

Transport integrals $\Omega^{(l,s)}(T)$ for binary collisions of open-shell atoms with uncertain interaction potentials

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General analytical expressions for the transport collision integrals $\Omega^{(l,s)}(T)$ for binary collisions of atoms that can interact through many different (repulsive-attractive as well as repulsive) potentials are derived. The integrals allow one to calculate the transport coefficients (viscosity, thermal conductivity, and ordinary and thermal diffusion coefficients) in gases dominated by collision systems driven by poorly understood multiple-force interactions. The approach is used to calculate the transport integrals for several collision systems, and the results are compared with the detailed *ab initio* calculations available for some well understood open-shell systems. [S1063-651X(98)08810-2]

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I. INTRODUCTION

Transport coefficients (viscosity, thermal conductivity, and ordinary and thermal diffusion coefficients) of weakly ionized gases and their mixtures can be obtained from the transport collision integrals $\Omega_{m-m}^{(l,s)}$ and $\Omega_{m-n}^{(l,s)}$ for all the binary collisions between the identical ($m-m$) and different ($m-n$) particles present in the gas (see Refs. [1-4], and references therein). The transport integrals for a binary collision can be calculated from the deflection function of the collision system if the interaction potential and the distribution of the impact energies of the colliding particles are known. The classical deflection function of a binary collision with impact energy E and impact parameter b in the field of a central potential $U(r)$ is [2]

$$\chi(g,b) = \pi - 2b \int_{r_m}^{\infty} \frac{dr}{r^2 \sqrt{1 - b^2/r^2 - U(r)/E}}, \quad (1)$$

where $E = \mu g^2/2$, μ and g are the reduced mass and the relative speed of the particles, respectively, r is the distance between the particles, and r_m is the distance of the closest approach of the particles. Subsequently, the l th-moment collision cross section is

$$Q^{(l)}(g) = 2\pi \int_0^{\infty} [1 - \cos^l \chi(g,b)] b db, \quad (2)$$

and the corresponding transport integrals for collisions in gas which is not far from local thermal equilibrium at temperature T , and which is dominated by the binary collisions driven by the potential $U(r)$, are

$$\Omega^{(l,s)}(T) = \left(\frac{kT}{2\pi\mu} \right)^{1/2} \int_0^{\infty} e^{-\gamma^2} \gamma^{2s+3} Q^{(l)}(g) d\gamma, \quad (3)$$

where $\gamma^2 = \mu g^2/2kT$.

The transport integrals (3) apply to collision systems of two particles which interact through a single potential $U(r)$. However, in many collision systems common in applica-

tions, the particles can interact (with different probabilities) through many different, both repulsive-attractive and repulsive, potentials (see Fig. 1). (For example, two ground-state oxygen atoms can interact through 18 different potentials.) The transport integrals $\Omega^{(l,s)}$ for such collisions must be statistically averaged over all the potentials possible in the collisions, and these average values should be used in calculations of the corresponding transport coefficients of the gases. The average transport integrals can be written as

$$\langle \Omega^{(l,s)}(T) \rangle = \left(\sum_{i=1}^{i_m} p_i \right)^{-1} \sum_{i=1}^{i_m} p_i \Omega_i^{(l,s)}(T) + \left(\sum_{j=1}^{j_m} p_j \right)^{-1} \sum_{j=1}^{j_m} p_j \Omega_j^{(l,s)}(T), \quad (4)$$

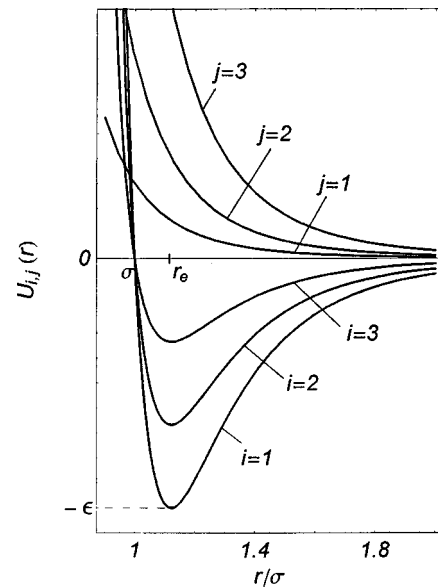


FIG. 1. Examples of potentials $U_{i,j}(r)$ occurring in multiple-force collisions of two atoms. Only the three lowest ($i=1,2,3$) repulsive-attractive potentials and the three lowest ($j=1,2,3$) repulsive potentials are shown. σ is the zero-potential distance and ϵ is the well depth of the lowest, $U_{i=1}(r)$, repulsive-attractive potential.

where subscripts i and j denote the repulsive-attractive and repulsive potentials, respectively, and where the first sum on the right-hand side is taken over all (i_m) repulsive-attractive potentials and the second sum is taken over all (j_m) repulsive potentials possible in the binary collision under consideration; $p_k/\sum_k p_k$ is the probability that the collision will be driven by the k th potential, and p_k is the electronic degeneracy of the diatom representing the binary collision driven by the k th potential.

