

THERMAL CONDUCTIVITY AND RESONANT
MULTIPOLE INTERACTIONS*

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ABSTRACT

The influence of multipole interactions on exchanges of rotational energy in molecular collisions is investigated by means of a simple two-state impact-parameter approximation. The calculations are restricted to linear molecules and to dipole and quadrupole fields. The effects of such exchanges on the thermal conductivity of gases and of gaseous mixtures is investigated in some detail, after correcting the kinetic theory of mixtures to include exchanges between unlike molecules. We find that dipole-quadrupole and quadrupole-quadrupole interactions can have a significant effect for molecules with low moments of inertia. In particular, quadrupole interactions are important in the hydrogen isotopes, and the calculated corrections for H_2 are consistent with recent experimental work by Harris. The theory seems capable of accounting for the anomalies observed by Baker and Brokaw in $HF + DF$ and $HCl + DCl$ mixtures in terms of multipolar "accidental" resonances.

I. INTRODUCTION

It has been known for many years that a number of polar gases have thermal conductivities anomalously low in comparison to their viscosities, the anomaly increasing with the polarity. Mason and Monchick¹ suggested that this was due to an exchange of rotational energy between two molecules during a distant encounter, whereby a glancing collision was transformed into a nearly head-on collision as far as the transport of rotational energy was concerned. Their calculation was limited to the case of exact resonance and long-range dipole forces, for which a simple impact-parameter approximation was possible. This resonant dipole exchange appeared to account for most of the anomaly.

Baker and Brokaw^{2,3} suggested an ingenious experimental test of the proposed mechanism: comparison of the thermal conductivity of a polar gas with that of its deuterated isotope (e.g., HCl and DCl). The masses and nearly all other relevant molecular parameters are equal for such molecules, except for the moments of inertia which differ by approximately a factor of two. For the pure isotopic gases the results seemed to substantiate the Mason-Monchick mechanism, but the results on an equimolar mixture of a polar gas and its deuterated isotope seemed too low, if resonant exchanges were neglected between molecules with different moments of inertia. Baker and Brokaw³ pointed out, however, that "accidental" resonances (actually near resonances) could occur in collisions between molecules like HCl and DCl where the moments of inertia differ by a factor of nearly two. An approximate calculation of this accidental resonance effect seemed to account for the results on HCl-DCl mixtures and was later applied to HF-DF mixtures.⁴ However, the calculation was rather intuitive, leaving the matter not settled

satisfactorily.

In this paper, we reconsider resonant exchange collisions between linear molecules with dipolar and quadrupolar force fields and the effects of such exchanges on heat transport in gases. Since what is desirable in an exploratory investigation of this sort is to locate and describe the gross features of the processes, some rather rough approximations have been made in the resonant exchange cross sections, i.e., rigour has been sacrificed for simplicity and universality. In essence, the cross-section calculation is based on a two-state impact-parameter approximation, the justification being that the effects are small and derive most of their contribution from glancing collisions. We may then apply the "selection rules" for dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions, namely that the change in the principal rotational quantum number is ± 1 for a molecule with a dipole and ± 2 for one with a quadrupole. The quadrupole terms lead to a number of resonances additional to those suggested for dipolar force fields alone,¹ as well as to some additional "accidental" resonances for molecules whose moments of inertia differ by a factor of two.^{2,3} The effects of all three interactions prove to be appreciable in the thermal conductivity of HCl, DCl, HF, DF, and their mixtures. Quadrupole-quadrupole resonant exchange is found to have a negligible effect on the thermal conductivity of N₂, O₂, and CO₂ - molecules with large moments of inertia - but is important for H₂, D₂, and HD, a result consistent with some new experimental work⁵.

II. EXCHANGE PROBABILITIES

Let θ_A , ϕ_A , θ_B and ϕ_B be the polar angles specifying the orientations of two linear molecules, A and B, relative to the displacement vector R between their centers of mass, and let μ and θ be dipole and quadrupole moments, respectively. Then the dipole-dipole, quadrupole-quadrupole, and dipole-quadrupole interaction potentials are⁶

$$\phi(\mu, \mu) = \frac{-\mu_A \mu_B}{R^3} (2c_A c_B - s_A s_B c), \quad (1)$$

$$\phi(\theta, \theta) = \frac{3}{4} \frac{\theta_A \theta_B}{R^5} (1 - 5c_A^2 - 5c_B^2 + 17c_A^2 c_B^2 + 2s_A^2 s_B^2 c^2 - 16 s_A s_B c_A c_B c), \quad (2)$$

$$\phi(\mu, \theta) = \frac{3}{2} \frac{\mu_A \theta_B}{R^4} [c_A (3c_B^2 - 1) - 2s_A s_B c_B c], \quad (3)$$

with the shorthand notation

$$c_A = \cos \theta_A, \quad c_B = \cos \theta_B, \quad c = \cos (\phi_A - \phi_B),$$

$$s_A = \sin \theta_A, \quad s_B = \sin \theta_B.$$

The unperturbed wave functions for the rotational motion of linear molecules are the spherical harmonics $Y_j^m(\theta, \phi)$, where $j(j+1) \hbar^2/2I$ are the corresponding energies, j the principal rotational quantum number, m its magnetic projection and

I the moment of inertia.

In general, the introduction of angular-dependent forces induces transitions in the rotational quantum numbers j_A , m_A , j_B , and m_B , and in ℓ and m_ℓ , the orbital angular momentum quantum numbers describing the relative motion. Since, as will become evident in the following section, we are principally interested in long-range collisions, i.e., small exchange probabilities, an impact-parameter calculation of the transition probabilities is acceptable. This enables us to decouple the internal angular momenta and the orbital angular momentum of the trajectory. The rotational states of the two molecules may then be regarded as undergoing transitions induced by the time-dependent force due to the variation of the potentials of Eqs. (1) - (3) as the relative trajectory is traced. The calculation becomes particularly simple in our case of long-range resonant or near-resonant collisions, because straight-line trajectories and constant relative velocities may be used. But even in this simplified model it is necessary in general to solve a number of multiply-coupled first-order differential equations⁷, a formidable task without further approximation. The internal state of the system may be specified by expanding the wave function in the set of unperturbed wave functions of the two rotors,

$$\Psi = \sum_{\{i\}} a_{\{i\}}(t) Y_{j_A}^{m_A}(\theta_A, \phi_A) Y_{j_B}^{m_B}(\theta_B, \phi_B) = \sum_{\{i\}} a_{\{i\}}(t) Y_{j_A}^{m_A}(A) Y_{j_B}^{m_B}(B), \quad (4)$$

where $\{i\}$ stands for the set of quantum numbers j_A , m_A , j_B , m_B . Then the set of equations to be solved is

$$i \hbar \dot{a}_{\{i\}} = \sum_{\{k\}} \langle \{i\} | \varphi(t) | \{k\} \rangle a_{\{k\}}(t) \exp(-i\Delta E_{\{ik\}}t/\hbar), \quad (5)$$

where

$$\langle \{i\} | \varphi(t) | \{k\} \rangle = \left\langle Y_{j_A}^{m_A}(A) Y_{j_B}^{m_B}(B) | \varphi(t) | Y_{j'_A}^{m'_A}(A) Y_{j'_B}^{m'_B}(B) \right\rangle, \quad (6a)$$

$$\Delta E_{\{ik\}} = E(j'_A, j'_B) - E(j_A, j_B). \quad (6b)$$

The transition probabilities are obtained from the solutions of Eqs(5). A clue to an appropriate approximation when the transition probabilities are not small is provided by a consideration of the case where only two states, in exact resonance, interact with each other. In this case, it is convenient to replace our original basis set by the gerade and ungerade wave functions⁸,

$$\psi_{g,u} = 2^{-1/2} \left[Y_j^m(A) Y_{j'}^{m'}(B) \pm Y_{j'}^{m'}(A) Y_j^m(B) \right], \quad (7)$$

which do not mix during a collision. The interaction then splits the energy levels by an amount

$$\Delta E_{g,u} = |E_g - E_u| = 2|\lambda|, \quad (8a)$$

where λ is the solution to the secular equation

$$\det \left[\lambda \delta_{m_A m'_A} \delta_{m_B m'_B} \pm \left\langle Y_j^{m_A(A)} Y_{j'}^{m_B(B)} | \varphi | Y_j^{m'_A(A)} Y_{j'}^{m'_B(B)} \right\rangle \right] = 0. \quad (8b)$$

It follows from this form that there is no splitting unless the "selection rules" detailed below are satisfied. Equations (5) now take the form

$$i \hbar \dot{a}_{g,u} = \pm \lambda(t) a_{g,u},$$

or

$$a_{g,u} = \exp \left[\pm (i/\hbar) \int_{-\infty}^t \lambda(t) dt \right]. \quad (9)$$

The probability for the transition $j m, j' m' \rightarrow j' m'$, $j m$ takes the well-known form⁷,

$$P_{ex} = \sin^2 \left[\hbar^{-1} \int_{-\infty}^{\infty} \lambda(t) dt \right]. \quad (10)$$

The approximation that we propose by analogy with the foregoing is to consider only two states at a time. For each pair of states, then Eqs.(5) become

$$i \hbar \dot{a}_{\{i\}} = \left\langle \{i\} | \varphi(t) | \{k\} \right\rangle a_{\{k\}}(t) \exp(-i \Delta E_{\{ik\}} t / \hbar), \quad (11a)$$

$$i \hbar \dot{a}_{\{k\}} = \left\langle \{k\} | \varphi(t) | \{i\} \right\rangle a_{\{i\}}(t) \exp(+i \Delta E_{\{ik\}} t / \hbar). \quad (11b)$$

If at $t = -\infty$, $a_{\{i\}}(-\infty) = 1$, the transition probability is given by $|a_{\{k\}}(+\infty)|^2$.

For $\Delta E \tau \ll \hbar$, where τ is the measure of the duration of the collision, the problem reduces to the so-called near resonance case, and we get Eq.(9) as the solution to Eq.(11), with $|\lambda|$ given by the matrix element $|\langle \{i\} | \varphi | \{k\} \rangle|$. We must emphasize that $|\lambda|$ does not have the meaning of an energy splitting as in the exact resonance case and that the similarity between the two expressions is due to the choice of approximation. Obviously this approximation neglects effects due to the interaction of a given state with more than one other state. Because no allowance is made for the reduction of a probability amplitude by transitions into competing states, this tends to overestimate the transition probabilities, possibly leading to a total probability greater than unity for transitions from one state to all others. This error is partially counter balanced by another; namely, a ladder mechanism whereby transitions are possible between states not directly coupled. The larger the computed transition probabilities, the more serious are these errors⁸. However, as will be obvious in the following sections, we will be interested in evaluating accurate values of P_{ex} primarily in regions of large impact parameter where $P_{ex} \leq 1/4$, thus hopefully minimizing the shortcomings of the method.

