \sum_k \beta_k^l D_{mk}^l(\omega) \tag{2.10}$$

is a combination of components of the matrix $D^l_{mk}(\omega)$ that is invariant under the transformations of the point symmetry group of the molecule[6].

For states that do not differ much from equilibrium states one can evidently drop all but the first few terms with l comparable with unity from the sum in (2.9). In view of this and the fact that $\langle J \| \hat{\rho} \| J\rangle$ is a partial probability and therefore tends to zero as J tends to infinity, we shall assume that the density matrix $\hat{\rho}$ is quasidiagonal in the QRS representation. We should also point out that it is meaningless to use the density matrix in the QRS representation except when

$$\overline{\hat{J}^2} = \mathrm{Sp}\,\hat{\rho}\hat{J}^2 \gg 1.$$

Since in the QRS representation the density matrix is diagonal in J to terms of the order of 1/J, we replace the function $D^l_{mk}(\omega)$ in (2.10) by an equivalent operator that is diagonal in J:

$$D_{mk}^l(\omega) \to \gamma_l(J)Y_{lm}(\hat{\mathbf{J}})Y_{lk}^*(\hat{\mathbf{J}}'),$$

where $Y_{lm}(\hat{J}) = (\hat{J}\nabla)^l Y_{lm}(\mathbf{r})$ is a spherical tensor operator constructed from the operators $\hat{J}_i$ for the components of the rotational angular momentum. The functions $Y_{lm}(\hat{J})$, $Y_{lk}(\hat{J}')$, and $\gamma_l(J)$ for l = 0–4 are given explicitly in[6]. As a result of this substitution, the density matrix for the rotational degrees of freedom will depend only on the operators $\hat{J}_i$ and $\hat{J}_{i'}$.

In accordance with the fact that the density matrix $\hat{\rho}$ is quasidiagonal, we can use (2.4) to obtain the following equation for linear molecules:

$$\hat{\rho} = \sum_J (2J+1)\int\frac{do}{4\pi}|\mathbf{J}\rangle\rho(\mathbf{J})|\mathbf{J}| + O\left(\frac{1}{J}\right), \quad \rho(\mathbf{J}) = \langle\mathbf{J}|\rho|\mathbf{J}\rangle. \tag{2.11}$$

It is convenient to expand the matrix element $\rho(J)$ in the complete set of functions $D^l_{m0}(\varphi\theta 0)$:

$$\rho(\mathrm{J})=\sum_{lm}\rho_{lm}(J)D_{m0}{}^{l}(\varphi\theta 0). \tag{2.12}$$

To find the coefficients $\rho_{lm}(\mathrm{J})$ we first substitute (2.12) into (2.11) and make use of (2.3) to obtain

$$\langle JM'|\rho|JM\rangle=\sum_{lm}\rho_{lm}(J)\langle lmJM|JM'\rangle\langle l0JJ|JJ\rangle, \tag{2.13}$$

where $\langle j_1m_1j_2m_2|jm\rangle$ is a Clebsch-Gordan coefficient. Then multiplying (2.13) by $\langle l'm'JM|JM'\rangle$ and summing over M and M′, we find

$$\rho_{lm}(J)=\frac{2l+1}{2J+1}\langle l0JJ|JJ\rangle^{-1}\sum_{M'M}\langle lmJM|JM'\rangle\langle JM'|\hat\rho|JM\rangle. \tag{2.14}$$

Finally, using (2.12) and (2.14), we obtain

$$\rho(J)=\sum_{lm}D_{m0}{}^{l}(\varphi\theta 0)\frac{2l+1}{2J+1}\langle l0JJ|JJ\rangle^{-1}\sum_{M'M}\langle lmJM|JM'\rangle\langle JM'|\hat\rho|JM\rangle. \tag{2.15}$$

For top-type molecules the formula analogous to (2.15) has the form

$$\rho(J)=\sum_{lm,st}D_{m0}{}^{l}(\varphi\theta 0)D_{t0}{}^{s*}(\psi\sigma 0)\frac{(2l+1)(2s+1)}{(2J+1)^2}\langle l0JJ|JJ\rangle^{-1}\langle s0JJ|JJ\rangle^{-1}\cdot$$
$$\times\sum_{M'M,K'K}\langle lmJM|JM'\rangle\langle stJK|JK'\rangle\langle JK'M'|\hat\rho|JKM\rangle. \tag{2.16}$$