The integrals (4) with $(l,s)=(1,1)$, $(1,2)$, $(1,3)$, and $(2,2)$ allow one to calculate (using, for example, the Chapman-Enskog transport theory) all basic second-order transport coefficients in gases not far from local thermal equilibrium. The main objective of this work is to develop a general approach to find analytical estimates for the average collision integrals (4), including the multiple-force collisions where many different interaction potentials are possible but the information about the potentials is very limited. Such a situation is common in many applications of high-temperature gases.

II. THE TRANSPORT INTEGRALS FOR REPULSIVE-ATTRACTIVE INTERACTIONS

Most of the repulsive-attractive potentials that occur in the binary collisions under consideration cannot be approximated with high accuracy in the entire range of interaction distance by a simple mathematically convenient function. In addition, some of the potentials can have one (or more) local maximum. Since the fraction of the latter potentials is usually small, and since the magnitudes of the well depths and the distances at which atom-atom potentials are zero are the dominating factors in the dynamics of the binary collisions, we ignore the potentials with the local maxima and approximate the repulsive-attractive potentials by the Lennard-Jones (12,6) potentials (see the discussion in Sec. VI). Consequently, the i th repulsive-attractive potential with well depth ϵ_i and the zero-potential distance σ_i is

$$U_i(r) = 4\epsilon_i \left[\left(\frac{\sigma_i}{r} \right)^{12} - \left(\frac{\sigma_i}{r} \right)^6 \right]. \quad (5)$$

Most of the repulsive-attractive curves in multiple-force collisions of neutral atoms can be approximated, with accuracy acceptable in applications, by the potential (5).

The cross sections (2) for a binary collision with impact velocity g and driven by a single (i)th potential (5) can be given as [2]

$$Q_i^{(l)}(g) = 2\pi\sigma_i^2 I_\chi^{(l)}(g^*), \quad (6)$$

where

$$I_\chi^{(l)*}(g^*) = \int_0^\infty [1 - \cos^l \chi(g^*, b^*)] b^* db^*, \quad (7)$$

$$g^{*2} = \mu g^2 / 2\epsilon_i, \quad (8)$$

and

$$b^* = b / \sigma_i. \quad (9)$$

The transport integrals for collisions driven by the i th potential (5) at temperature T are

$$\Omega_i^{(l,s)}(T) = \pi\sigma_i^2 \left(\frac{kT}{2\pi\mu} \right)^{1/2} I_g^{(l,s)*}(T_i^*), \quad (10)$$

where

$$I_g^{(l,s)*}(T_i^*) = \frac{2}{T_i^{*s+2}} \int_0^\infty e^{-g^{*2}/T_i^*} g^{*2s+3} I_\chi^{(l)*}(g^*) dg^*, \quad (11)$$

and

$$T_i^* = kT / \epsilon_i. \quad (12)$$

The value of kT in gases at temperatures below 10 000 K is significantly smaller than the well depths ϵ_i of most of the interaction potentials in the collision systems dominating the transport properties of gases common in applications. The reduced impact energy g^{*2} in most such collisions is smaller than 0.8, and the collisions are the ‘‘orbiting’’ collisions if their impact parameters b^* are close to the corresponding ‘‘orbiting’’ impact parameters b_o^* (see below). Numerical analysis in a broad range of g^* and b^* showed that if such a collision is driven by the potential (5), then there are three distinctive regions of the reduced impact parameter b^* .

(1) b^* is close to the orbiting impact parameter b_o^* . The functions $[1 - \cos \chi(g^*, b^*)]$ and $[1 - \cos^2 \chi(g^*, b^*)]$ oscillate very rapidly with average values equal to one and one-half, respectively. The contribution of the functions to the integrals (7) in the narrow region where $b^* \approx b_o^*$ is much smaller than the contribution of the functions in the other regions of b^* . Therefore the former contribution is neglected in the following considerations.

(2) b^* is greater than b_o^* . When b^* is slightly greater than b_o^* , the functions $[1 - \cos \chi(g^*, b^*)]$ and $[1 - \cos^2 \chi(g^*, b^*)]$ are close to two and one, respectively, and they both decrease very rapidly with increase of b^* . At values of b^* not much greater than b_o^* , the functions have weak dependence on g^* and their dependence on b^* is always almost exponential,

$$1 - \cos^l \chi(g^*, b^*) \approx (3-l) \exp\{-20[(b^{*2}/b_o^{*2}) - 1]\}. \quad (13)$$

(3) b^* is smaller than b_o^* . In this case, the maximum value of the integrand $[1 - \cos \chi(g^*, b^*)]$ equals two (at $b_o^{*2} = 0$ and at $b^{*2} \approx b_o^{*2}$), and the position of the integrand minimum (equal to zero) is weakly dependent on g^* and is close to $b_o^{*2}/2$. In addition, the b^{*2} dependence of the derivative of the integrand $[1 - \cos \chi(g^*, b^*)]$ with respect to b^{*2} is always close to a parabolic function centered at $b_o^{*2}/2$,

$$1 - \cos \chi(g^*, b^*) \approx \frac{8}{b_o^{*4}} \left(b^{*2} - \frac{b_o^{*2}}{2} \right)^2. \quad (14)$$