In general, the number of "resonating" states, i.e., close-lying states satisfying the condition $\Delta E \ll \hbar/\tau$, is severely restricted. The vanishing of the potential energy matrix elements for the multipole interactions considered here restricts them even further. Thus, for linear polar molecules the only non-vanishing off-diagonal terms occur for $j'_A = j_A \pm 1$, $j'_B = j_B \pm 1$; for linear

quadrupolar molecules, the selection rule is $j'_A = j_A \pm 2$, $j'_B = j_B \pm 2$, and for dipole-quadrupole interactions the selection rule is $j'_A = j_A \pm 1$, $j'_B = j_B \pm 2$ and vice versa. The resonance condition further restricts the number of values of j_A and j_B to be considered to those obeying the relation

$$\frac{j_A(j_A+1)}{I_A} + \frac{j_B(j_B+1)}{I_B} = \frac{j'_A(j'_A+1)}{I_A} + \frac{j'_B(j'_B+1)}{I_B}. \quad (12)$$

We shall say that two states are in exact resonance if the above conditions are fulfilled with $j'_A = j_B$ and $j'_B = j_A$ (which requires $I_A = I_B$), and that there is an accidental resonance if the conditions are otherwise fulfilled, or nearly fulfilled.

For $I_A = I_B$, the only exact resonances occur for dipole-dipole and quadrupole-quadrupole interactions, for which $j_A = j_B \pm 1$ and $j_A = j_B \pm 2$, respectively. However, in dipole-quadrupole interactions an accidental resonance can occur if $j_\mu = 2j_\theta - 2$ for excitation of the dipole or if $j_\mu = 2j_\theta + 3$ for de-excitation. The other case of interest here is $I_B = 2I_A$, for which accidental exact resonances are possible for dipole-dipole interactions and some dipole-quadrupole interactions. These are:

$$\begin{array}{lll} \mu_A \mu_B: & j_B = 2j_A + 2 & \text{for A excitation,} \\ & j_B = 2j_A - 1 & \text{for A de-excitation;} \\ \\ \theta_A \mu_B: & j_B = 4j_A + 6 & \text{for A excitation,} \\ & j_B = 4j_A - 3 & \text{for A de-excitation.} \end{array}$$

In addition, accidental near resonances occur for $\mu_A \Theta_B$ interactions if $j_B \approx j_A, j_A \gg 1$ and for $\Theta_A \Theta_B$ interactions if $j_B \approx 2j_A, j_A \gg 1$. These cases are all important for thermal conductivity which tends to weight large values of j .

The following matrix elements for the potentials of Eqs. (1) - (3) are obtained by use of well-known formulas^{6b}. We write a_{ex} for the coefficient of the factors - $\mu_A \mu_B / R^3, (3/4) \Theta_A \Theta_B R^{-5}$, and $(3/2) \mu_A \Theta_B R^{-4}$ in the matrix eigenvalue λ :

dipole-dipole interaction ($j'_A = j_A + 1, j'_B = j_B - 1$):

$$a_{ex}^{\mu\mu} = \frac{1}{2} \left[1 - \left(\frac{m_A}{j_A} \right)^2 \right]^{1/2} \left[1 - \left(\frac{m_B}{j_B} \right)^2 \right]^{1/2} \delta_{m'_A m_A} \delta_{m'_B m_B} \\ - \frac{1}{8} \left(1 \pm \frac{m_A}{j_A} \right) \left(1 \pm \frac{m_B}{j_B} \right) \delta_{m'_A, m_A \pm 1} \delta_{m'_B, m_B \mp 1}, \quad (13)$$

Quadrupole-quadrupole interaction ($j'_A = j_A + 2, j'_B = j_B - 2$):

$$a_{ex}^{\Theta\Theta} = \frac{9}{8} \left[1 - \left(\frac{m_A}{j_A} \right)^2 \right] \left[1 - \left(\frac{m_B}{j_B} \right)^2 \right] \delta_{m'_A m_A} \delta_{m'_B m_B} \\ - \frac{1}{2} \left[1 - \left(\frac{m_A}{j_A} \right)^2 \right]^{1/2} \left[1 - \left(\frac{m_B}{j_B} \right)^2 \right]^{1/2} \left(1 \pm \frac{m_A}{j_A} \right) \left(1 \pm \frac{m_B}{j_B} \right) \delta_{m'_A, m_A \pm 1} \delta_{m'_B, m_B \mp 1} \\ + \frac{1}{8} \left(1 \pm \frac{m_A}{j_A} \right) \left(1 \pm \frac{m_B}{j_B} \right) \delta_{m'_A, m_A \pm 2} \delta_{m'_B, m_B \mp 2}, \quad (14)$$

Dipole-quadrupole interactions ($j'_A = j_A + 1$, $j'_B = j_B - 2$)

$$\begin{aligned}
 a_{\text{ex}}^{\mu\theta} = & (3/8) \left[1 - \left(\frac{m_A}{j_A} \right)^2 \right]^{1/2} \left[1 - \left(\frac{m_B}{j_B} \right)^2 \right] \delta_{m'_A, m_A} \delta_{m'_B, m_B} \\
 & + (1/4) \left[1 - \left(\frac{m_B}{j_B} \right)^2 \right]^{1/2} \left(1 \pm \frac{m_A}{j_A} \right) \left(1 \pm \frac{m_B}{j_B} \right) \delta_{m'_A, m_A \pm 1} \delta_{m'_B, m_B \pm 1}.
 \end{aligned} \tag{15}$$

With our simple approximation and the semiclassical impulse approximation⁹, we can immediately integrate Eq. (10) along a straight-line trajectory to obtain

$$P_{\text{ex}}^{\mu\mu} = \sin^2 \left(2\mu_A \mu_B a_{\text{ex}}^{\mu\mu} / \hbar g b^2 \right), \tag{16}$$

$$P_{\text{ex}}^{\theta\theta} = \sin^2 \left(\theta_A \theta_B a_{\text{ex}}^{\theta\theta} / \hbar g b^4 \right), \tag{17}$$

$$P_{\text{ex}}^{\mu\theta} = \sin^2 \left(3\pi \mu_A \theta_B a_{\text{ex}}^{\mu\theta} / 4 \hbar g b^3 \right), \tag{18}$$

where the a_{ex} are given by Eqs. (13)-(15), b is the impact parameter, and g is the relative velocity of the collision. These exchange probabilities depend on the quantum numbers m and j as well as on b and g ; we need the cross-sections obtained by averaging over m_A and m_B and integrating over b :

$$\left\langle Q_{\text{ex}}^{\mu\mu} \right\rangle_{\text{av.}} = \frac{2\pi}{(2j_A+1)(2j_B+1)} \sum_{m_A=-j_A}^{j_A} \sum_{m_B=-j_B}^{j_B} \int_0^\infty P_{\text{ex}}^{\mu\mu} b db,$$

$$\begin{aligned}
&= \frac{2\pi}{(2j_A+k)(2j_B+1)} \sum_{m_A=-j_A}^{j_A} \sum_{m_B=-j_B}^{j_B} \frac{\mu_A \mu_B}{\hbar g} \frac{\pi}{2} |a_{\text{ex}}^{\mu\mu}|, \\
&\equiv \frac{\pi^2 \mu_A \mu_B}{\hbar g} \left\langle |a_{\text{ex}}^{\mu\mu}| \right\rangle_{\text{av}}.
\end{aligned} \tag{19}$$

Similarly, we find that

$$\left\langle Q_{\text{ex}}^{\Theta\Theta} \right\rangle_{\text{av}} = \frac{\pi^{3/2}}{2} \left(\frac{\Theta_A \Theta_B}{\hbar g} \right)^{1/2} \left\langle |a_{\text{ex}}^{\Theta\Theta}|^{1/2} \right\rangle_{\text{av}}, \tag{20}$$

$$\left\langle Q_{\text{ex}}^{\mu\Theta} \right\rangle_{\text{av}} = \frac{3^{1/2}}{\Gamma(5/3)} \left(\frac{\pi^4}{18} \right)^{2/3} \left(\frac{\mu_A \Theta_B}{\hbar g} \right)^{2/3} \left\langle |a_{\text{ex}}^{\mu\Theta}|^{2/3} \right\rangle_{\text{av}}. \tag{21}$$

The exchange cross-sections $\left\langle Q_{\text{ex}} \right\rangle_{\text{av}}$ depend not only on g , but on j_A and j_B also through the coefficients $\left\langle |a_{\text{ex}}| \right\rangle_{\text{av}}$. Fortunately, (1) the dependence is very weak for large j and (2) a good approximation--at least for linear dipole molecules¹--is obtained by taking only the first terms in Eqs. (13) - (15) into account (i.e., by considering only $\Delta m = 0$ transitions). The values so obtained are shown in Table I. An estimate of the error involved can be obtained by comparing the dipole-dipole coefficient, 0.308, with 0.435, obtained by Sutton¹⁰, who summed up the splittings, $|\lambda|$, obtained by London⁶ with his "unsharp" resonance theory of dipole interactions. For use in subsequent calculations, we adopt the accurate dipole coefficient,

0.435. Because of the many approximations, we cannot expect the coefficients to be more than semi-quantitative. Some calculations by one of us (C. N.) indicate that this is so and that although the present formulae are suitable for our purposes at present, it would be desirable to have a better approximation.

III. ENERGY EXCHANGE AND THERMAL CONDUCTIVITY

Resonant exchange reactions seldom have much influence on macroscopic properties, perhaps the best known case of any importance being their effect on the thermal conductivity of dipolar gases¹. The preceding section shows, however, that resonant exchanges may occur for dipole-quadrupole and quadrupole-quadrupole interactions as well. Accordingly, in this section we extend the earlier treatment of Mason and Monchick¹ to quadrupole and dipole interactions of linear molecules and to resonant exchanges between unlike molecules in mixtures. For comparison with experiment we have chosen the systems H_2 , N_2 , O_2 , CO_2 , HCl , DCl , HF and DF , and the mixtures HCl - DCl and HF - DF .

