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Transport Properties of Ground State Nitrogen Atoms

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Transport properties of dilute monatomic gases depend on the two body atom–atom interaction potential. When two ground state (^4S) nitrogen atoms interact, they can follow any of four potential energy curves corresponding to the N_2 molecule; the X $^1\Sigma_g^+$, A $^3\Sigma_u^+$, $^5\Sigma_g^+$, and $^7\Sigma_u^+$ curves. Transport collision integrals for the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states have been calculated by representing the potentials for these states with the Hulburt–Hirschfelder potential. The $^5\Sigma_g^+$ state has a large local maximum which requires changes in the computational procedure used previously; a modified Hulburt–Hirschfelder potential has been used to represent the potential for this state. Collision integrals for the $^7\Sigma_u^+$ state have been obtained by direct use of a recent theoretical potential for this state. The collision integrals are compared with results obtained in previous studies.

INTRODUCTION

Knowledge of the thermophysical properties of nitrogen (and air) at high temperatures is important in the chemistry and physics of the upper atmosphere[1] and in applications including high temperature coal gasification,[2] plasmas,[3] and atmospheric reentry by spacecraft.[4] Since the thermophysical properties of a mixture of gases depend on the thermophysical properties of the individual components,[5] it is important to have accurate results for the nitrogen atoms. Experimental thermophysical property data is sparse[6-10] for atomic nitrogen because of the high temperatures required.

As a result, it is necessary to rely on theory to obtain the transport properties of nitrogen atoms. The theory used is the kinetic theory of gases. According to this approach, the transport properties depend on the two-body interactions between chemical species. When two ground state (^4S) nitrogen atoms interact, they can follow[11] any of four potential energy curves (states) corresponding to the N_2 molecule; the ground $X\,^1\Sigma_g^+$ state and the $A\,^3\Sigma_u^+$, $^5\Sigma_g^+$, and $^7\Sigma_u^+$ states. The interatomic potentials for these states all possess attractive minima although the potential minima for the $^5\Sigma_g^+$ and $^7\Sigma_u^+$ states are very shallow.

THE N-N INTERACTION POTENTIALS

Each of these four states of nitrogen must be considered in determining the ground state transport properties, using the best available interaction potential for each state. Currently the best available potential energy curves for the $X\,^1\Sigma_g^+$ and $A\,^3\Sigma_u^+$ states of N_2 are the "experimental" Rydberg–Klein–Rees (RKR) results of Vanderslice *et al.*,[11,12] Steele *et al.*,[13] and Gilmore.[14] Theoretical calculations for the ground state are also available.[15-17] Potential energy curves for the $^5\Sigma_g^+$ state have been estimated from spectroscopic data[11,18] and

theoretical calculations are also available.[19,20] Here, the multiconfiguration, self-consistent field (SCF) results of Krauss and Neumann[20] are probably most accurate. Spectroscopic information is not available about the $^7\Sigma_u^+$ state, but valence bond calculations are available[11,21] and there is a recent[22] SCF calculation of the potential energy curve for this state.

The two previous detailed calculations of the transport properties of nitrogen atoms[23,24] have involved the modeling of some of the potentials mentioned above by fitting these potentials with empirical potentials for which transport collision integrals have been calculated.[25-28] The empirical potentials used in these calculations[23,24] are the attractive inverse power (AIP) potential, the exponential-six (ES) potential, the Morse potential (MP), and the exponential repulsive (ER) potential. The potentials used are shown in Table I. The results of Capitelli and Devoto[24] should be more accurate for two reasons. First, they fit the RKR results for the

TABLE I. Empirical fitting of the N–N interatomic potentials for transport property calculations.

| State | Yun and Mason[a] | | Capitelli and Devoto[b] | |
	Potential fitted	Empirical potential[a]	Potential fitted	Empirical potential[b]
$^1\Sigma_g^+$	RKR[c]	AIP	RKR[c]	MP[f]
$^3\Sigma_u^+$	RKR[c]	AIP	RKR[c]	MP[f]
$^5\Sigma_g^+$	Vanderslice *et al.*[c]	ES	Carroll[d]	MP
$^7\Sigma_u^+$	Vanderslice *et al.*[c]	ER	Meador[e]	ER

[a]Reference 23.   [d]Reference 18.
[b]Reference 24.   [e]Reference 21.
[c]Reference 11.   [f]Reference 46.