Analysis of the g^* and b^* dependences of the integrand $[1 - \cos^2 \chi(g^*, b^*)]$ can now be simplified by use of the relationship (14) in conjunction with the fact that $[1 - \cos^2 \chi] = (1 - \cos \chi)[2 - (1 - \cos \chi)]$. As a result, one obtains

$$1 - \cos^2 \chi(g^*, b^*) = 16 \left(\frac{b^*}{b_o^*} \right)^2 - 80 \left(\frac{b^*}{b_o^*} \right)^4 + 128 \left(\frac{b^*}{b_o^*} \right)^6 - 64 \left(\frac{b^*}{b_o^*} \right)^8. \quad (15)$$

Using relationship (15) and neglecting small quantities, the integrals (7) can be written

$$\begin{aligned} I_{\chi}^{(1)*}(g^*) &= \int_0^{\infty} [1 - \cos \chi(g^*, b^*)] b^* db^* \\ &\simeq \frac{8}{b_o^{*4}} \int_0^{b_o^*} [b^{*2} - (b_o^{*2}/2)]^2 b^* db^* \\ &\quad + 2 \int_{b_o^*}^{2b_o^*} \exp\{-20[(b^{*2}/b_o^{*2}) - 1]\} b^* db^* \\ &= \frac{23}{60} b_o^{*2}, \end{aligned} \quad (16)$$

and

$$\begin{aligned} I_{\chi}^{(2)*}(g^*) &= \int_0^{\infty} [1 - \cos^2 \chi(g^*, b^*)] b^* db^* \\ &\simeq \left(4 \frac{b^*}{b_o^*} \right)^2 \int_0^{b_o^*} [1 - 5(b^*/b_o^*)^2 + 8(b^*/b_o^*)^4 \\ &\quad - 4(b^*/b_o^*)^6] b^* db^* \\ &\quad + \int_{b_o^*}^{2b_o^*} \exp\{-20[(b^{*2}/b_o^{*2}) - 1]\} b^* db^* \\ &= \frac{7}{24} b_o^{*2}. \end{aligned} \quad (17)$$

We replaced the infinite integration limits in the expressions (16) and (17) by $2b_o^*$ for mathematical convenience. However, the replacement is justified by the fact that the values of the integrands $[1 - \cos \chi(b^*)]$ and $[1 - \cos^2 \chi(b^*)]$ for $b^* > 2b_o^*$ are orders of magnitude smaller than the mean values of the integrands in the interval $0 \leq b^* \leq b_o^*$.

In the case of binary collisions driven by the potential (5) and with g^{*2} less than 0.8, the orbiting impact parameter is given in the limit of small g^* as

$$b_o^{*2} \simeq \frac{13}{4} \frac{1}{g^{*2/3}}. \quad (18)$$

Relationships (11) and (16)–(18) allow one to obtain the integrals $I_g^{(l,s)*}(T_i^*)$ which are of interest in studies of transport coefficients in gases where kT is less than ϵ_i . In particular,

$$I_g^{(1,1)*}(T_i^*) = \frac{5}{4} \Gamma\left(\frac{8}{3}\right) T_i^{*-1/3}, \quad I_g^{(1,2)*}(T_i^*) = \frac{5}{2} \Gamma\left(\frac{11}{3}\right) T_i^{*-1/3}, \quad (19)$$

$$\begin{aligned} I_g^{(1,3)*}(T_i^*) &= \frac{5}{4} \Gamma\left(\frac{14}{3}\right) T_i^{*-1/3}, \\ I_g^{(2,2)*}(T_i^*) &= \frac{15}{16} \Gamma\left(\frac{11}{3}\right) T_i^{*-1/3}, \end{aligned} \quad (20)$$

where $\Gamma(x)$ is the gamma function of argument x ; $\Gamma\left(\frac{8}{3}\right) = 1.505$, $\Gamma\left(\frac{11}{3}\right) = 4.012$, and $\Gamma\left(\frac{14}{3}\right) = 14.711$.

In a gas not far from local thermal equilibrium at temperature T , an overwhelming fraction of binary collisions have impact energies E smaller than $3kT$. In most of the repulsive-attractive collisions discussed here, values of kT are much (or at least significantly) smaller than the collision potential well depths ϵ_i , and consequently, the collision reduced impact energies g^{*2} and the reduced speeds g^* are smaller than one. Thus our assumption that the well depths of the repulsive-attractive potentials are substantially greater than kT requires the upper limit of the integral in the expression (11) be not greater than one. However, taking, as a mathematical convenience, this limit infinite is justified by the fact that the contribution of the integrals from the interval $1 \leq g^* \leq \infty$ is negligible [the values of the integrands in the expression (11) are very small when $g^* > 1$].