A. PURE GASES

Since some of the effects are rather small, the use of a linearized formula for the heat conductivity might mask the effect of resonant exchanges. We have therefore used the complete formula in which inelastic collisions are included fully, and not just as a first-order correction. We indicate the argument in some detail first for a pure gas, since the procedure and notation are the same for the much more complicated case of a mixture. For

a pure gas, it has been shown that the exact result, within the framework of the Wang Chang-Uhlenbeck-deBoer form of kinetic theory, is^{1,11}

$$\frac{\lambda m}{\eta} = \frac{5}{2} c_{V \text{ tr}} + \left(\frac{\rho \mathcal{D}_{\text{int}}}{\eta} \right) c_{\text{int}} - \left(\frac{2c_{\text{int}}}{\pi \zeta} \right) \left(\frac{5}{2} - \frac{\rho \mathcal{D}_{\text{int}}}{\eta} \right)^2 \left[1 + \frac{2}{\pi \zeta} \left(\frac{5c_{\text{int}}}{3k} + \frac{\rho \mathcal{D}_{\text{int}}}{\eta} \right) \right]^{-1}, \quad (22)$$

where λ is the thermal conductivity, η the viscosity, m the molecular mass, $c_{V \text{ tr}} = 3k/2$ the constant volume translational heat capacity per molecule, c_{int} the internal heat capacity per molecule, ζ the collision number for inelastic collisions other than resonant collisions, ρ the gas density, and \mathcal{D}_{int} the diffusion coefficient for internal energy. The entire effect of resonant collisions is contained in \mathcal{D}_{int} by way of a collision integral defining \mathcal{D}_{int} ,

$$\left(\rho \mathcal{D}_{\text{int}} \right)^{-1} = \left(8/3 c_{\text{int}} T \right) \left\langle (\epsilon_i - \bar{\epsilon}) \left[(\epsilon_i - \epsilon_j) \gamma^2 - (\epsilon_k - \epsilon_\ell) \gamma \gamma' \cos \chi \right] \right\rangle, \quad (23)$$

where i and j refer to internal states before collision, k and ℓ to internal states after collision, ϵ_i is the energy of the i -th internal state divided by kT , γ^2 is the relative translational kinetic energy before collision divided by kT and γ'^2 the same after collision, and χ is the angle of deflection in the collision in center of mass coordinates. The collision

integral $\langle \dots \rangle$ (not to be confused with the $\langle \dots \rangle_{av}$ already used) is, for a collision between species A and B,

$$\begin{aligned} \langle F \rangle = & \left(\frac{kT}{2\pi\mu_{AB}} \right)^{1/2} \frac{1}{Q_A Q_B} \sum_{ijkl} \int_0^\infty d\gamma \int_0^{2\pi} d\phi \int_0^\pi d\chi \\ & \times \left[F \gamma^3 \exp(-\gamma^2 - \epsilon_{Ai} - \epsilon_{Bj}) I_{ij}^{kl} \sin \chi \right], \end{aligned} \quad (24)$$

where i and k are internal states of A and j and ℓ internal states of B, F is any function of the dynamical variables before and after collision, I_{ij}^{kl} is the differential scattering cross section into the solid angle $\sin\chi d\chi d\phi$ for the process $i, j \rightarrow k, \ell, \gamma \rightarrow \gamma'$; Q_A and Q_B are internal partition functions

$$Q_A = \sum_i \exp(-\epsilon_{Ai}),$$

and μ_{AB} is the reduced mass of the colliding AB pair.

To show the effect of resonant exchange, we rewrite the collision integral $\langle \dots \rangle$ of Eq. (23), now denoted as I_1 for brevity, as

$$\begin{aligned} I_1 = & \left\langle (\epsilon_i - \bar{\epsilon}) (\epsilon_i - \epsilon_j) (\gamma^2 - \gamma\gamma' \cos\chi) \right\rangle \\ & + \left\langle (\epsilon_i - \bar{\epsilon}) (\Delta\epsilon_i - \Delta\epsilon_j) (\gamma^2 - \gamma\gamma' \cos\chi) \right\rangle \end{aligned}$$

$$- \left\langle (\epsilon_i - \bar{\epsilon}) (\Delta\epsilon_i - \Delta\epsilon_j) \gamma^2 \right\rangle, \quad (25)$$

where $\Delta\epsilon_i = \epsilon_k - \epsilon_i$ and $\Delta\epsilon_j = \epsilon_\ell - \epsilon_j$. For most collisions the last two terms represent corrections for inelastic collisions which are presumably small except in the case of resonant collisions ($\Delta\epsilon_i = -\Delta\epsilon_j$) which may occur out to large values of the impact parameter. In that case, we may rewrite Eq. (25) as

$$I_1 \approx (I_1)_{\text{dir}} + 2 \left\langle (\epsilon_i - \bar{\epsilon}) \Delta\epsilon_i (\gamma^2 - \gamma\gamma' \cos\chi) P_{\text{ex}} \right\rangle_{\text{res}} - 2 \left\langle (\epsilon_i - \bar{\epsilon}) \Delta\epsilon_i \gamma^2 P_{\text{ex}} \right\rangle_{\text{res}}, \quad (26)$$

where P_{ex} is the probability of resonant exchange and characteristically is a rapidly oscillating function of b (with an average value of $1/2$) for all b less than some critical value b_c , and a monotonically vanishing function of b for $b > b_c$. The term $(I_1)_{\text{dir}}$ represents the collision integral for internal energy diffusion without resonant exchange but including all other collisions, and is of magnitude $(c_{\text{int}}/k)(kT/2\pi\mu)^{1/2} \pi\sigma^2$, where σ is an ordinary gas-kinetic collision diameter such that $\chi \approx 0$ for $b \geq \sigma$. The second term on the right is of magnitude $(c_{\text{int}}/k)(kT/2\pi\mu)^{1/2} \pi\sigma^2 f_{\text{res}}$, where f_{res} is the fraction of collisions for which the two molecules are in resonance, and the third term is of magnitude $(c_{\text{int}}/k)(kT/2\pi\mu)^{1/2} \pi b_c^2 f_{\text{res}}$. Since $f_{\text{res}} \ll 1$, the second term is negligible, but because $b_c \gg \sigma$, the third term is not and contributes a

significant correction term to \mathcal{D}_{int} . The expression thus becomes

$$I_1 \approx (I_1)_{\text{dir}} + 2 \left\langle (\epsilon_i - \bar{\epsilon})(\epsilon_i - \epsilon_k) \gamma^2 P_{\text{ex}} \right\rangle_{\text{res}}. \quad (27)$$

For dipole-dipole and quadrupole-quadrupole resonances $\epsilon_k = \epsilon_j$ and $\epsilon_l = \epsilon_i$ and Eq. (27) becomes Eq. (70) of reference 1. This is no longer true if we admit dipole-quadrupole resonances and thus we are forced to use the more general form, Eq. (27).

Assuming that the scattering pattern is almost independent of the initial or final internal states except for a scaling factor consisting of a total transition probability, the so-called independent scattering pattern approximation, we can carry out the averaging over b , m_A , and m_B in the correction term of Eq. (27), converting P_{ex} to $\left\langle Q_{\text{ex}} \right\rangle_{\text{av}}$ of Eq. (19). We can now sum over the principal quantum numbers of all pairs of resonant states and integrate over all velocities, as previously shown in detail for dipole-dipole interactions¹. After substituting for $\left\langle Q_{\text{ex}} \right\rangle_{\text{av}}$ from Eqs. (19 - 21), the final results for \mathcal{D}_{int} may be written as

$$\mathcal{D}_{\text{int}} = \left(\mathcal{D}_{\text{int}} \right)_{\text{dir}} \left(1 + \Delta_{\text{ex}}^{\mu\mu} + \Delta_{\text{ex}}^{\mu\theta} + \Delta_{\text{ex}}^{\theta\theta} \right)^{-1}, \quad (28)$$

where $\left(\mathcal{D}_{\text{int}} \right)_{\text{dir}}$ comes from $(I_1)_{\text{dir}}$, and the Δ_{ex} terms come from the resonant correction term of Eq. (27) and are given by

$$\Delta_{\text{ex}}^{\mu\mu} = g^{\mu\mu} \frac{9\pi^2}{16} \left(\frac{m}{2kT} \right)^{1/2} \left(\frac{\theta_{\text{rot}}}{T} \right)^{3/2} \left(\frac{\mu^2}{h} \right) \frac{\left\langle |a_{\text{ex}}^{\mu\mu}| \right\rangle_{\text{av}}}{\sigma_{\text{dir}}^2 \Omega_{\text{dir}}^*}, \quad (29)$$

$$\Delta_{\text{ex}}^{\theta\theta} = g^{\theta\theta} \frac{21\pi}{8} \Gamma\left(\frac{7}{4}\right) \left(\frac{m}{kT}\right)^{1/4} \left(\frac{\theta_{\text{rot}}}{T}\right)^{3/2} \left(\frac{\theta^2}{\hbar}\right)^{1/2} \frac{\langle |a_{\text{ex}}^{\theta\theta}|^{1/2} \rangle_{\text{av}}}{\sigma^2 \Omega_{\text{dir}}^{(1,1)*}}, \quad (30)$$

$$\Delta_{\text{ex}}^{\mu\theta} = g^{\mu\theta} \frac{7\pi}{15} \left(\frac{3\pi}{5}\right)^{1/2} \left(\frac{2\pi^2}{3}\right)^{1/3} \left(\frac{m}{kT}\right)^{1/3} \left(\frac{\theta_{\text{rot}}}{T}\right)^{3/2} \left(\frac{\mu\theta}{\hbar}\right)^{2/3} \frac{\langle |a_{\text{ex}}^{\mu\theta}|^{2/3} \rangle_{\text{av}}}{\sigma^2 \Omega_{\text{dir}}^{(1,1)*}}, \quad (31)$$

in which $\theta_{\text{rot}} = \hbar^2/2kI$ is the characteristic rotational temperature and $\Omega_{\text{dir}}^{(1,1)*}$ is the reduced collision integral for diffusion without resonant exchange. The coefficients g are the corrections to be applied for replacing quantum summations by integrations, and are

$$g^{\mu\mu} = \frac{(Q_{\text{class}}/Q)^2}{(c_{\text{int}}/k)} \frac{8}{3} \left(\frac{2}{\pi}\right)^{1/2} \left(\frac{\theta_{\text{rot}}}{T}\right)^{5/2} \sum_{n=1}^{\infty} n^2 (4n^2 - 1) e^{-2n^2 \theta_{\text{rot}}/T}, \quad (32)$$

$$g^{\theta\theta} = \frac{(Q_{\text{class}}/Q)^2}{c_{\text{int}}/k} \frac{2}{3} \left(\frac{2}{\pi}\right)^{1/2} \left(\frac{\theta_{\text{rot}}}{T}\right)^{5/2} \times \sum_{n=1}^{\infty} (2n-1)(2n+1)^2 (2n+3) e^{-2(n^2+n+1)\theta_{\text{rot}}/T}, \quad (33)$$

$$g^{\mu\theta} = \frac{(Q_{\text{class}}/Q)^2}{(c_{\text{int}}/k)} \frac{50}{3} \left(\frac{5}{\pi}\right)^{1/2} \left(\frac{\theta_{\text{rot}}}{T}\right)^{5/2} \times \sum_{n=1}^{\infty} n(n+1)(2n+1)^2 e^{-(5n^2+5n+2)\theta_{\text{rot}}/T}. \quad (34)$$

Some values of these coefficients are given in Table II and shown in Fig. 1. For symmetric linear molecules the values of $\Delta_{\text{ex}}^{\mu\mu}$ and $\Delta_{\text{ex}}^{\mu\theta}$ are zero of course because $\mu = 0$. $\Delta_{\text{ex}}^{\theta\theta}$ is not zero and must be modified for the existence of ortho and para forms. This is taken into account by summing only over the even or the odd rotational levels in $g^{\theta\theta}$; these are also displayed in Table II and Fig. 1.