Formulas (2.13), (2.15), and (2.16) determine the relation between the QRS and $|\mathrm{JKM}\rangle$ representations; moreover, it is evident from (2.15) and (2.16) that, while the density matrix ρ is quasidiagonal in the QRS representation to terms of the order of 1/J for arbitrary θ and φ, generally speaking it is not quasidiagonal in the $|\mathrm{JKM}\rangle$ representation for values of K and M of the order of unity.

3. THE KINEMATIC PART OF THE QUASICLASSICAL KINETIC EQUATION FOR GASES HAVING ROTATIONAL DEGREES OF FREEDOM

In this section we shall discuss the form of the left-hand side (1.9) of the quasiclassical kinetic equation for a gas in the presence of an external magnetic or electric field for the general case in which the gas molecules have rotational degrees of freedom. Such a discussion becomes necessary if, for example, one is to investigate the effect of external fields on the transport coefficients for molecular gases. We note that in the presence of a field that can be treated as a perturbation, the QRS functions can be used only as zeroth approximation functions. If the field has no effect in this approximation, then in place of the states $|\lambda\rangle$ we must use the states $|\tilde\lambda\rangle$ that satisfy the equation

$$\{\hat H^{(0)}+\hat{\mathscr{H}}'\}|\tilde\lambda\rangle=E|\tilde\lambda\rangle, \tag{3.1}$$

in which $\hat H^{(0)}$ is an operator for which the states $|\lambda\rangle$ are exact eigenfunctions, $\hat{\mathscr{H}}'$ is the perturbation operator, and E is the eigenvalue of the "perturbed" operator $\{\hat H^{(0)}+\hat{\mathscr{H}}'\}$ for the eigenfunction $|\tilde\lambda\rangle$.

a) Nonparamagnetic molecules in a magnetic field

Let **a**, **b**, and **c** be unit vectors in the directions of the axes of a coordinate system fixed to the molecule and conforming to its symmetry[6]. Then for the Hamiltonian operator for a nonparamagnetic molecule in a magnetic field **B** we have

$$\hat{\mathscr{H}}=\hat{\mathscr{H}}_0+\hat{\mathscr{H}}',$$

where

$$\hat{\mathscr{H}}_0=A(a_i\hat J_i)^2+B(b_i\hat J_i)^2+C(c_i\hat J_i)^2, \tag{3.2}$$

A, B, and C being the rotational constants of the molecule. In writing (3.2) we have assumed that the axes of the coordinate system $\{x', y', z'\}$ are parallel to the principal axes of the tensor of inertia of the molecule. In the general case this is valid provided the point symmetry of the molecule is no lower than C_{2v} or D_{2h}; hence in the following we shall consider only molecules with such symmetry. For symmetric top molecules we must put A = B in (3.2); for linear molecules, A = B and C = 0; and for spherical molecules, A = B = C. Here the perturbation operator is

$$\hat{\mathscr{H}}'=-(\hat{\boldsymbol{\mu}}\mathbf{B}), \tag{3.3}$$

where $\hat\mu$ is the operator for the magnetic moment of the molecule. In the general case $\hat{\mathscr{H}}'$ should also include terms depending on the nuclear spin; however, we can drop them since we are interested in the case of large J ($\mathrm{J}\gg 1$) and the magnetic fields are usually such as to decouple the rotational and nuclear magnetic moments[13].

Using the gyromagnetic tensor g_{ik}, we write the molecular magnetic moment operator $\hat\mu$ as follows:

$$\hat\mu_i=g_{ik}\hat J_k. \tag{3.4}$$

In most cases the properties of the gyromagnetic tensor are determined by the geometric symmetry of the molecule[14]; hence we write

$$g_{ik}=g_1a_ia_k+g_2b_ib_k+g_3c_ic_k. \tag{3.5}$$

For linear and symmetric-top molecules, $g_1 = g_2$ and

$$g_{ik}=g_1\delta_{ik}+(g_3-g_1)c_ic_k. \tag{3.6}$$

Finally, for spherical molecules we have $g_1 = g_2 = g_3$, and the gyromagnetic tensor is fully isotropic: $g_{ik} = g\delta_{ik}$.