The expressions and conclusions derived in this section can also be used for Lennard-Jones interactions where $0.8 \leq g^{*2} \leq 1$. This is because the dependences of the integrands $[1 - \cos \chi]$ and $[1 - \cos^2 \chi]$ on b^* and g^* are similar to the corresponding dependences for collisions with $g^{*2} < 0.8$. The fact that rapid oscillations of the integrands exist when $b^* \approx b_o^*$ and $g^{*2} < 0.8$ but are absent when $g^{*2} > 0.8$ has little impact on the validity of the extension of the approach of this section on the collisions with $g^{*2} > 0.8$. This is because even though the amplitude of the oscillations changes from zero to two (when $l=1$) and from zero to one (when $l=2$), the interval of b^* where it takes place is very narrow—it is much smaller than the value of the orbiting impact parameter b_o^* .

Expressions (10), (19), and (20) lead to the following transport integrals for collisions of particles interacting through the single-force potential (5) with $\epsilon_i > kT$:

$$\Omega_i^{(1,1)}(T_i^*) = \frac{5}{4} \Gamma\left(\frac{8}{3}\right) \left(\frac{\pi kT}{2\mu} \right)^{1/2} \sigma_i^2 \left(\frac{\epsilon_i}{kT} \right)^{1/3}, \quad (21)$$

$$\Omega_i^{(1,2)}(T_i^*) = \frac{5}{2} \Gamma\left(\frac{11}{3}\right) \left(\frac{\pi kT}{2\mu} \right)^{1/2} \sigma_i^2 \left(\frac{\epsilon_i}{kT} \right)^{1/3}, \quad (22)$$

$$\Omega_i^{(1,3)}(T_i^*) = \frac{5}{4} \Gamma\left(\frac{14}{3}\right) \left(\frac{\pi kT}{2\mu} \right)^{1/2} \sigma_i^2 \left(\frac{\epsilon_i}{kT} \right)^{1/3}, \quad (23)$$

and

$$\Omega_i^{(2,2)}(T_i^*) = \frac{15}{16} \Gamma\left(\frac{11}{3}\right) \left(\frac{\pi kT}{2\mu} \right)^{1/2} \sigma_i^2 \left(\frac{\epsilon_i}{kT} \right)^{1/3}. \quad (24)$$

Taking the above into account and using the first term of the relationship (4), the averaged collision integrals $\langle \Omega_i^{(l,s)}(T) \rangle$ can be written as

$$\begin{aligned} \langle \Omega_i^{(l,s)}(T) \rangle &= \left(\sum_{i=1}^{i_m} p_i \right)^{-1} \sum_{i=1}^{i_m} p_i \Omega_i^{(l,s)*}(T_i^*) \\ &= \pi f^{(l,s)} \left(\frac{kT}{2\pi\mu} \right)^{1/2} \left(\sum_{i=1}^{i_m} p_i \right)^{-1} \\ &\quad \times \sum_{i=1}^{i_m} p_i \sigma_i^2 \left(\frac{\epsilon_i}{kT} \right)^{1/3}, \end{aligned} \quad (25)$$

where, as before, the sums are taken over all (i_m) repulsive-attractive potentials possible to occur in the collision, p_i is the electronic degeneracy of the diatomic state representing the collision driven by the i th potential, and

$$f^{(1,1)} = \frac{5}{4} \Gamma\left(\frac{8}{3}\right) = 1.881, \quad f^{(1,2)} = \frac{5}{2} \Gamma\left(\frac{11}{3}\right) = 10.030, \quad (26)$$

$$f^{(1,3)} = \frac{5}{4} \Gamma\left(\frac{14}{3}\right) = 18.389, \quad f^{(2,2)} = \frac{15}{16} \Gamma\left(\frac{11}{3}\right) = 3.761. \quad (27)$$

Expression (25) can now be rewritten as

$$\langle \Omega_i^{(l,s)}(T) \rangle = \pi \sigma_1^2 f^{(l,s)} \left(\frac{kT}{2\pi\mu} \right)^{1/2} \left(\frac{\epsilon_1}{kT} \right)^{1/3} \langle S \rangle, \quad (28)$$

where

$$\langle S \rangle = \left(\sum_{i=1}^{i_m} p_i \right)^{-1} \sum_{i=1}^{i_m} \left\{ p_i \left(\frac{\sigma_i}{\sigma_1} \right)^2 \left(\frac{\epsilon_i}{\epsilon_1} \right)^{1/3} \right\}. \quad (29)$$

The term $p_i / \sum_{i=1}^{i_m} p_i$ in Eq. (29) is the probability that the diatomic state representing the collision is in the i th repulsive-attractive state, that is, the probability that the state interaction potential has the zero potential distance σ_i and well depth ϵ_i . Thus $\langle S \rangle$ is the averaged (over all repulsive-attractive states of the diatom) value of the product $(\sigma_i / \sigma_1)^2 (\epsilon_i / \epsilon_1)^{1/3}$.