In many cases the quantum effects are small and the following asymptotic formulae suffice:

$$g^{\mu\mu} = e^{-2\theta_{\text{rot}}/3T} \left(1 - \frac{1}{3} \frac{\theta_{\text{rot}}}{T} + \dots \right), \quad (35)$$

$$g^{\theta\theta} = e^{-13\theta_{\text{rot}}/6T} \left(1 - \frac{4}{3} \frac{\theta_{\text{rot}}}{T} + \dots \right), \quad (36)$$

$$g^{\mu\theta} = e^{-17\theta_{\text{rot}}/12T} \left(1 - \frac{5}{6} \frac{\theta_{\text{rot}}}{T} + \dots \right), \quad (37)$$

The low temperature limiting forms of these coefficients are

$$g^{\mu\mu} = \frac{2}{3} \left(\frac{2}{\pi} \right)^{1/2} \left(\frac{T}{\theta_{\text{rot}}} \right)^{3/2} + \dots, \quad (38)$$

$$g^{\theta\theta} \begin{pmatrix} \text{even} \\ \text{odd} \end{pmatrix} = \frac{1}{12} \left(\frac{2}{\pi} \right)^{1/2} \left(\frac{T}{\theta_{\text{rot}}} \right)^{3/2} + \dots, \quad (39)$$

$$g^{\theta\theta} (\text{Total}) = \frac{5}{2} \left(\frac{2}{\pi} \right)^{1/2} \left(\frac{T}{\theta_{\text{rot}}} \right)^{3/2} e^{-4\theta_{\text{rot}}/T} + \dots, \quad (40)$$

$$g^{\mu\theta} = 25 \left(\frac{5}{\pi} \right)^{1/2} \left(\frac{T}{\theta_{\text{rot}}} \right)^{3/2} e^{-10\theta_{\text{rot}}/T} + \dots \quad (41)$$

To give an idea of the magnitude of the quadrupole-quadrupole exchange effect, we show in Table III the calculated values of $\Delta_{\text{ex}}^{\theta\theta}$ for N_2 , O_2 , CO_2 , and H_2 at 300°K . The contribution is negligible for the first three, but not for H_2 which even shows a distinct ortho-para effect. The reason for the difference is the low moment of inertia of H_2 , which leads to a large spacing of the rotational energy levels and thus to a different energy distribution of the ortho and para forms at low temperatures.

A more extended calculation of $\Delta_{\text{ex}}^{\theta\theta}$ as a function of temperature is shown in Fig. 2 for H_2 , D_2 , and HD . The parameters used are listed in Table IV. The effect on \mathcal{D}_{int} amounts to roughly 30% except at very low and very high temperatures. Since the rotational degrees of freedom in H_2 carry at most about 25% of the total energy flux, the effect of quadrupole resonant exchange amounts to only 7% of the total thermal conductivity of H_2 . Thus the effect is not large, but still capable of experimental detection. Harris⁵ used a differential method to measure the deviation of thermal conductivity of para-hydrogen at 77°K and 311°K from the theoretical formula which neglects resonance corrections. The results are shown in Fig. 2 and, within mutual errors, are consistent with the effect predicted by the theoretical formulae developed here and in the previous section. Unfortunately, the situation is not entirely unambiguous because of possible surface accommodation effects in the experiments. Recent results¹² on the thermal conductivity difference of o- D_2 and n- D_2 near 20°K are inconclusive: using the formulae of the next subsection and assuming that the diffusion cross sections for o-o, p-p, and o-p D_2 collisions are equal, it is possible to arrive at a theoretical

formula like that of Uebelhack, et al.,¹² corrected for resonant collisions. The theoretical difference, like theirs, is too small, and, with resonant corrections, has an even smaller temperature dependence. The rest of the difference may probably be attributed to small differences in the collision cross sections of the ortho and para forms of D₂. These latter effects - less than 0.1% - are masked, however, at higher temperatures, and the theoretical differences in ortho and para forms - $\sim 1\%$ in H₂ at 300°K and at 200°K in D₂ - should be observable.

The relative importance of dipole-dipole, quadrupole-quadrupole, and dipole-quadrupole resonant exchange is shown in Table V for HF, DF, HCl, and DCl at the temperatures at which Baker and Brokaw^{3,4} made their measurements; the parameters used are listed in Table VI. It is apparent that the dipole-dipole exchange is the most important, but that the other contributions are not entirely negligible; that is, although the θ - θ and μ - θ exchanges contribute only a few percent to the overall effect on the thermal conductivity, this can be a significant contribution for some purposes. For instance, if one wishes to use thermal conductivity measurements and Eq. (22) to calculate collision numbers for inelastic collisions, it is important to have accurate values of \mathcal{D}_{int} . This is illustrated by the last two columns of Table V, which show rotational collision numbers calculated from the conductivity measurements of Baker and Brokaw. The effect of including quadrupole-quadrupole and dipole-quadrupole resonant exchange is to increase the rotational collision numbers, ζ_{rot} , to more physically reasonable values. Incidentally, if all resonant exchange is neglected, the absurd result of negative ζ_{rot} is obtained. The values of ζ_{rot} for HCl may be compared with the value $\zeta_{\text{rot}} \approx 7$ collisions at

0°C, obtained from acoustic absorption measurements¹³. However, our values for ζ_{rot} should not be taken too literally, because we have not included any correction for the effect of inelastic collisions on \mathcal{D}_{int} . In particular, the calculations of Sandler¹⁴ for the models of rigid loaded spheres and rigid spherocylinders suggest that inelastic collisions (other than resonant collisions) may affect \mathcal{D}_{int} by a few percent, increasing \mathcal{D}_{int} for $\zeta_{\text{rot}} \gtrsim 2.8$ and decreasing it for $\zeta_{\text{rot}} \lesssim 2.8$. If this trend holds for the polar molecules of Tabel V, the values of ζ_{rot} in the last column of the table would be decreased slightly for HF, DF and HCl, and increased appreciably for DCl, a result which appears physically plausible.

B. MIXTURES

The complete expression for the thermal conductivity of a gas mixture within the framework of the Wang Chang-Uhlenbeck-de Boer theory is still very complicated^{11,15}. But if we regard it as merely an interpolation formula between the conductivities of the pure components, always forcing the expression to give the correct pure component results, a simple but useful approximation can be obtained by formally neglecting all inelastic collision terms in the complete expression¹¹. The result is equivalent to the Hirschfelder-Eucken expression¹⁶, which reads, for a binary mixture of gases A and B,

$$\lambda_{\text{mix}}^{(\text{HE})} = \lambda_{\text{mix}}^{(\text{mon})} + \frac{\lambda_A - \lambda_A^{(\text{mon})}}{1 + \frac{x_B \mathcal{D}_{\text{Aint},A}}{x_A \mathcal{D}_{\text{Aint},B}}} + \frac{\lambda_B - \lambda_B^{(\text{mon})}}{1 + \frac{x_A \mathcal{D}_{\text{Bint},B}}{x_B \mathcal{D}_{\text{Bint},A}}}, \quad (42)$$

where $\lambda_{\text{mix}}(\text{mon})$, $\lambda_A(\text{mon})$, and $\lambda_B(\text{mon})$ are the conductivities of the mixture, component A and component B calculated as if the gases were monatomic,^{6,16} e.g.,

$$\lambda_A(\text{mon}) = \frac{5}{2} c_{\text{vtr}} \frac{\eta_A}{m_A}, \text{ etc.}, \quad (43)$$

λ_A and λ_B are the true conductivities of pure component A and B, x_A and x_B are their mole fractions, and m_A is the molecular mass. The diffusion coefficients are now of two types: one for diffusion through molecules of the same type, namely, $\mathcal{D}_{\text{Aint},A}$ and $\mathcal{D}_{\text{Bint},B}$; which are given by Eq. (23), and one for diffusion through molecules of different type. These are given by¹¹

$$\left(n \mathcal{D}_{\text{Aint},B} \right)^{-1} = 16 \left(\mu_{AB} / 3 c_{\text{Aint}} T \right) I_2^{AB}, \quad (44)$$

$$I_2^{AB} = \left\langle \left(\epsilon_{Ai} - \bar{\epsilon}_A \right) \left[\left(\epsilon_{Ai} - \bar{\epsilon}_A \right) \gamma^2 - \left(\epsilon_{Ak} - \bar{\epsilon}_A \right) \gamma \gamma' \cos \chi \right] \right\rangle_{AB}, \quad (45)$$

where n is the total number density of the mixture. Analogous expressions hold for $\mathcal{D}_{\text{Bint},A}$ and I_2^{BA} , obtained by interchange of subscripts.