We write the left-hand side of the quasiclassical kinetic equation for molecules with rotational degrees of freedom as follows:

$$\mathscr{L}\rho=\left\{\frac{\partial}{\partial t}+\dot J_i\frac{\partial}{\partial J_i}+\dot J_{i'}\frac{\partial}{\partial J_{i'}}\right\}\rho,$$
$$\dot J_i=i\langle[\hat{\mathscr{H}},\hat J_i]\rangle,\quad \dot J_{i'}=i\langle[\hat{\mathscr{H}},\hat J_{i'}]\rangle, \tag{3.7}$$

where the averages are to be taken over the states (3.1). We note that using the six variables J_i and $J_{i'}$ to describe the rotational degrees of freedom, which is done in order to simplify the calculations, does not lead to contradictions because the condition

$$J_x^2+J_y^2+J_z^2=J_{x'}^2+J_{y'}^2+J_{z'}^2=J^2.$$

is to be imposed on the variables. With the aid of (3.2) and (3.3), we obtain

$$\dot J_i=[\boldsymbol{\mu}\mathbf{B}]_i,\quad \mu_k=\langle\hat\mu_k\rangle=-\frac{\partial\Delta E}{\partial B_k},\quad \Delta E=\langle\hat{\mathscr{H}}'\rangle. \tag{3.8}$$

Then using (3.8), we find

$$\dot J_i\frac{\partial}{\partial J_i}=-i\gamma_{\mathrm{eff}}B_i\hat L_i, \tag{3.9}$$

where the $\hat L_i$, the operators for the angular momentum components, depend on θ and φ, and

$$\gamma_{\mathrm{eff}}=g_1\sin^2\sigma\cos^2\psi+g_2\sin^2\sigma\sin^2\psi+g_3\cos^2\sigma\quad\text{for}\quad g_1\neq g_2\neq g_3,$$
$$\gamma_{\mathrm{eff}}=g_1+(g_3-g_1)\cos^2\sigma\quad\text{for}\quad g_1=g_2\neq g_3,$$
$$\gamma_{\mathrm{eff}}=g\quad\text{for}\quad g_1=g_2=g_3. \tag{3.10}$$

In accordance with (3.7) we obtain the following expression for the operator $\dot J_{i'}\partial/\partial J_{i'}$:

$$\dot{J}_{i'}\frac{\partial}{\partial J_{i'}}=-i\mathscr{B}_{i'}J_{i'}\hat{L}_{i'},$$

$$\mathscr{B}_{x'}=2[A-g_1(\mathbf{BJ})J^{-2}],\quad \mathscr{B}_{y'}=2[B-g_2(\mathbf{BJ})J^{-2}],$$
$$\mathscr{B}_{z'}=2[C-g_3(\mathbf{BJ})J^{-2}], \tag{3.11}$$

where the $\hat{L}_{i'}$ depend on σ and ψ. Using the relation $J_{i'}L_{i'}=0$, it is not difficult to show that

$$\dot{J}_{i'}\frac{\partial}{\partial J_{i'}}=-i\{\mathscr{B}_{z'}-\mathscr{B}_{x'}\}J_{z'}\hat{L}_{z'}$$

for symmetric-top molecules, and $\dot{J}_{i'}\partial/\partial J_{i'}=0$ for linear and spherical-top molecules.