The force constant for the i th Lennard-Jones interaction is

$$k_i^{LJ} = \left. \frac{d^2 U_i(r)}{dr^2} \right|_{r=r_{e,i}} = \frac{72\epsilon_i}{r_{e,i}^2}, \quad (30)$$

where $r_{e,i}$ is the distance at the minimum of the potential well depth ϵ_i .

The force constant for motion of the reduced mass μ in the field of a harmonic potential is

$$k_i^H = \frac{4\mu \pi^2 \omega_{e,i}^2}{h^2}, \quad (31)$$

where h is Planck's constant, and $\omega_{e,i}$ is the spectroscopic constant for the harmonic motion.

Since $k_i^{LJ} \approx k_i^H$ when $r \rightarrow r_{e,i}$, the expressions (30) and (31) give

$$\frac{r_{e,i}}{r_{e,1}} \approx \frac{\omega_{e,1}}{\omega_{e,i}} \left(\frac{\epsilon_i}{\epsilon_1} \right)^{1/2}, \quad (32)$$

where the subscript $i=1$ denotes the properties of the lowest repulsive-attractive potential for the collision system.

Allen and Longair have suggested [5] the following approximate rule for the electronic states of most diatomic systems:

$$\omega_{e,i} r_{e,i}^3 n_i^{1/2} \approx \text{const}, \quad (33)$$

where n_i , called ‘‘group number,’’ depends on the periodic group classification of the interacting atoms (the particular group in the periodic system in which the atoms appear) and on the diatom electronic configuration. Using the rule in the relationship (32) one obtains

$$\frac{r_{e,i}}{r_{e,1}} = \frac{\sigma_i}{\sigma_1} = \left(\frac{n_1 \epsilon_1}{n_i \epsilon_i} \right)^{1/4}, \quad (34)$$

where the term $(n_1 \epsilon_1 / n_i \epsilon_i)^{1/4}$ was studied extensively by Allen and Longair [5], Clark and Stoves [6], and Wu and Yang [7]. They found that the values of the term are very close to one in almost all electronic configurations of almost all diatomic molecules. Therefore we assume in what follows that the ratio σ_i / σ_1 is equal to one for all values of i .

The potential well depths ϵ_1 of most of the diatoms are equal to 3–6 eV. The typical value of the energy kT of particles in weakly ionized gases common in applications ranges from about 0.2 to about 1 eV. Therefore, and because of the fact that the statistical weights of the higher repulsive-attractive states of the diatoms representing the collisions under consideration are usually somewhat higher than the statistical weights of the lower repulsive-attractive states of the diatoms, the relationship (29) can be written as

$$\langle S \rangle \approx \frac{1}{2}. \quad (35)$$

Subsequently, the average transport integrals (25) for the repulsive-attractive interactions possible in typical binary collisions are

$$\langle \Omega_i^{(l,s)}(T) \rangle = \pi \sigma_1^2 \frac{f^{(l,s)}}{2} \left(\frac{kT}{2\pi\mu} \right)^{1/2} \left(\frac{\epsilon_1}{kT} \right)^{1/3}. \quad (36)$$

III. THE TRANSPORT INTEGRALS FOR REPULSIVE INTERACTIONS

Most of the repulsive potentials occurring in multiforce collisions cannot be accurately approximated in the entire range of the interaction distance by a simple function. In addition, some (small) fraction of the potentials can be non-monotonic with respect to r . We ignore the nonmonotonic potentials, and approximate the monotonic ones by some convenient functions which reliably reproduce the potentials in the vicinity of $r \approx r_{o,j}$ where $U_j(r_{o,j}) \approx kT$ [it was shown [2] that the most important region of the repulsive interaction is where $U_j(r \approx r_{o,j}) \approx kT$]. These functions are

$$U_j(r \approx r_{o,j}) = \frac{c_j}{r^{t_j}}, \quad (37)$$

where c_j and t_j are the parameters of the j th repulsive potential.

The transport integrals (3) for binary collisions driven by a single (j th) repulsive potential (37) can be given as [8]

TABLE I. The values of the integrals $A_j^{(l)}$ given in Eq. (39).

t_j	$A_j^{(1)}$	$A_j^{(2)}$
2	0.398	0.528
3	0.311	0.353
4	0.298	0.308
6	0.306	0.283
8	0.321	0.279
10	0.333	0.278
12	0.346	0.279
14	0.356	0.280
∞	0.500	0.333

$$\Omega_j^{(l,s)}(T) = \left(\frac{\pi kT}{2\mu} \right)^{1/2} \left(\frac{t_j c_j}{kT} \right)^{2/t_j} A_j^{(l)} \Gamma[s+2-(2/t_j)], \quad (38)$$

where

$$A_j^{(l)} = \int_0^\infty [1 - \cos^l \chi(\beta_j)] \beta_j d\beta_j, \quad (39)$$

and

$$\beta_j = \left(\frac{\mu g^2}{2t_j c_j} \right)^{1/t_j}. \quad (40)$$

The values of the integrals $A_j^{(l)}$ are finite for all values of t_j greater than one (see Table I).