The corrections to I_2 for accidentally resonant exchange are obtained from Eq. (45) by arguments like those used for I_1 ; the results are

$$I_2^{AB} \approx \left(I_2^{AB} \right)_{\text{dir}} + \left\langle \left(\epsilon_{Ai} - \bar{\epsilon}_A \right) \left(\epsilon_{Ai} - \epsilon_{Ak} \right) \gamma^2 P_{\text{ex}}^{AB} \right\rangle_{AB, \text{res}}, \quad (46a)$$

$$I_2^{BA} \approx \left(I_2^{BA} \right)_{\text{dir}} + \left\langle \left(\epsilon_{Bj} - \bar{\epsilon}_B \right) \left(\epsilon_{Bj} - \epsilon_{B\ell} \right) \gamma^2 P_{\text{ex}}^{BA} \right\rangle_{AB, \text{res}}. \quad (46b)$$

The factor of 2 in I_1 is missing from these correction terms because of the distinguishability of the colliding pair; this is related to the fact that $\mathcal{D}_{\text{Aint},A}$ is not the limit of $\mathcal{D}_{\text{Aint},B}$ as $B \rightarrow A$. The evaluation of the correction terms proceeds as for pure gases, and, with an easy extension of the previous notation, leads to the expressions

$$\mathcal{D}_{\text{Aint},B} = \left(\mathcal{D}_{\text{Aint},B} \right)_{\text{dir}} \left[1 + \frac{1}{2} \left(\Delta_{AB}^{\mu\mu} + \Delta_{AB}^{\theta\theta} + \Delta_{AB}^{\mu\theta} + \Delta_{AB}^{\theta\mu} \right) \right]^{-1}, \quad (47a)$$

$$\mathcal{D}_{\text{Bint},A} = \left(\mathcal{D}_{\text{Bint},A} \right)_{\text{dir}} \left[1 + \frac{1}{2} \left(\Delta_{BA}^{\mu\mu} + \Delta_{BA}^{\theta\theta} + \Delta_{BA}^{\mu\theta} + \Delta_{BA}^{\theta\mu} \right) \right]^{-1}, \quad (47b)$$

For $I_B = 2I_A$, only the correction terms $\Delta_{AB}^{\mu\mu}$, $\Delta_{BA}^{\mu\mu}$, $\Delta_{AB}^{\theta\mu}$, and $\Delta_{BA}^{\mu\theta}$ correspond to exact resonances; the others are only near resonances, although they have been treated as exact: this entails counting half-integral values of j . The order of subscripts on the Δ 's corresponds to the order on the internal diffusion coefficient, and the order of the superscripts denotes the order of the transition. That is, $\Delta_{AB}^{\mu\theta}$ is the correction to $\mathcal{D}_{\text{Aint},B}$ for a dipole transition on A and a quadrupole transition on B, whereas $\Delta_{AB}^{\theta\mu}$ is the correction for a quadrupole transition on A and a dipole transition on B. The detailed expressions for the Δ 's are given in an appendix.

The relative importance of the exchange corrections for unlike collisions is illustrated in Table VII for HF-DF and HCl-DCI collisions at the temperatures

for which thermal conductivity measurements have been made^{3,4}. These should be compared with the corresponding values for like collisions in Table V. It is again apparent that the dipole-dipole exchange correction is the most important, but that the others may not be negligible. The dipole-dipole and quadrupole-quadrupole exchange corrections for unlike collisions are always smaller than the corresponding corrections for like collisions, but the reverse is true for some of the dipole-quadrupole corrections. However, the total exchange corrections are generally smaller for unlike than for like collisions.

In attempting to account for their results on the thermal conductivity of equimolar HX+DX mixtures, Baker and Brokaw^{3,4} assumed the following relations. Note a factor of two difference in the definition of our resonant corrections and theirs.

$$\frac{1}{2} \Delta_{HX-DX}^{\mu\mu} = \Delta_{HX-HX}^{\mu\mu}, \quad (48a)$$

$$\Delta_{DX-HX}^{\mu\mu} = \Delta_{DX-DX}^{\mu\mu}. \quad (48b)$$

Comparison of Tables V and VII shows that these relations are followed only very roughly. From the expressions in the appendix we find instead the following relations holding in the classical limit (with $I_{DX} = 2I_{HX}$, $m_{DX} = m_{HX}$, $\mu_{DX} = \mu_{HX}$, $\Theta_{DX} = \Theta_{HX}$):

$$\frac{1}{2} \Delta_{HX-DX}^{\mu\mu} = \frac{6^{1/2}}{9} \Delta_{HX-HX}^{\mu\mu}, \quad (49a)$$

$$\begin{aligned}
\frac{1}{2} \Delta_{DX-HX}^{\mu\mu} &= \frac{4(3)^{1/2}}{27} \Delta_{DX-DX}^{\mu\mu} \\
&= \frac{1}{6} \Delta_{HX-DX}^{\mu\mu} .
\end{aligned}
\tag{49b}$$

The same relations hold for the quadrupole-quadrupole exchange corrections, and analogous relations among the various dipole-quadrupole exchange corrections.

Following the procedure of Baker and Brokaw^{3,4} we have displayed the calculated and experimental results in Figs. 3 and 4 as the deviations of the thermal conductivities of equimolar HX+DX mixtures from the linear average of the pure HX and DX components. Three calculated curves are shown as broken curves: one with Δ_{AB} set equal to zero, one including only the Δ_{AB} corresponding to exact resonances, and one including both exact and near resonances. It is evident that the inclusion of unlike exchange in the Hirschfelder-Eucken calculation reduces the discrepancy with experiment, but does not completely eliminate it. One way of improving the agreement would be to multiply all the unlike resonant corrections by 2; $\lambda_{mix}(HE)$ would now reduce to λ_A as $A \rightarrow B$, but has no other theoretical justification.

The complete Wang Chang-Uhlenbeck-deBoer expression for the mixture thermal conductivity takes the form

$$\lambda_{mix} = \lambda_{mix}^{tr} + \lambda_{mix}^{int} ,
\tag{50}$$

where both the translational and internal contributions are given by ratios of complicated determinants^{11,15}. The elements $L_{qq'}^{rs,r's'}$ of the determinants are

linear combinations of collision integrals of the form of Eq. (24)¹⁵. These have been expressed in reference 11 in terms of various relaxation times, diffusion coefficients and other experimental quantities, subject to several approximations, some of which must be revised if resonant exchange collisions are to be taken into account properly. Briefly, the most important approximation is the neglect of the so-called complex collisions, i.e., collisions that involve more than one quantum jump; in particular, collisions in which the internal states of both colliding molecules change are neglected. Clearly this approximation would discard resonant collisions and so must be used with care. It is safe to neglect complex collisions in the expressions for the elements $L_{qq'}^{01,01}$, which dominate the behavior of λ_{mix}^{tr} , since they explicitly involve only the inelastic collisions other than resonant collisions. The same is true of the elements $L_{qq'}^{10,01}$ and $L_{qq'}^{01,10}$. The second approximation assumes that the angular scattering distribution is the same in all channels except for a scaling factor, the total transition probability. This will be called the independent scattering pattern assumption. This permits a number of terms to be dropped from the elements $L_{qq'}^{01,10}$ and $L_{qq'}^{10,01}$. Thermal diffusion measurements in ortho and para hydrogen at low temperatures indicate that these terms are indeed small although by no means negligible in all circumstances¹⁷. The result of these considerations is to leave the expressions for $L_{qq'}^{10,10}$, $L_{qq'}^{10,01}$, and $L_{qq'}^{01,10}$ given in reference 11 unchanged.

The foregoing approximations must be applied more carefully to the elements $L_{qq'}^{01,01}$, which dominate the behavior of λ_{mix}^{int} . When this is done, a new term, something like a rotational relaxation number but due only to

resonant collisions, appears in the diagonal elements $L_{qq'}^{01,01}$. In the notation of reference 11, for the two component case, $q=A,B$,

$$L_{AA}^{01,01} = L_{AA}^{01,01} + \Delta L_{AA}^{01,01}, \quad (51)$$

$$L_{AA}^{01,01} = \frac{4kT}{p\bar{v}_{Aint,A} c_{A,int}} \left(x_A^2 + x_A x_B \frac{\bar{v}_{Aint,A}}{\bar{v}_{Aint,B}} \right), \quad (52a)$$

$$\Delta L_{AA}^{01,01} = \frac{-8k}{\pi(c_{Aint})^2} \left[\frac{x_A^2 m_A c_{Arot}}{k\eta_A \zeta_{AA}} + \frac{6}{5} x_A x_B \frac{m_A}{m_B} \frac{T A_{AB}^*}{p \bar{v}_{AB}} \left(\frac{c_{Arot}}{\zeta_{AB}} + \frac{c_{Arot}^{1/2} c_{Brot}^{1/2}}{\tilde{\zeta}_{AB}} \right) \right], \quad (52b)$$

where A_{AB}^* is the ratio of collision integrals defined in reference 11. $L_{BB}^{01,01}$ is obtained by interchanging subscripts. The new term $\tilde{\zeta}_{AB}$ arises from the following collision integral

$$\left\langle \Delta \epsilon_{Ai} \Delta \epsilon_{Bj} p_{ex}^{AB} \right\rangle_{AB,res} \equiv \frac{T}{\pi \eta_{AB}} \frac{c_{Arot}^{1/2} c_{Brot}^{1/2}}{\tilde{\zeta}_{AB}}, \quad (53)$$

where η_{AB} is a fictitious viscosity defined in terms of a collision integral¹¹. Note that $\tilde{\zeta}_{AB} = \tilde{\zeta}_{BA}$, a symmetry that is not true for the usual collision numbers ζ_{AB} . $\tilde{\zeta}$ itself may be separated into the contributions from the different types

of exchange interactions as follows:

$$\frac{1}{\zeta_{AB}} = \frac{1}{\zeta_{\mu\mu}} + \frac{1}{\zeta_{\theta\theta}} + \frac{1}{\zeta_{\mu\theta}} + \frac{1}{\zeta_{\theta\mu}} \quad , \quad (54)$$

where $\zeta_{AB}^{\alpha\beta} = \zeta_{BA}^{\beta\alpha}$. The evaluation of these collision integrals is quite similar to that of the analogous $\Delta_{AB}^{\alpha\beta}$ and leads to quite similar expressions which are given in the appendix.

The new term ζ_{AB} also appears in the off-diagonal elements $L_{AB}^{01,01}$ and $L_{BA}^{01,01}$, as does a new type of diffusion collision integral, I_3^{AB} :

$$\begin{aligned} L_{AB}^{01,01} = & \frac{48}{5\pi} \frac{x_A x_B A_{AB}^*}{c_{Aint} c_{Bint} n D_{AB}} \frac{c_{Arot}^{1/2} c_{Brot}^{1/2}}{\zeta_{AB}} \\ & + \frac{64}{3} \frac{\mu_{AB} x_A x_B}{c_{Aint} c_{Bint} T} I_3^{AB} \quad , \end{aligned} \quad (55)$$

where

$$I_3^{AB} = \left\langle \left(\epsilon_{Ai} - \bar{\epsilon}_A \right) \left[\left(\epsilon_{Bj} - \bar{\epsilon}_B \right) \gamma^2 - \left(\epsilon_{B\ell} - \bar{\epsilon}_B \right) \gamma \gamma' \cos \chi \right] \right\rangle_{AB} \quad (56)$$

Neglect of complex collisions and the assumption of independent scattering patterns reduces $L_{AB}^{01,01}$, $B \neq A$, to zero. We will retain these assumptions for all collisions other than resonant collisions: their contribution will then

be nil. The contribution of resonant collisions to I_3^{AB} may then be evaluated according to arguments like those used for I_1 and I_2 , and we find

$$I_3^{AB} \approx - \left\langle \left(\epsilon_{Ai} - \bar{\epsilon}_A \right) \left(\epsilon_{Ai} - \epsilon_{Ak} \right) \gamma^2 p_{ex}^{AB} \right\rangle_{AB, res}, \quad A \neq B. \quad (57)$$

These corrections are the same as the corrections occurring in Eqs. (46) for I_2 and have already been evaluated. The presence of these correction terms in the off-diagonal elements of $L^{01,01}$ makes up for the missing factor of 2 in the correction terms of I_2 : the mixture formulae will now reduce properly to the single gas conductivity in the limit of a mixture of a gas with itself. The determinant element of Eq. (35) may now be approximated by

$$L_{AB}^{01,01} \approx - \frac{4x_A x_B}{c_{Aint} c_{Bint} n \mathcal{D}_{AB}} \left(\frac{c_{Aint}}{2} \Delta_{AB} - \frac{12}{5\pi} A_{AB}^* \frac{c_{Aint}^{1/2} c_{Bint}^{1/2}}{\tilde{\zeta}_{AB}} \right), \quad (58)$$

where Δ_{AB} is the same group of corrections that appear in Eq. (47a) and in the appendix.