For reasonable values of the field strength **B**, the terms proportional to the field strength in (3.11) are small as compared with the corresponding field-independent terms and can be dropped. For example, for NH_3 molecules we have[14,15] $C = 6.29\ \mathrm{cm}^{-1}$, $A = 9.96\ \mathrm{cm}^{-1}$, $g_3 = 0.48\ \mu_n$, and $g_1 = 0.56\ \mu_n$ (μ_n is the nuclear magneton), so in a 1 kOe field the corresponding ratio is of the order of 10^{-7}. It is evident from the relationships adduced that $\dot{J}_{i'}\sim\omega_0$, where ω_0 is the frequency of the free rotation of the molecule. Since ω_0 is much larger than the collision frequency τ^{-1} we have

$$\dot{J}_{i'}\partial\rho/\partial J_{i'}=0. \tag{3.12}$$

in the zeroth approximation in $\omega_0\tau$. We note that the use of Eq. (3.12) to eliminate the "fast" variables is similar in import to the averaging over the rapid rotation that was considered in[1] for diatomic molecules.

A density matrix of the form

$$\rho=\rho(J,\ A\sin^2\sigma\cos^2\psi+B\sin^2\sigma\sin^2\psi+C\cos^2\sigma) \tag{3.13}$$

can serve as the solution to Eq. (3.12) for molecules with C_{2v} and D_{2h} symmetry, and a density matrix of the form

$$\rho=\rho(J,\ \cos\sigma), \tag{3.14}$$

for symmetric-top molecules. For spherical-top and linear molecules, $\dot{J}_{i'}\partial/\partial J_{i'}=0$, and there are no limitations of the type of (3.13) and (3.14). Hence, in accordance with (2.9) one must take into account only the point symmetry of the molecule. We also note that Eqs. (3.13) and (3.14). mean simply that after averaging over the rapid rotation of the molecule, the density matrix can depend only on integrals of the rotational motion.

b) Polar molecules in an electric field

For the Hamiltonian $\mathscr{H}$ for a molecule with a dipole moment d in an electric field E we have

$$\mathscr{H}=\mathscr{H}_0+\mathscr{H}',\quad \mathscr{H}'=-(\mathbf{dE}).$$

For molecules of various symmetry types, $\mathscr{H}_0$ is given by Eq. (3.2). We shall also consider fully asymmetric molecules. In this case $\hat{H}_0$ is also given by Eq. (3.2) provided the axes of the coordinate system $\{x',y',z'\}$ are parallel to the principal axes of the tensor of inertia of the molecule. The dipole moment operator $\hat{d}_i$ for an asymmetric molecule can be written as follows:

$$\hat{d}_i=d_1a_i+d_2b_i+d_3c_i.$$

One must put $d_1 = d_2 = 0$ for molecules with C_{2v} symmetry, symmetric tops, and linear molecules with $C_{\infty v}$ symmetry. As in the case treated above we have Eq. (3.8), so here we have

$$i\langle[\hat{\mathscr{H}},\hat{J}_i]\rangle=[\mathbf{d}\times\mathbf{E}]_i,\quad \mathbf{d}=-\frac{\partial\Delta E}{\partial\mathbf{E}},\quad \Delta E=\langle\hat{\mathscr{H}}'\rangle. \tag{3.15}$$

Using (3.15), we obtain

$$\dot{J}_i\frac{\partial}{\partial J_i}=-i\gamma_{\mathrm{eff}}E_i\hat{L}_i,$$
$$\gamma_{\mathrm{eff}}=J^{-1}\{d_1\sin\sigma\cos\psi+d_2\sin\sigma\sin\psi+d_3\cos\sigma\} \tag{3.16}$$

The coefficient γ_{eff} vanishes for linear molecules with $C_{\infty v}$ symmetry. In an electric field the expression for $\dot{J}_{i'}\partial/\partial J_{i'}$ takes the form

$$\dot{J}_{i'}\frac{\partial}{\partial J_{i'}}=-i\mathscr{E}_{i'}J_{i'}\hat{L}_{i'},$$

$$\mathscr{E}_{x'}=2A-\frac{d_1}{J_{x'}}(\mathbf{EJ})J^{-2},\quad \mathscr{E}_{y'}=2B-\frac{d_2}{J_{y'}}(\mathbf{EJ})J^{-2},\quad \mathscr{E}_{z'}=2C-\frac{d_3}{J_{z'}}(\mathbf{EJ})J^{-2}. \tag{3.17}$$

Equation (3.17) is valid for asymmetric molecules. For symmetric-top molecules we have

$$\dot{J}_{i'}\frac{\partial}{\partial J_{i'}}=-i\{\mathscr{E}_{z'}-\mathscr{E}_{x'}\}J_{z'}\hat{L}_{z'}$$

and for linear molecules with $C_{\infty v}$ symmetry, $\dot{J}_{i'}\partial/\partial J_{i'}=0$.