$^1\Sigma_g^+$ and $^3\Sigma_u^+$ states over the entire range of interatomic separations, including the repulsive "wall" as well as the attractive long-range part of the potential fit by Yun and Mason.[23] At the high temperatures where atomic nitrogen exists, the repulsive wall makes an important contribution to the transport properties.[29] In addition, Capitelli and Devoto[24] used the results of Carroll[18] and of Meador[21] for the $^5\Sigma_g^+$ and $^7\Sigma_u^+$ states, respectively. These results are probably more accurate than the results of Vanderslice et al.[11] which were used in the calculations of Yun and Mason.[23]

A computer code has recently been developed[30,31] which calculates the transport collision integrals for the Hulburt—Hirschfelder (HH) potential. The HH potential is probably the best general purpose empirical potential for fitting atom—atom interactions with an attractive minimum in the potential.[13,32-35] The computed results give good agreement with experimental transport properties for argon[36] and for the alkali metal vapors.[37,38] In addition, the HH potential can reproduce the local maxima often found at "large" internuclear separations for atom—atom interactions.[39-43]

In reduced form, the HH potential is given by[39,44,45]

$$V_{HH}^*(r^*) = \exp[-2a(r^*/d - 1)] - 2\exp[-a(r^*/d - 1)]$$

$$+ \beta\left(\frac{r^*}{d} - 1\right)^3\left[1 + \gamma\left(\frac{r^*}{d} - 1\right)\right]\exp[-2a(r^*/d - 1)],$$

(1)

where

$$V^* = \frac{V}{\epsilon}, \quad r^* = \frac{r}{\sigma}, \quad d = \frac{r_e}{\sigma}, \quad a = \frac{\omega_e}{2\sqrt{B_e\,\epsilon'}}, \quad \beta = ca^3,$$

$$\gamma = ba, \quad c = 1 + a_1\sqrt{\frac{\epsilon'}{a_0}}, \quad b = 2 - \frac{\frac{7}{12} - \epsilon'\frac{a_2}{a_0}}{c}, \quad a_0 = \frac{\omega_e^2}{4B_e},$$

$$a_1 = -1 - \frac{\alpha_e\omega_e}{6B_e^2}, \quad a_2 = \frac{5}{4}a_1^2 - \frac{2\omega_e\chi_e}{3B_e}.$$

Also, r is the interatomic separation, ϵ is the depth of the potential well, r_e is the interatomic separation corresponding to ϵ, ϵ' is well depth in wave numbers, ω_e is the fundamental vibrational frequency, $\omega_e\chi_e$ is the anharmonicity constant, B_e is the rotational constant, α_e is the rotation-vibration coupling constant, and σ is the smallest interatomic separation at which the potential is zero (the "effective" hard sphere diameter). The empirical HH potential has six parameters, all of them determined from spectroscopic data. The HH potential reduces to the Morse potential if $c = 0$.

Comparisons of the empirical potentials used in previous calculations[23,24] of the transport properties and of the HH potential with the RKR results[11] are shown in Tables II and III for the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states of N_2, respectively. The spectroscopic constants used in the HH potential are from Huber and Herzberg.[47] Agreement between the HH and RKR results is excellent for the $^1\Sigma_g^+$ state. Agreement between these results is good for the $^3\Sigma_u^+$ state except at small values of r. This is somewhat surprising since, in general, HH and RKR results are in good agreement[13,36-39] at small values of r. For both states, the HH potential gives better agreement with the RKR results than do the results ob-

TABLE III. Comparison of the HH, Morse[a,b] and AIP[c] potentials with the RKR[d] potential for the $^3\Sigma_u^+$ state of N_2.