The potential parameters c_j can be obtained from the values of the potentials $U_j(r)$ at one particular interaction distance, say, $r = r_{o,j}$. Then, the constant c_j in the function (37) reproducing the j th repulsive potential is

$$c_j = kT r_{o,j}^{t_j}, \quad (41)$$

and the transport integral (38) can be written as

$$\Omega_j^{(l,s)} = \pi r_{o,j}^2 \left(\frac{kT}{2\pi\mu} \right)^{1/2} t_j^{2/t_j} A_j^{(l)} \Gamma(s+2-2/t_j). \quad (42)$$

Typically, the exponents t_j of the potentials (37) approximating the repulsive potentials of binary collisions at $r \sim r_{o,j}$ have relatively low (but rarely smaller than two) values. When t_j is not large, the product $(r_{o,j}/\sigma_1)^2 t_j^{2/t_j} A_j^{(l)} \Gamma(s+2-2/t_j)$ for different values of j does not differ significantly from the value of the product for $t_j=3$. Assuming this value for t_j , one obtains for the average value of the product in the vicinity of $r_{o,j}$

$$\left\langle \frac{r_{o,j}}{\sigma_1^2} t_j^{2/t_j} A_j^{(l)} \Gamma(s+2-2/t_j) \right\rangle \approx 4A_3^{(l)} \Gamma(s+\frac{4}{3}), \quad (43)$$

where $A_3^{(l)}$ are given in Table I. Subsequently, the average transport integral (42) can be written as

$$\langle \Omega_j^{(l,s)}(T) \rangle = \pi \sigma_1^2 \left(\frac{kT}{2\pi\mu} \right)^{1/2} 4A_3^{(l)} \Gamma(s+\frac{4}{3}). \quad (44)$$

IV. THE TRANSPORT INTEGRALS AVERAGED OVER ALL INTERACTIONS

The average transport integral for atom-atom collisions where many repulsive as well as repulsive-attractive interaction potentials are possible can be written as

$$\langle \Omega^{(l,s)}(T) \rangle = \langle \Omega_i^{(l,s)}(T) \rangle + \langle \Omega_j^{(l,s)}(T) \rangle, \quad (45)$$

or, according to relationships (36) and (44), as

$$\langle \Omega^{(l,s)}(T) \rangle = \pi \sigma^2 \left(\frac{kT}{2\pi\mu} \right)^{1/2} \left[\frac{f^{(l,s)}}{2} \left(\frac{\epsilon}{kT} \right)^{1/3} + 4A_3^{(l)} \Gamma(s+\frac{4}{3}) \right], \quad (46)$$

where $A_3^{(1)}=0.311$ and $A_3^{(2)}=0.353$, $f^{(l,s)}$ are given in expressions (26) and (27), and where we denoted $\epsilon \equiv \epsilon_1$ and $\sigma \equiv \sigma_1$ as the parameters of the lowest repulsive-attractive potential possible in the collision system.

V. THE TRANSPORT INTEGRALS FOR RIGID-SPHERE INTERACTIONS

Transport cross sections for collision of two rigid spheres of radii R_1 and R_2 ($\sigma = R_1 + R_2$) are

$$Q^{(1)} = \pi(R_1 + R_2)^2, \quad (47)$$

and

$$Q^{(2)} = \frac{2\pi}{3} (R_1 + R_2)^2, \quad (48)$$

and the corresponding transport integrals are

$$\Omega^{(1,1)}(T) = \left(\frac{\pi kT}{2\mu} \right)^{1/2} (R_1 + R_2)^2, \quad (49)$$

$$\Omega^{(1,2)}(T) = 3 \left(\frac{\pi kT}{2\mu} \right)^{1/2} (R_1 + R_2)^2, \quad (50)$$

$$\Omega^{(1,3)}(T) = 12 \left(\frac{\pi kT}{2\mu} \right)^{1/2} (R_1 + R_2)^2, \quad (51)$$

and

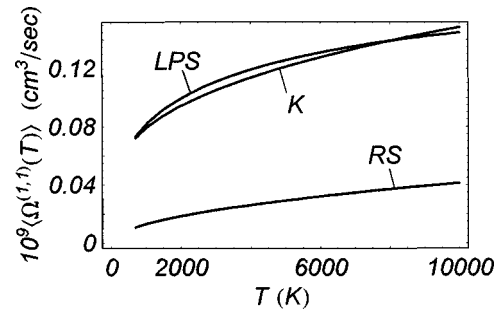


FIG. 2. The potential-averaged transport integrals $\langle \Omega^{(1,1)}(T) \rangle$ for collision of two ground-state nitrogen atoms $N(^4S_{3/2})$. Curve LPS gives the results of the detailed *ab initio* calculations of Levin, Partridge, and Stallcop (Ref. [10]), curve K gives the results of the present work [Eq. (46)], and curve RS gives the results obtained from the rigid-sphere model of the collision.