The terms proportional to the field strength in (3.17) are small as compared with the field-independent terms and can be neglected. For example, for NH_3 molecules ($d = 1.50$) with $E = 300$ V/cm the corresponding ratio is of the order of 10^{-4}. As in the case of a magnetic field, the remaining terms in (3.17) will be the largest in the kinetic equation, so that Eq. (3.12) will be valid in the zeroth approximation in $\omega_0\tau$.

Up to now we have been considering the linear approximation in the field strength. The higher order corrections need be taken into account only when the fields are strong enough to require it or the effect of interest vanishes in the linear approximation (the case of linear molecules in an electric field). In the last case, taking the z axis in the direction of the electric field we obtain the following expression for the second order correction $\Delta E^{(2)}$:

$$\Delta E^{(2)}_{J,M}=\sum_{J'}\frac{|\langle JM|\mathscr{H}'|J'M\rangle|^2}{A[J^2-J'^2]}. \tag{3.18}$$

Using (3.18), we obtain the following expression in the second order of perturbation theory for $\gamma^{(2)}_{\mathrm{eff}}$ for a linear molecule with $C_{\infty v}$ symmetry:

$$\gamma^{(2)}_{\mathrm{eff}}=\frac{3d^2}{4AJ^4}(\mathbf{EJ}).$$

c) Paramagnetic molecules in a magnetic field

In paramagnetic molecules, the effect of rotation always predominates over multiplet splitting when the rotational quantum number K is large; hence Hund's case b[16] is realized by such molecules. In view of this, we choose to describe the free molecule in terms of the states $|\Lambda KNSJ\theta\varphi\rangle$, where Λ is the projection of the orbital angular momentum L onto the axis of the molecule, K is the rotational angular momentum, N is the total orbital angular momentum, S is the spin of the molecule, J is the total angular momentum of the molecule, and θ and φ are angles specifying the orientation of the total angular momentum in the laboratory system. In this case the operator for the interaction with the field has the form

$$\hat{\mathscr{H}}'=-\mu_0(\hat{L}_i+2\hat{S}_i)B_i, \tag{3.19}$$

where μ_0 is the Bohr magneton and $\hat{S}_i$ and $\hat{L}_i$ are the operators for the spin and orbital angular momentum, respectively, of the electrons in the molecule. Operator (3.19) is diagonal in all the quantum numbers except J, so the left-hand side of the quasiclassical kinetic equation can be expressed in the usual form:

$$\mathscr{L}\rho=J_i\frac{\partial}{\partial J_i}\rho,\quad J_i=[\boldsymbol{\mu}\times\mathbf{B}]_i,\ \boldsymbol{\mu}=-\frac{\partial\Delta E}{\partial\mathbf{B}}.$$

With the aid of the expression for the Zeeman splitting of the terms of a diatomic molecule[17] we obtain

$$J_i\frac{\partial}{\partial J_i}=-i\gamma_{\text{eff}}B_i\hat{L}_i,$$

$$\gamma_{\text{eff}}=-\left[\frac{2\sigma}{J}+\frac{\Lambda^2+\sigma-\sigma^2+s(s+1)}{J^2}\right]\mu_0,\quad \sigma=J-N, \tag{3.20}$$

where σ is the projection of the spin onto the direction of the total angular momentum **J**.