$r(10^{-10}$ m)	V(HH)/V(RKR)	V(MP)/V(RKR)	V(AIP)/V(RKR)
1.046	0.455	0.214	41.149
1.054	0.582	0.386	35.777
1.062	0.679	0.519	31.265
1.070	0.751	0.621	27.461
1.080	0.828	0.727	23.898
1.089	0.872	0.793	21.022
1.099	0.911	0.851	18.447
1.108	0.927	0.882	16.335
1.120	0.954	0.924	14.247
1.131	0.963	0.943	12.545
1.145	0.977	0.967	10.877
1.160	0.983	0.981	9.406
1.180	0.991	0.997	7.922
1.203	0.991	1.001	6.584
1.240	0.989	1.002	5.081
1.356	0.976	0.990	2.746
1.405	0.974	0.990	2.263
1.442	0.974	0.992	1.994
1.474	0.976	0.997	1.810
1.503	0.979	1.004	1.674
1.532	0.980	1.010	1.555
1.558	0.985	1.021	1.471
1.584	0.990	1.033	1.397
1.609	0.998	1.047	1.339
1.633	1.008	1.066	1.294
1.657	1.020	1.086	1.257
1.682	1.031	1.108	1.222
1.706	1.046	1.135	1.199
1.732	1.060	1.161	1.174
1.756	1.083	1.198	1.165

[a]Reference 24.   [c]Reference 23.
[b]Reference 46.   [d]Reference 11.

TABLE II. Comparison of the HH, Morse[a,b] and AIP[c] potentials with the RKR[d] potential for the $^1\Sigma_g^+$ state of N_2.

$r(10^{-10}$ m)	V(HH)/V(RKR)	V(MP)/V(RKR)	V(AIP)/V(RKR)
0.896	1.013	0.878	40.494
0.904	1.020	0.909	35.032
0.912	1.016	0.926	30.449
0.921	1.013	0.941	26.409
0.931	1.009	0.952	22.850
0.942	1.003	0.960	19.716
0.956	1.003	0.972	16.738
0.973	1.003	0.982	13.994
0.994	1.000	0.988	11.453
1.027	1.001	0.997	8.742
1.146	1.000	0.999	4.215
1.213	1.000	0.997	3.116
1.261	0.999	0.995	2.591
1.302	0.999	0.996	2.255
1.339	1.000	0.999	2.019
1.375	1.001	1.001	1.830
1.410	1.002	1.006	1.679
1.447	0.998	1.006	1.538
1.477	0.998	1.023	1.464
1.512	1.013	1.031	1.374

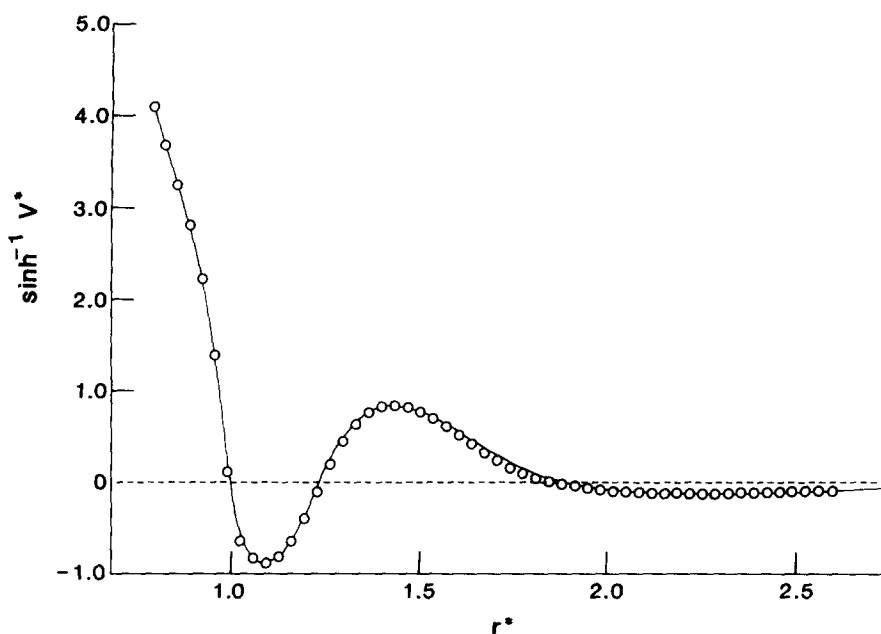[a]Reference 24.   [c]Reference 23.
[b]Reference 46.   [d]Reference 11.

FIG. 1. Plot of $\sinh^{-1}(V^*)$ as a function of r^* for the $^5\Sigma_g^+$ state of N_2. The circles are the results of Krauss and Neumann (Refs. 20 and 48); the line is the fit to the modified HH potential. This "pseudo-logarithmic" scale is approximately semilogarithmic for large V^* and approximately linear for small V^*, and can accommodate the large variations in magnitude and changes of sign in V^* with a single graph.

tained using the Morse potential. The AIP potential gives poor agreement with the RKR results.