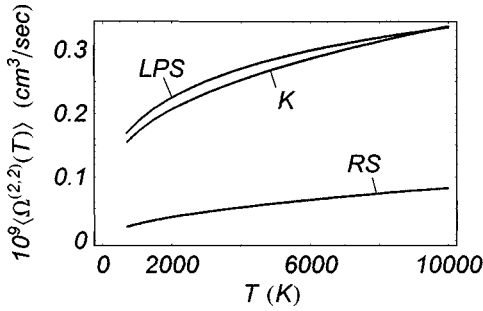


FIG. 3. The potential-averaged transport integrals $\langle \Omega^{(2,2)}(T) \rangle$ for collision of two ground-state nitrogen atoms $N(4S_{3/2}^o)$. The meaning of the symbols is the same as in Fig. 2.

$$\Omega^{(2,2)}(T) = 2 \left(\frac{\pi kT}{2\mu} \right)^{1/2} (R_1 + R_2)^2, \quad (52)$$

where, as before, μ is the reduced mass of the colliding spheres.

VI. RESULTS AND DISCUSSION

The multiple-force transport integrals have been studied for a long time (see Refs. [2,9,10], and references therein) but only recently have detailed *ab initio* calculations and experimental data made it possible to assemble quite complete and accurate sets of the potentials for multiple-force collision systems containing ground-state nitrogen and oxygen atoms and ions. Using the potentials, Levin, Partridge, and Stallcop made detailed semiclassical calculations of the average transport integrals for the systems. We compare in Figs. 2–7 the transport integrals (46) [when $(l,s) \equiv (1,1)$ and $(2,2)$] for $N(4S_{3/2}^o)$ - $N(4S_{3/2}^o)$, $O(3P_2)$ - $O(3P_2)$, and $N(4S_{3/2}^o)$ - $O(3P_2)$ binary collisions with the corresponding results of Levin *et al.* and, in the case of the $O(3P_2)$ - $O(3P_2)$ collisions, with the results of Dalgarno and Smith [11]. We also include in the figures the transport integrals obtained assuming that the colliding atoms are rigid spheres with the collision diameter equal to the zero-potential distance σ of the lowest repulsive-attractive potential. The average transport integrals $\langle \Omega^{(l,s)}(T) \rangle$ of the present work and the average transport integrals $\sigma^2 \bar{\Omega}_{n,s}(T)$ given in the tables in Ref. [10] are related as follows:

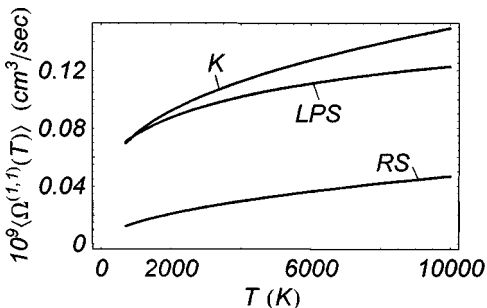


FIG. 4. The potential-averaged transport integrals $\langle \Omega^{(1,1)}(T) \rangle$ for collision of two ground-state oxygen atoms $O(3P_2)$. The meaning of the symbols is the same as in Fig. 2.

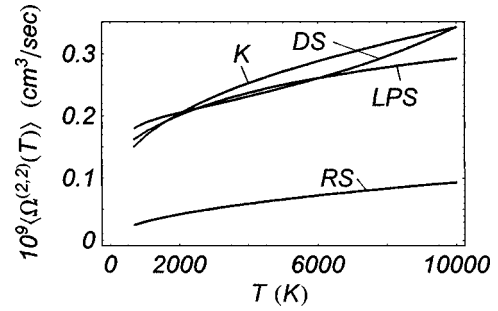


FIG. 5. The potential-averaged transport integrals $\langle \Omega^{(2,2)}(T) \rangle$ for collision of two ground-state oxygen atoms $O(3P_2)$. Curve DS gives the results of Dalgarno and Smith (Ref. [11]). The meaning of the other symbols is the same as in Fig. 4.

$$\Omega^{(2,2)}(T) = \left(\frac{kT}{2\pi\mu} \right)^{1/2} \frac{\sigma^2 \bar{\Omega}_{n,s}(T)}{F(n,s)}, \quad (53)$$

where

$$F(n,s) = \frac{4(l+1)}{\pi(s+1)! [2l+1 - (-1)^l]}. \quad (54)$$

As can be seen in Figs. 2–7, the expression (46) gives a reasonable first-order approximation to the average transport integrals $\langle \Omega^{(l,s)}(T) \rangle$ for the three collision systems. [The agreement of the integrals (46) for (l,s) other than $(1,1)$ and $(2,2)$ with the corresponding *ab initio* results for these systems is similar to that seen in Figs. 2–7.] The accuracy of the approximation in the temperature range from 300 to 10 000 K is not worse than about 15% for all the collisions. Such accuracy is acceptable in studies of transport coefficients of many gases which are common in modern applications but where interaction potentials of some (or all) multiple-force collisions are uncertain. One should notice that the rigid-sphere model is an inappropriate representation of the dynamics of multiple-force binary collisions.