4. COLLISION PROBABILITIES FOR NONSPHERICAL MOLECULES WITH ROTATIONAL DEGREES OF FREEDOM

In discussing the scattering of nonspherical molecules with rotational degrees of freedom we shall be primarily interested in such dependence of the collision probability $w(\lambda\lambda_1\to\lambda'\lambda_1')$ on the directions of the relative velocity and rotational angular momenta of the colliding molecules as may be allowed by the molecular symmetry. In order to obtain this dependence one must expand the scattering operator $\hat{T}$ in a manner that takes the lack of spherical symmetry of the scattering of rotating molecules explicitly into account[6]. Using the notation of[18] for products of spherical tensor operators, this expansion for the scattering of molecules by molecules can be written as follows:

$$\hat{T}=\sum_{ll_1L}T_{ll_1L}(\hat{K}^{(0)},r)\,[B^l(\omega)\times B^{l_1}(\omega_1)]^L Y^L(\mathbf{r}), \tag{4.1}$$

where the subscript 1 indicates the second molecule in the collision, **r** is the radius vector joining the centers of mass of the colliding molecules, and $\hat{K}^0$ corresponds to the operator $\hat{K}$ defined in (1.4) with the spherically symmetric operator $\hat{\mathscr{H}}^{(0)}_{\text{rot}}$ for the rotational energy, which is given by

$$\hat{\mathscr{H}}^{(0)}_{\text{rot}}={}^1/_3(A+B+C)\hat{J}^2.$$

The invariant combination $B^l_m(\omega)$ of elements of the matrix $D^l_{mk}(\omega)$ is defined by Eq. (2.10). We note that if $\hat{T}$ is invariant under inversion, the T_{ll_1L} vanish except when $l+l_1+L$ is even.

For scattering from an atom (from a spherically symmetric particle) one must put $l_1=0$ in (4.1).

Using expansion (4.1) for a collision probability w invariant under inversion and time reversal, one can obtain the following expression for the case of local scattering in the center of mass system (the necessary properties of the combinations $B^l_m(\omega)$ are discussed in the Appendix):

$$w(\lambda\lambda_1\to\lambda'\lambda_1')=\frac{2\pi}{\hbar}W(\mathbf{q},\{\mathbf{J}\},\{\sigma\psi\})\,\delta(E_\lambda+E_{\lambda_1}-E_{\lambda'}-E_{\lambda_1'}), \tag{4.2}$$

where $q=\mathbf{k}'-\mathbf{k}$ is the change in the relative momentum in the collision, and the symbol $\{c\}$ represents a set of four quantities: $\{y^i\}=\{y,y',y_1,y_1'\}$. The nonspherical expansion for the quantity W in (4.2) has the following form:

$$W=\sum_{mn}W_{mn},\quad W_{mn}=\alpha_{mn}\mathscr{A}_m\mathscr{B}_n,$$

where $m=\{\mathscr{L},\{S\},QQ_1\}$, $n=\{\{R\},F,F_1\}$,

$$\alpha_{mn}=\alpha_{mn}(q,\{J\})=\sum_{\nu\nu'}a_{\nu\nu'}(q,\{J\})\left[\frac{(2Q+1)(2Q_1+1)}{2\mathscr{L}+1}\right]^{1/2}.$$

$$\times\langle L0L'0|\mathscr{L}0\rangle\begin{Bmatrix}l & l_1 & L\\ l' & l_1' & L'\\ Q & Q_1 & \mathscr{R}\end{Bmatrix}b_{\mu\mu_1}(\{J\})\,b_{\eta\eta_1}(\{J\})\,c_{ll'F}c_{l_1l_1'F_1},$$

$$\nu=\{ll_1L\},\quad \mu=\{ll',SS',Q\},\quad \eta=\{ll',RR',F\},$$
$$b_{\mu\mu_1}(\{J\})=b_\mu(J,J')\;b_{\mu_1}(J_1,J_1'),$$

$$b_\mu(JJ')=\langle J'J'J'-J'|S'0\rangle\langle J-JJJ|S0\rangle\begin{Bmatrix}J' & J & l\\ J' & J & l'\\ S' & S & Q\end{Bmatrix};$$

$$\mathscr{A}_m=Y^{\mathscr{L}}\{[Y^{S'}\times Y^{S}]^Q\times[Y^{S_1'}\times Y^{S_1}]^{Q_1}\}^{\mathscr{L}},$$
$$\mathscr{B}_n=(\operatorname{Re}\beta^F\beta^{F_1})\,[Y^{R'}\times Y^{R}]^F[Y^{R_1'}\times Y^{R_1}]^{F_1}.$$