The SCF calculations[20] for the $^5\Sigma_g^+$ state of N_2 indicate that this state has a local maximum at 2.21×10^{-10} m. Indeed, the barrier height is essentially the same as the potential minimum $(1.6 \times 10^{-20}$ J) at 1.69×10^{-10} m. This is shown in Fig. 1. Mullikan's calculations[19] also indicate the presence of a local maximum. A comparison of the results of Krauss and Neumann,[20] Carroll,[18] and Vanderslice et al.[11] is shown in Table IV. Clearly, the earlier results[11,18] do not agree very well with the results of Krauss and Neumann.[20] The earlier results have a potential wall that appears to be more steep and the long-range part of the potential energy curve is nearly flat, with no local maximum.

The results of delta-function model calculations by Meador[21] and by Vanderslice et al.[11] for the $^7\Sigma_u^+$ state are compared in Table V. The results differ by about

20%. The SCF calculations of Ferrante and Stwalley[22] which, like the earlier results, can be reasonably well represented by an ER potential, at least at high temperatures, are also shown in Table V. The earlier results[11,21] do not agree very well with the results of Ferrante and Stwalley[22] at small r but agreement is better at larger r. It is somewhat surprising that the results of Vanderslice et al.[11] give the better overall agreement. The potential of Ferrante and Stwalley[22] does have an attractive minimum $(0.083 \times 10^{-20}$ J at 3.71 $\times 10^{-10}$ m) since they include the effects of the multipole expansion coefficients C_6, C_8, and C_{10} in their calculation.

ATOMIC NITROGEN TRANSPORT PROPERTIES

The viscosity η of a pure dilute gas is given by[5]

$$\eta = 2.669 \times 10^{-6} \ \frac{\sqrt{MT}}{\sigma^2 \Omega^{(2,2)*}} \ \left(\frac{kg}{m \cdot s} \right) \ , \tag{2}$$

TABLE IV. Comparison of proposed interaction potentials V for the $^5\Sigma_g^+$ state of N_2: V in 10^{-19} J.

$r(10^{-10}$ m)	V(Krauss and Neumann[a])	V(Carroll[b])	V(Vanderslice et al.[c])
1.217	4.933	11.10	427.3
1.323	2.115	2.012	2.249
1.429	0.750	0.069	0.612
1.535	0.019	−0.216	−0.141
1.693	−0.163	−0.141	−0.027
1.852	−0.064	−0.059	−0.003
2.011	0.079	−0.022	0.0
2.223	0.157	−0.006	
2.434	0.111	−0.002	
2.805	0.011	0.0	
3.069	−0.010		
3.281	−0.016		
3.916	−0.014		
4.022	−0.014		

[a]Reference 20.   [b]Reference 18.   [c]Reference 11.

TABLE V.   Comparison of proposed interaction potentials V for the $^7\Sigma_u^+$ state of N_2; V in 10^{-19} J.

$r(10^{-10}$ m)	V(Ferrante and Stwalley[a])	V(Meador[b])	V(Vanderslice *et al.*[c])
1.30	26.17	11.90	14.21
1.50	13.52	6.92	8.19
1.75	5.93	3.51	4.12
2.00	2.60	1.78	2.07
2.25	1.14	0.90	1.04
2.50	0.50	0.46	0.53
2.75	0.22	0.22	0.26
3.00	0.10	0.11	0.13
3.20	0.05	0.06	0.08

[a]Reference 22.   [b]Reference 21.   [c]Reference 11.

where M is the molecular weight in g/mol, T is the temperature in K, and $\sigma^2\Omega^{(2,2)*}$ is the viscosity collision integral in units of 10^{-20} m^2 (Å^2). The self-diffusion coefficient D is given by

$$D = 2.694\times10^{-7}\ \frac{\sqrt{T^3/M}}{p\sigma^2\Omega^{(1,1)*}}\ \left(\frac{m^2}{s}\right),\tag{3}$$

where p is the pressure in units of 0.1 MPa (1 bar) and $\sigma^2\Omega^{(1,1)*}$ is the diffusion collision integral in units of 10^{-20} m^2(Å^2). The translational contribution to the thermal conductivity λ_{tr} is given by

$$\lambda_{tr} = 8.322\times10^{-2}\ \frac{\sqrt{T/M}}{\sigma^2\Omega^{(2,2)*}}\ \left(\frac{W}{m\cdot K}\right).\tag{4}$$

Since the effect of excited electronic states is not being considered, the internal contribution to the thermal conductivity λ_{int} is zero.