Values of $\tilde{\zeta}_{AB}$ for multipole exchanges in HX-DX collisions are given in Table VIII at the temperatures for which thermal conductivities have been measured. They are similar in magnitude to the usual collision numbers for like collisions given in Table V. To obtain values for ζ_{AB} , the usual collision numbers for unlike collisions, we have assumed that the structure of the target

molecule is relatively unimportant and have taken

$$\zeta_{AB} = \zeta_{AA} , \zeta_{BA} = \zeta_{BB} . \quad (59)$$

The values of ζ_{AA} and ζ_{BB} in Table V assure that the conductivities of the pure components will be reproduced correctly.

The results are shown in Figs. 3 and 4 as the unbroken lines. Three curves have been calculated: no unlike resonances, exact unlike resonances counted, and both exact and near resonances counted for unlike collisions. It is apparent that the effect of resonant exchange is appreciably greater in the complete kinetic theory expression than in the Hirschfelder-Eucken approximation. The results without unlike exchange are clearly much too high; the effect of including unlike exchange is in the right direction and of the correct magnitude. There remain, however, small discrepancies of detail. Thus the calculated results for HF+DF are always slightly too high, even with near resonance included. But for this system the resonant corrections are so large (see Tables V and VII) that it seems likely that the simplified two-state theory of Section II is inadequate. Inclusion of near-resonant exchange collisions for HCl+DCl is sufficient to lower the calculated point below the experimental points, and indeed to change the sign of the deviation from linearity. This might indicate that near-resonant exchange should not be weighted as heavily as exact resonance, but the theory of Section II is much too simple to deal with a question of that sort. The effect of omitting the new term, $\tilde{\zeta}$, is very small (less than 10% of the total deviation from the average)

and in the positive direction. This was to be expected since ζ_{AB} and ζ_{BA} cancel in the limit of a gas with itself and HCl+DCl and HF+DF are, after all, isotopic mixtures. Besides the numerical discrepancies, the predicted temperature dependence is not quite right. But again, in view of the many approximations involved, the details should probably not be taken too seriously, except to indicate that resonant effects are evident in HX+DX mixtures, and that marked improvement is made by including multipole interaction effects higher than dipole-dipole.

IV. DISCUSSION

We believe that the present results show the importance of including other multipole interactions as well as dipole-dipole interactions in calculations of the thermal conductivity of gases and gas mixtures containing molecules of low moments of inertia. Such interactions seem capable of accounting for the anomalies observed in HF+DF and HCl+DCl mixtures. However, the numerical details should not be taken too literally, because many approximations have been made. In particular, the whole theory of resonant exchange used here is based on a two-state approximation, and the integrals occurring have been computed by an impact parameter approximation. Furthermore, the numerical values of the exchange coefficients, $\langle |a_{ex}|^2 \rangle_{av}$, have been calculated roughly (Table I). In addition to these approximations in the collision theory, approximations have also been made in the kinetic theory. Complex collisions have been neglected, and the independent scattering pattern approximation has been made in many of the

matrix elements. The effect of inelastic collisions¹⁴ on \mathcal{D}_{int} has been neglected and spin polarization¹⁸ has been ignored. The values of ζ_{AB} and ζ_{BA} have been estimated only roughly via Eq. (59). These are all thought to be small effects, but the remaining discrepancies with experiment are now in the realm of small effects. We may thus close on an optimistic note--for calculations of thermal conductivity, the present theory is adequate to approximately 1 or 2%.

APPENDIX

The unlike exchange corrections for the internal-energy diffusion coefficients are as follows. For exact resonance,

$$\Delta_{AB}^{\mu\mu} = g_{AB}^{\mu\mu} \frac{3\pi^2}{8} \left(\frac{2\mu_{AB}}{3kT} \right)^{1/2} \left(\frac{\theta_{Arot}}{T} \right)^{3/2} \left(\frac{\mu_{AB}}{\hbar} \right) \frac{\langle |a_{ex}^{\mu\mu}| \rangle_{av}}{\sigma_{AB}^2 \Omega_{AB}^{(1,1)*}}, \quad (A1)$$

$$\Delta_{BA}^{\mu\mu} = \frac{2}{3} \Delta_{AB}^{\mu\mu} \left(g_{BA}^{\mu\mu} / g_{AB}^{\mu\mu} \right), \quad (A2)$$

$$\Delta_{AB}^{\Theta\mu} = -g_{AB}^{\Theta\mu} \frac{190}{243} \left(\frac{3}{\pi} \right)^{1/2} \left(\frac{\pi^4}{18} \right)^{2/3} \left(\frac{2\mu_{AB}}{kT} \right)^{1/3} \left(\frac{\theta_{Arot}}{T} \right)^{3/2} \\ \times \left(\frac{\theta_{AB}^{\mu\Theta}}{\hbar} \right)^{2/3} \frac{\langle |a_{ex}^{\mu\Theta}|^{2/3} \rangle_{av}}{\sigma_{AB}^2 \Omega_{AB}^{(1,1)*}}, \quad (A3)$$

$$\Delta_{BA}^{\Theta\mu} = -\frac{1}{19} \Delta_{AB}^{\Theta\mu} \left(g_{BA}^{\Theta\mu} / g_{AB}^{\Theta\mu} \right), \quad (A4)$$

where the semiclassical asymptotic expressions for the g coefficients are

$$g_{AB}^{\mu\mu} = e^{-2\theta_{Arot}/3T} \left(1 - \frac{1}{9} \frac{\theta_{Arot}}{T} + \dots \right), \quad (A5)$$

$$g_{BA}^{\mu\mu} = e^{-\theta_{Arot}/3T} \left(1 - \frac{1}{3} \frac{\theta_{Arot}}{T} + \dots \right) , \quad (A6)$$

$$g_{AB}^{\theta\mu} = e^{-17\theta_{Arot}/12T} \left(1 - \frac{67}{38} \frac{\theta_{Arot}}{T} + \dots \right) , \quad (A7)$$

$$g_{BA}^{\mu\theta} = e^{-13\theta_{Arot}/12T} \left(1 - \frac{19}{2} \frac{\theta_{Arot}}{T} + \dots \right) , \quad (A8)$$

For near resonance,

$$\Delta_{AB}^{\theta\theta} = g_{AB}^{\theta\theta} \frac{7\pi}{2} \left(\frac{1}{6} \right)^{1/2} \Gamma\left(\frac{7}{4}\right) \left(\frac{2\mu_{AB}}{kT} \right)^{1/4} \left(\frac{\theta_{Arot}}{T} \right)^{3/2}$$

$$\times \left(\frac{\theta_A \theta_B}{\hbar} \right)^{1/2} \frac{\langle |a_{ex}^{\theta\theta}|^2 \rangle_{av}}{\sigma_{AB}^2 \Omega_{AB}^{(1,1)*}} , \quad (A9)$$

$$\Delta_{BA}^{\theta\theta} = \frac{2}{3} \Delta_{AB}^{\theta\theta} \left(g_{BA}^{\theta\theta} / g_{AB}^{\theta\theta} \right) , \quad (A10)$$

$$\Delta_{AB}^{\mu\theta} = g_{AB}^{\mu\theta} \frac{40}{9} \left(\frac{2}{\pi} \right)^{1/2} \left(\frac{\pi^4}{18} \right)^{2/3} \left(\frac{2\mu_{AB}}{kT} \right)^{1/3} \left(\frac{\theta_{Arot}}{T} \right)^{3/2} \\ \times \left(\frac{\mu_A \theta_B}{\hbar} \right)^{2/3} \frac{\langle |a_{ex}^{\mu\theta}|^2 \rangle_{av}}{\sigma_{AB}^2 \Omega_{AB}^{(1,1)*}}, \quad (A11)$$

$$\Delta_{BA}^{\theta\mu} = \frac{3}{8} \Delta_{AB}^{\mu\theta} \left(g_{BA}^{\theta\mu} / g_{AB}^{\mu\theta} \right), \quad (A12)$$

where the semiclassical expressions for the g coefficients are

$$g_{AB}^{\theta\theta} = e^{-43\theta_{Arot}/24T} \left(1 - \frac{11}{18} \frac{\theta_{Arot}}{T} + \dots \right), \quad (A13)$$

$$g_{BA}^{\theta\theta} = e^{-35\theta_{Arot}/24T} \left(1 - \frac{61}{48} \frac{\theta_{Arot}}{T} + \dots \right), \quad (A14)$$

$$g_{AB}^{\mu\theta} = e^{-25\theta_{Arot}/24T} \left(1 - \frac{2}{3} \frac{\theta_{Arot}}{T} + \dots \right), \quad (A15)$$

$$g_{BA}^{\theta\mu} = e^{-17\theta_{Arot}/24T} \left(1 - \frac{11}{36} \frac{\theta_{Arot}}{T} + \dots \right). \quad (A16)$$

The resonant rotational relaxation collision numbers are closely related to the corresponding Δ_{AB} ,

$$\frac{1}{\zeta_{AB}^{\mu\mu}} = \frac{1}{\zeta_{BA}^{\mu\mu}} = \frac{5\pi}{36A_{AB}^*} |\Delta_{AB}^{\mu\mu}| h_{AB}^{\mu\mu} , \quad (A17)$$

$$\frac{1}{\zeta_{AB}^{\theta\theta}} = \frac{1}{\zeta_{BA}^{\theta\theta}} = \frac{5\pi}{42A_{AB}^*} |\Delta_{AB}^{\theta\theta}| h_{AB}^{\theta\theta} , \quad (A18)$$

$$\frac{1}{\zeta_{AB}^{\mu\theta}} = \frac{1}{\zeta_{BA}^{\theta\mu}} = \frac{3\pi}{32A_{AB}^*} |\Delta_{AB}^{\mu\theta}| h_{AB}^{\mu\theta} , \quad (A19)$$

$$\frac{1}{\zeta_{AB}^{\theta\mu}} = \frac{1}{\zeta_{BA}^{\mu\theta}} = \frac{3\pi}{38A_{AB}^*} |\Delta_{AB}^{\theta\mu}| h_{AB}^{\theta\mu} . \quad (A20)$$