$$Y^{\mathscr{L}}=Y^{\mathscr{L}}(\mathbf{q}),\quad Y^{S^i}=Y^{S^i}(\mathbf{J}^i),\quad Y^{R^i}=Y^{R^i}(\sigma^i\psi^i) \tag{4.3}$$

and the quantities $c_{ll'F}$ are defined in the Appendix. The coefficients $a_{\nu\nu'}(q,\{J\})$ in (4.3) have the following properties:

$$a_{\nu\nu'}(q,\{J\})=\dot{a}_{\nu'\nu}(q,\{J\}), \tag{4.4a}$$

$$a_{\nu\nu'}(q,\{J\})=a_{\nu\nu'}(q,\{J\}^t),\quad \{J\}^t=\{J',J,J_1',J_1\}, \tag{4.4b}$$

Condition (4.4a) is associated with the fact that W is real, and (4.4b), with the invariance of W under time reversal.

Using the expression obtained above for the collision probability W and Eq. (4.4b) we can establish the relation between the probabilities for the direct ($w(\lambda\lambda_1\to\lambda'\lambda_1')$) and inverse ($w(\lambda'\lambda_1'\to\lambda\lambda_1)$) collisions. We note at once that the equation $w=w'$ can easily be obtained on the assumption that T is Hermitian, since in that case

$$|\langle a|\hat{T}|b\rangle|^2=|\langle b|\hat{T}|a\rangle|^2.$$

In the general case, however, the following relation obtains:

$$W_{mn}'=(-1)^{\Xi}W_{mn},\quad \Xi=\mathscr{L}+\sum S^i+\sum R^i. \tag{4.5}$$

Hence for the spherically symmetric probability $W^{(0)}$ ($\mathscr{L}=S^i=R^i=0$) the equality $w=w'$ obtains for all molecules. For the nonspherical part of the collision probability, the values possible for the sum X depend on the point symmetry of the molecules. Let us examine a few particular cases.

1. Let us consider only the "zeroth" invariant combination $\mathscr{B}n_0$, where $n_0=\{\{R\},00\}$. Then in accordance with the properties of the 9j symbols in the expression for $b_{\eta\eta_1}(\{J\})$, the following equalities should obtain: $R'=R$, $R_1'=R_1$, $l'=l$, and $l_1'=l_1$. When $l'=l$ and $l_1'=l_1$, the α_{mn} differ from zero only for even values of $S'+S+Q$ and $S_1'+S_1+Q_1$. In this approximation, therefore, the sum in (4.5) is equal to $\mathscr{L}+Q+Q_1$. There are three cases in which $\mathscr{L}+Q+Q_1$ will always be even:

a) when $Q_1=0$ (then $Q=\mathscr{L}$) (this case corresponds to scattering by an atom;

b) when $L=L'$; and

c) when $\mathscr{L}=0$ (then $Q=Q_1$).

When the nonsphericity parameter ϵ is small (ϵ is proportional to the ratio of the terms in (4.1) with $l\neq0$ to the terms with $l=0$) the molecular partner in the collision can be treated as spherically symmetric, then in accordance with case a), the approximation with the zeroth invariant combination $\mathscr{B}n_0$ leads to the result $w=w'$. We note that in this approximation $l=l'$ and w is quadratic in the nonsphericity parameter ϵ.

2. It is not difficult to see that, because of the properties of the 9j symbols, the equalities $J=J'$ and

$J_1 = J_1'$ must obtain for the term in W linear in the nonsphericity parameter, for which $l = l_1 = l_{\min}$ and $l' = l_1' = 0$ ($l_{\min}$ is the minimum value of l allowed by the symmetry). It can be shown that in this approximation with $\{S\}$ and $\{R\}$ small as compared with J and J_1, the ratio of the 9j symbol with even $S'-S$ to the 9j symbol with odd $S'-S$ will be of the order of J when l is even, and of the order of 1/J when l is odd. In other words, the statement

$$\sum S^i + \sum R^i - \text{is even}$$

is correct with an accuracy of 1/J. Thus, in this approximation the equality $w = w'$ holds with an accuracy of 1/J for molecules whose symmetry forbids odd values of l and l_1. The molecular symmetry point groups for which l can only be even[6] are C_{2h}, C_{4h}, C_{6h}, D_{3d}, D_{5d}, D_{2h}, D_{4h}, D_{6h}, O_h, and I_h; moreover, the point groups for which $l_{\min}$ is even are D_{2d}, D_{4d}, D_{6d}, D_{3h}, and D_{5h}.