It is difficult to say what the accuracy of the expression (46) is for collisions of atoms other than the nitrogen and oxygen atoms because no complete and reliable sets of the potentials are available for interactions of the atoms. [Accurate potentials for collision of two ground-state hydrogen atoms are well known, but the number of possible potentials is too small (only one repulsive-attractive and one repulsive potential) to consider the H-H system for testing the

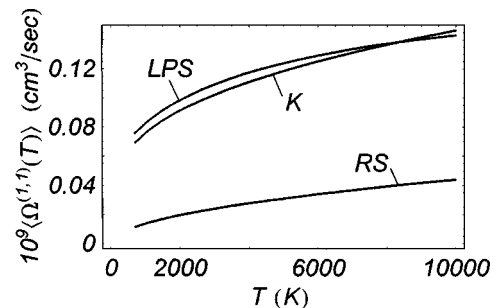


FIG. 6. The potential-averaged transport integrals $\langle \Omega^{(1,1)}(T) \rangle$ for collision of a ground-state nitrogen atom $N(4S_{3/2}^o)$ with a ground-state oxygen atom $O(3P_2)$. The meaning of the symbols is the same as in Fig. 2.

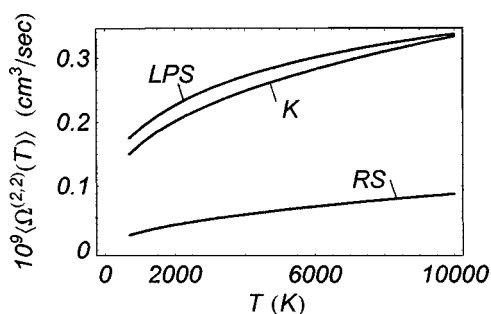


FIG. 7. The potential-averaged transport integrals $\langle \Omega^{(2,2)}(T) \rangle$ for collision of a ground-state nitrogen atom $N(^4S_{3/2})$ with a ground-state oxygen atom $O(^3P_2)$. The meaning of the symbols is the same as in Fig. 2.

accuracy of the relationship (46).] However, judging on the basis of the comparison shown in Figs. 2–7 and on the fact that the relationship (46) was derived from *first principles*, the accuracy of the relationship (46) should not be worse than 20% for most multiple-force collisions of neutrals in gases at temperatures below 10 000 K. The ratio of the accuracy of the expression (36) [an estimate of the contribution of the repulsive-attractive potentials to the transport integrals $\langle \Omega^{(l,s)}(T) \rangle$] to the accuracy of the expression (44) (an estimate of the contribution of the repulsive potentials to the integrals) may differ from one collision system to another because the expressions were derived using different averaging procedures. It seems, however, that the temperature dependence of the ratio is such that at temperatures below 10 000 K the overall accuracy of the integrals (46) is always within the margin (less than about 15%) which is acceptable in studies of collisions driven by poorly understood multiple-force potentials.

We assumed in the present work the Lennard-Jones potentials (5) for the repulsive-attractive atom-atom interactions, with the potential parameters ϵ_i and σ_i taken from the Wigner-Witmer curves for the diatoms representing the collisions. Use of realistic model potentials other than the potential (5) would not lead to such a simple analytical expression as the transport integral (46). In addition, the large volume of work [1] on gas transport coefficients in a broad range of single-force interaction potentials (Lennard-Jones, Sutherland, Krieger, etc.) at temperatures below 2000 K shows that all these potentials produce only small differences in the transport coefficients as long as the potential param-

eters ϵ and σ have the same values. Therefore, expression (46) should give realistic estimates of the average transport integrals for gases dominated by atom-atom collisions at temperatures below 2000 K as well as at substantially higher temperatures (up to 10 000 K), although it may be somewhat less accurate in the latter case. The accuracy of the expression at these high temperatures cannot be verified beyond the comparisons of the formula with the *ab initio* calculations shown in Figs. 2–7 since no measurements of the transport coefficients in gases at high temperatures are available. However, one should keep in mind that at temperatures close to 10 000 K, the contribution of collisions involving charged particles (a product of the gas ionization) will be at least as important for accurate interpretation of the measurements as the contribution of the atom-atom collisions. Analysis of the impact of the charged particles on transport properties of high-temperature gases is beyond the scope of this work, but it would be difficult to make because a general and accurate description of low-energy interactions of electrons and ions with atoms is not available. Also, the approach of the present work, based on superposition of the effects of *binary* collisions, is not suitable for derivation of the transport integrals for long-range (*many-body*) interactions such as the *e-e* collisions.

The transport integral (46) was derived from classical formalism of collisional dynamics and the other transport integrals shown in Figs. 2–7 were obtained from semiclassical formalism. These formalisms are expected to be quite accurate also at temperatures much lower than room temperature. However, at temperatures well below 50 K quantum-mechanical corrections to the integrals may be necessary [12].

Finally, one should add that the approach of this work can also be applied to multiple-force binary collisions of particles other than atoms (for example, a collision of an atom with a molecule) if the needed interaction potentials for the collisions are available.

ACKNOWLEDGMENTS

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