The h coefficients are quantum corrections; their semiclassical expressions are

$$h_{AB}^{\mu\mu} = e^{\theta_{Arot}/6T} \left(1 - \frac{1}{4} \frac{\theta_{Arot}}{T} + \dots \right) \left(1 - \frac{1}{9} \frac{\theta_{Arot}}{T} + \dots \right)^{-1} , \quad (A21)$$

$$h_{AB}^{\theta\theta} = e^{\theta_{Arot}/6T} \left(1 - \frac{\theta_{Arot}}{T} + \dots \right) \left(1 - \frac{11}{18} \frac{\theta_{Arot}}{T} + \dots \right)^{-1}, \quad (A22)$$

$$h_{AB}^{\mu\theta} = e^{\theta_{Arot}/6T} \left(1 - \frac{1}{2} \frac{\theta_{Arot}}{T} + \dots \right) \left(1 - \frac{2}{3} \frac{\theta_{Arot}}{T} + \dots \right)^{-1} \quad (A23)$$

$$h_{AB}^{\theta\mu} = e^{\theta_{Arot}/6T} \left(1 - \frac{3}{4} \frac{\theta_{Arot}}{T} + \dots \right) \left(1 - \frac{67}{38} \frac{\theta_{Arot}}{T} + \dots \right)^{-1}. \quad (A24)$$

TABLE I

Average Values of Resonant Exchange Coefficients,
for use in Eqs. (19) - (21)

	$\Delta m=0$ (only)	Corrected
$\langle a_{\text{ex}}^{\mu\mu} \rangle_{\text{av}}$	0.308	0.435
$\langle a_{\text{ex}}^{\theta\theta} ^{1/2} \rangle_{\text{av}}$	1.308	1.308
$\langle a_{\text{ex}}^{\mu\theta} ^{2/3} \rangle_{\text{av}}$	0.514	0.514

TABLE II
Rotational Specific Heats and Quantum Correction Factors
for Resonant Exchange of Rotational Energy

$\frac{T}{\Theta_{\text{rot}}}$	C_{rot}/k		$\mu\mu$		$\frac{\Theta\Theta}{g}$		$\mu\Theta$
	even	odd	total	even	odd	total	
0	0	0	0	0	0	0	0
0.25	0.0000	0.0000	0.0650	0.0083	0.0083	0.0000	0.0000
0.50	0.0044	0.0000	0.7940	0.0235	0.0235	0.0002	0.0000
0.75	0.1070	0.0007	1.0925	0.0432	0.0432	0.0058	0.0000
1.00	0.4353	0.0106	1.0729	0.0665	0.0665	0.0276	0.0011
1.25	0.8748	0.0500	1.0380	0.0929	0.0929	0.0638	0.0081
1.50	1.2319	0.1312	1.0210	0.122	0.122	0.104	0.0286
1.75	1.4214	0.2476	1.0131	0.153	0.154	0.144	0.0657
2.0	1.4647	0.3816	1.0091	0.185	0.188	0.181	0.117
2.5	1.3428	0.6347	1.0051	0.245	0.260	0.249	0.240
3.0	1.1888	0.8126	1.0033	0.293	0.335	0.310	0.358
3.5	1.0904	0.9135	1.0023	0.329	0.406	0.364	0.453
4.0	1.0401	0.9633	1.0017	0.361	0.468	0.412	0.525
4.5	1.0171	0.9856	1.0013	0.392	0.518	0.454	0.578
5.0	1.0072	0.9948	1.0010	0.426	0.558	0.491	0.619
6.0	1.0016	0.9998	1.0007	0.495	0.611	0.553	0.677
7.0	1.0006	1.0004	1.0005	0.558	0.646	0.602	0.719
8.0	1.0004	1.0004	1.0004	0.610	0.673	0.641	0.750
9.0	1.0003	1.0003	1.0003	0.652	0.697	0.674	0.775
10.0	1.0002	1.0002	1.0002	0.685	0.718	0.701	0.795
12.0	1.0002	1.0002	1.0002	0.735	0.754	0.744	0.827
14.0	1.0001	1.0001	1.0001	0.771	0.783	0.777	0.850
16.0	1.0001	1.0001	1.0001	0.798	0.806	0.802	0.867
18.0	1.0001	1.0001	1.0001	0.819	0.825	0.822	0.881
20.0	1.0001	1.0001	1.0001	0.836	0.841	0.838	0.893
∞	1.0000	1.0000	1.0000	1.000	1.000	1.000	1.000

TABLE III

Effect of Resonant Quadrupole-Quadrupole Energy
Exchange on Thermal Conductivity at 300°K

Gas	$10^{26} \left \frac{\sigma}{\text{esu}} \right ^a$	Θ_{rot} °K	ϵ/k °K	$\frac{\sigma}{\text{\AA}}$	$\Delta_{\text{ex}}^{\Theta\Theta}$
N ₂	1.52	2.86	91.5 ^b	3.681 ^b	0.0096
O ₂	0.39	2.07	113 ^b	3.433 ^b	0.0017
CO ₂	4.3	0.56	190 ^b	3.996 ^b	0.0018
o-H ₂	0.662	85.4	37.2 ^c	2.97 ^c	0.278
p-H ₂	0.662	85.4	37.2 ^c	2.97 ^c	0.228

^aD.E. Stogryn and A.P. Stogryn, Mol. Phys. 11, 371 (1966)

^bReference 6

^cD.E. Diller and E.A. Mason, J. Chem. Phys. 44, 2604 (1966)

TABLE IV

Parameters Used in the Calculations for Figure 2

Gas	$10^{26} \theta ^a$ esu	θ_{rot} °K	ϵ/k^b °K	σ^b Å
H ₂	0.662	85.4	37.2	2.97
D ₂	0.649	42.7	35.0	2.976
HD	0.642	64.1	36.5	2.96

^aD.E. Stogryn and A.P. Stogryn, Mol. Phys. 11, 371 (1966)

^bD.E. Diller and E.A. Mason, J. Chem. Phys. 44, 2604 (1966)

TABLE V

Effect of Resonant Multipole-Multipole Energy
Exchange on the Thermal Conductivity
of Polar Diatomic Gases

Gas	T °K	Δ_{ex}				
		$\mu\mu$	$\Theta\Theta$	$\mu\Theta$	Calc. $\mu\mu$ only	rot $\mu\mu + \mu\Theta + \Theta\Theta$
HF	373.8	2.209	0.262	0.193	8.1	10.7
	422.3	1.855	0.236	0.171	7.8	10.7
DF	373.8	0.903	0.116	0.082	3.0	4.2
	422.3	0.767	0.102	0.072	2.6	3.8
HCl	300.1	0.456	0.199	0.094	4.1	13.3
	328.5	0.400	0.180	0.085	2.7	7.4
	374.8	0.329	0.156	0.072	1.8	4.8
	423.1	0.274	0.135	0.061	1.4	3.7
	471.4	0.232	0.119	0.053	1.2	3.5
DCI	300.1	0.176	0.081	0.037	0.8	2.2
	328.5	0.154	0.072	0.034	0.5	1.5
	374.8	0.126	0.062	0.028	0.2	1.0
	423.1	0.105	0.054	0.024	0.1	0.8
	471.4	0.089	0.047	0.020	0.1	0.8

TABLE VI
Parameters Used in the Calculations for Table V

Gas	$10^{18} \mu $ esu	$10^{26} \theta $ esu	θ_{rot} °K	ϵ/k °K	σ Å	δ_{max}
HF	1.83 ^a	2.6 ^c	30.16 ^a	400 ^d	2.394 ^d	2.0 ^d
DF	1.837 ^a	2.6 ^c	15.85 ^a	400 ^d	2.394 ^d	2.0 ^d
HCl	1.081 ^b	3.8 ^c	15.24 ^b	328 ^e	3.36 ^e	0.34 ^e
DCI	1.085 ^b	3.8 ^c	7.84 ^b	328 ^e	3.36 ^e	0.34 ^e

^aReference 4

^bReference 3

^cD.E. Stogryn and A.P. Stogryn, Mol. Phys. 11, 371 (1966)

^dPrivate communication from Dr. Roger Svehla

^eL. Monchick and E.A. Mason, J. Chem. Phys. 35, 1676 (1961)

TABLE VII

Multipole-Multipole Energy Exchange Corrections for
Unlike Collisions Between HX and DX.
Comparison Should be Made with the Corrections
for Like Collisions in Table V

Mixture	T °K	$\frac{1}{2} \Delta_{\text{HX-DX}}$				$\frac{1}{2} \Delta_{\text{DX-HX}}$			
		$\mu\mu$	$\theta\theta$	$\mu\theta$	$\theta\mu$	$\mu\mu$	$\theta\theta$	$\mu\theta$	$\theta\mu$
HF - DF	373.8	0.612	0.078	0.293	-0.095	0.206	0.025	0.001	0.058
	422.3	0.521	0.069	0.257	-0.085	0.175	0.023	0.001	0.051
HCl-DC1	300.1	0.126	0.058	0.140	-0.048	0.042	0.018	0.001	0.027
	328.5	0.110	0.051	0.126	-0.043	0.037	0.017	0.001	0.025
	374.8	0.090	0.044	0.106	-0.037	0.030	0.014	0.000	0.020
	423.1	0.075	0.038	0.090	-0.031	0.025	0.013	0.000	0.017
	471.4	0.064	0.034	0.079	-0.027	0.021	0.011	0.000	0.014

TABLE VIII

Rotational Collision Numbers for Multipole-Multipole
Energy Exchange in HX-DX Collisions

Mixture	T	$\tilde{\zeta}_{\text{HX-DX}} = \tilde{\zeta}_{\text{DX-HX}}$
	° K	
HF-DF	373.8	1.4
	422.3	1.6
HCl-DCI	300.1	4.2
	328.5	4.8
	374.5	5.7
	423.1	6.7
	471.4	7.7