3. Let us consider the case in which the quantities $a_{\nu\nu'}(q\{J\})$ in (4.3) are real (this corresponds to real values for $T_{ll_1L}(K^{(0)}, r)$ in (4.1)). It is not difficult, using the symmetry of the expressions in (4.3) under exchange of ν and ν', to show that $\Sigma S^i + \Sigma S^i$ must be even in this approximation. Hence here, as in the preceding case, the equality $w = w'$ holds for those molecules for which the possible values of l are even.

In concluding we note that for the case of linear molecules one must put $\{\psi\} = 0$ and $\{\sigma\} = \pi/2$ in (4.3); then the possible values for $\mathscr{L}$ and $\{R\}$ should be even.

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APPENDIX

Here we present some of the properties of the functions

$$B_m^l(\omega) = \sum_p \beta_p^l D_{mp}^l(\omega)$$

and the coefficients β_p^l used in section 4 in deriving formulas for the collision probability.

1. The functions $B_m^l(\omega)$ are normalized as follows:

$$\int d\omega\, B_m^{l*}(\omega) B_m^l(\omega) = 8\pi^2/(2l+1). \tag{A.1}$$

2. From the usual rule for the addition of angular momenta we find

$$B_m^l(\omega) B_{m_1}^{l_1}(\omega) = \sum_{LM} c_{ll_1L} \langle lml_1m_1 | LM\rangle B_M^L(\omega), \tag{A.2}$$

where

$$c_{ll_1L} = \frac{2L+1}{8\pi^2} \langle lml_1m_1 | LM\rangle^{-1} \int d\omega B_M^{L*}(\omega) B_m^l(\omega) B_{m_1}^{l_1}(\omega)\, \delta_{l+l_1+L,2\varkappa}, \tag{A.3}$$

and κ is an arbitrary integer.

3. Using the definition of the functions $B_m^l(\omega)$ and the normalizing condition (A.1), we find

$$\sum_p |\beta_p^l|^2 = 1. \tag{A.4}$$

4. With the aid of the formula for the integral of the product of three D functions[12], we find

$$c_{ll_1L} = \sum_{pp_1P} \langle lpl_1p_1 | LP\rangle (\beta_P^L)^* \beta_p^l \beta_{p_1}^{l_1} \delta_{l+l_1+L,2\varkappa}. \tag{A.5}$$

5. Using Eq. (A.2) and known properties of the D functions[12], we obtain

$$\sum_{pp_1} \beta_p^l \beta_{p_1}^{l_1} \langle lpl_1p_1 | L(p+p_1)\rangle = c_{ll_1L} \beta_{p+p_1}^L. \tag{A.6}$$

6. Equation (A.6) can be solved to give

$$\beta_p^l \beta_{p_1}^{l_1} = \sum_L c_{ll_1L} \langle lpl_1p_1 | L(p+p_1)\rangle \beta_{p+p_1}^L. \tag{A.7}$$

7. In accordance with the symmetry of the operator T, the function $[B^l(\omega) \times B^{l_1}(\omega_1)]^L$ in (4.1) behaves under inversion and complex conjugation like the spherical harmonic $Y_{lm}(\mathbf{r})$. This makes it possible to determine the behavior under inversion and complex conjugation of the β_p^l, which depend on the shape of the molecule. Having defined inversion for the Euler angles as a rotation of the coordinate system $\{x', y', z'\}$ through an angle π about the y' axis, we have

$$\hat{I}(\beta_p^l \beta_{p_1}^{l_1}) = (-1)^{p+p_1} \beta_{-p}^l \beta_{-p_1}^{l_1}, \quad (\beta_p^l \beta_{p_1}^{l_1})^* = (-1)^{p+p_1} \beta_{-p}^l \beta_{-p_1}^{l_1}. \tag{A.8}$$

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