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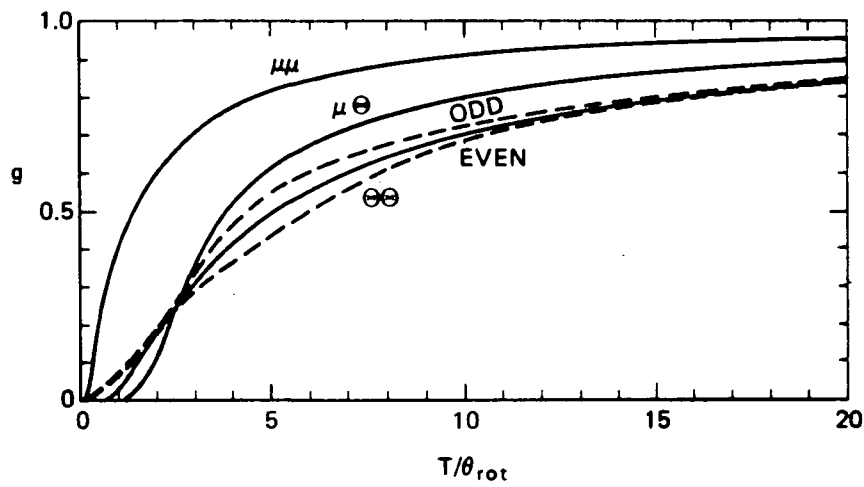


Fig. 1

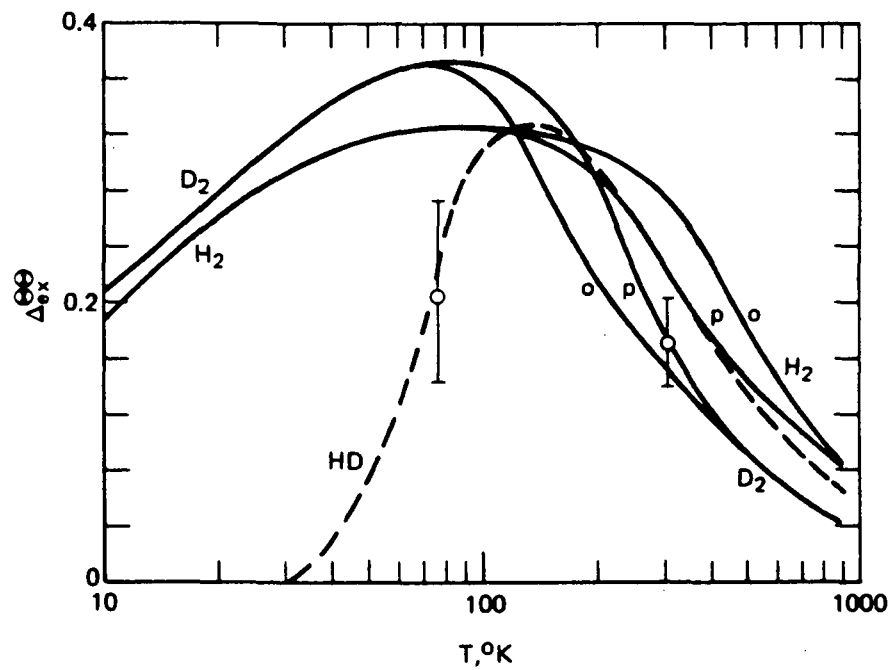


Fig. 2

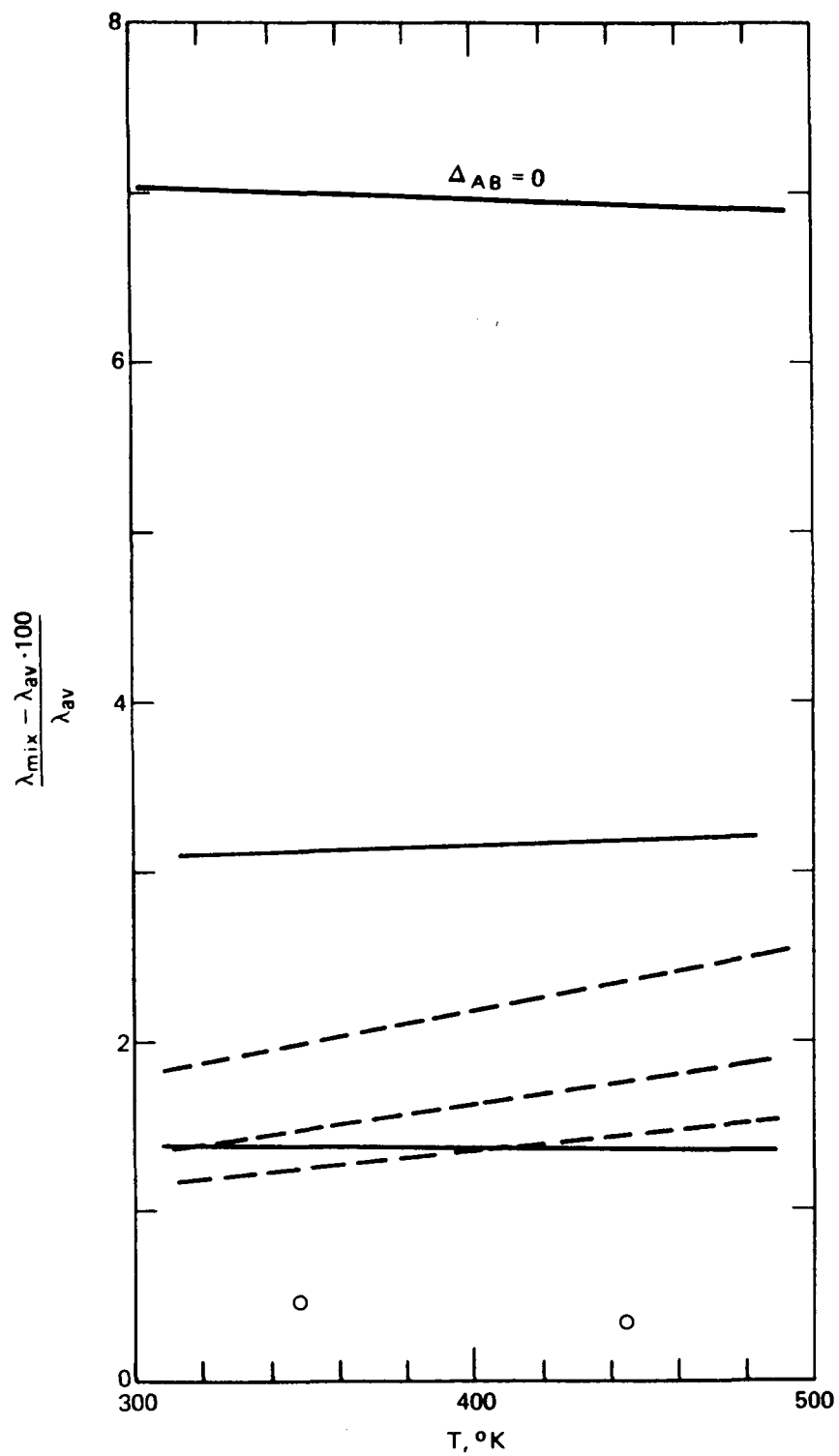


Fig. 3

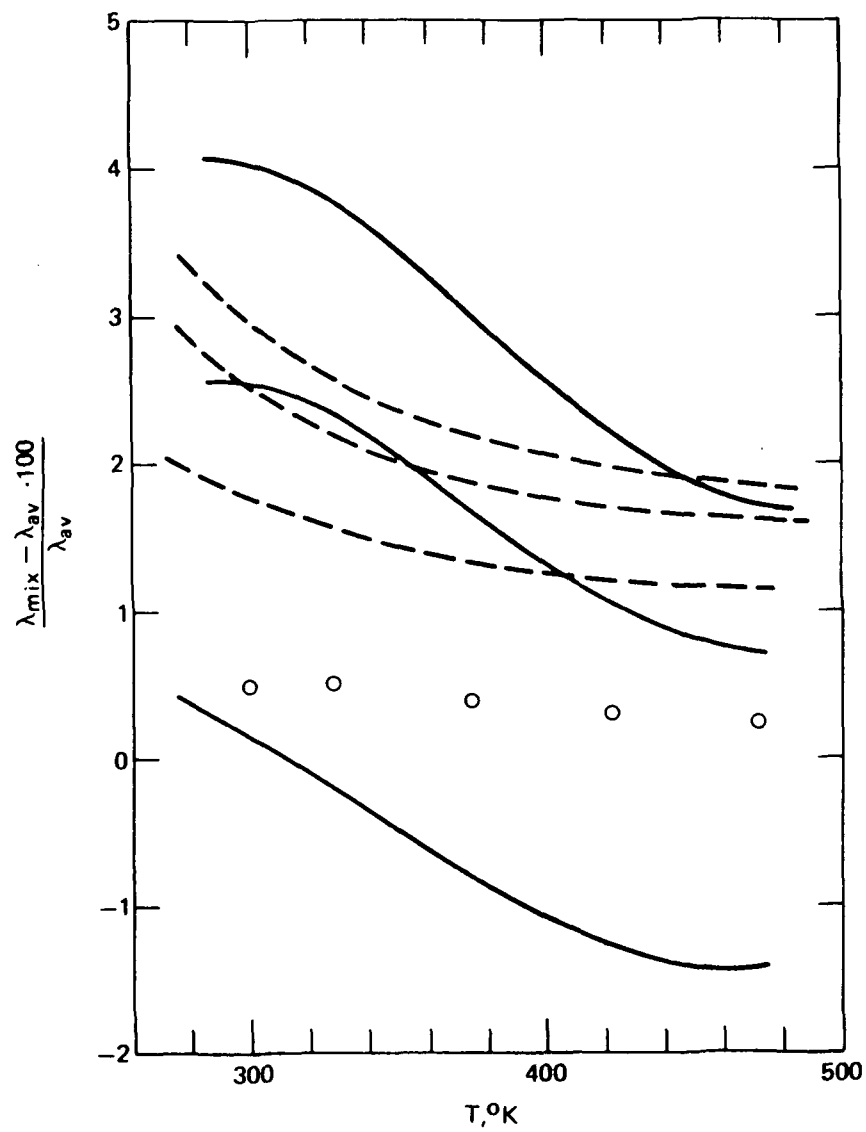


Fig. 4

FIGURE CAPTIONS

- Fig. 1. Quantum correction factors $g^{\mu\mu}$, $g^{\mu\theta}$, and $g^{\theta\theta}$ for resonant exchange of rotational energy, as appearing in Eqs. (29) - (31). The dashed curves for quadrupole-quadrupole exchange apply to symmetric molecules, and refer to summations over even or odd rotational energy levels.
- Fig. 2. Resonant quadrupole-quadrupole correction to D_{int} for hydrogen isotopes. The experimental points refer to p-H₂.
- Fig. 3. Deviation of the thermal conductivities of equimolar HF+DF mixtures from a linear average. Solid curves are the present theory and dashed curves are the Hirschfelder-Eucken approximation. In each case the upper curve is obtained with all unlike exchange corrections Δ_{AB} set to zero, the next lower curve includes only the Δ_{AB} for exact resonances, and the lowest curve includes both exact and near resonances.
- Fig. 4. Same as Fig. 3, for equimolar HCl+DCl mixtures.