Thus, the only information required to calculate the transport properties are the values of the collision integrals, obtained by integrating over all possible impact parameters and energies of binary collisions. In this work, the collision integrals have been calculated for the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states by using the computer code for the HH potential[30,31] and the spectroscopic constants given in Huber and Herzberg.[47] The HH parameters for the $^1\Sigma_g^+$ state are

$$a = 2.9514,\qquad \beta = 2.1475,$$

$$\gamma = 3.0039,\qquad d = 1.3118,$$

$$\epsilon = 1.5870\times10^{-18}\ \text{J},\quad \sigma = 8.3678\times10^{-11}\ \text{m},$$

and those for the $^3\Sigma_u^+$ state are

$$a = 3.5410,\qquad \beta = 5.8936,$$

$$\gamma = 3.0751,\qquad d = 1.2515,$$

$$\epsilon = 5.6636\times10^{-19}\ \text{J},\quad \sigma = 1.0280\times10^{-10}\ \text{m}.$$

Spectroscopic constants are not available for the $^5\Sigma_g^+$ state, so the HH potential cannot be obtained in the usual manner. The solution of Krauss and Neumann[20] for the $^5\Sigma_g^+$ potential is presented in the form[48] of a discrete set of potential values for evenly spaced values of r, as shown by the circles of Fig. 1. One possible procedure

to obtain the $^5\Sigma_g^+$ collision integrals would be to fit the potential of Krauss and Neumann[20] to the HH function and then to use the computer code of Ref. 30. Unfortunately, it is not possible to obtain an adequate fit with a single set of HH parameters.

However, a good fit can be obtained with two minor modifications of the HH potential. First, different sets of parameters are used for $r^* < r_e$ and $r^* > r_e$. Second, for $r^* > r_e$ the potential is changed to

$$V^*(r^*) = \epsilon^*\left\{\exp[-2a(r^*/d - 1)] - 2\exp[-a'(r^*/d - 1)]\right.$$
$$\left. + \beta\left(\frac{r^*}{d} - 1\right)^3\left[1 + \gamma\left(\frac{r^*}{d} - 1\right)\right]\exp[-2a(r^*/d - 1)]\right\},$$
$$\tag{5}$$

which differs from the usual HH potential by an overall constant factor ϵ^* and the replacement of the parameter a by the new parameter a' in the second term of Eq. (5). This replacement is necessary for the $^5\Sigma_g^+$ potential because a is normally fixed by the second derivative at the minimum, which in the present case is very large. For large r^*, the HH potential is dominated by its second term, but because of the very large value required for a, the second term is negligible at the distance of the secondary minimum. This dilemma can be avoided if d' is chosen to be substantially smaller than a. Because of these modifications, the minimum in the potential functions is no longer located at d nor is its value equal to -1 at d unless the constant ϵ^* is appropriately chosen.

With positive values of V^* at small r^* omitted, the potential of Krauss and Neumann[20,48] was fit to the form given in Eq. (5). A nonlinear least squares fitting algorithm was used with weight factors included to ensure an accurate fit at the maximum and the second minimum. The location and value of the primary minimum of the resulting potential were determined numerically. Then the potential values for r^* less than the location of the primary minimum were similarly fitted to an ordinary HH function, subject to the constraint that the potential and its first derivative be continuous at the minimum where it is joined to Eq. (5).

The potential parameters determined in this way are, for $r^* < 1.0909$,

$a = 8.8086$, $\beta = 86.9094$, $\gamma = 2.4211$, $d = 1.0909$,

and, for $r^* > 1.0909$,

$\epsilon^* = 0.91136$, $a = 4.7482$, $d' = 2.2106$,

$\beta = 1184.354$, $\gamma = 0.1624$, $d = 1.0545$.

Also, the well depth and the effective hard sphere diameter are

$$\epsilon = 1.4900 \times 10^{-20} \text{ J} , \quad \sigma = 1.5507 \times 10^{-10} \text{ m} .$$

The above potential is plotted as the solid line in Fig. 1. The fit to the potential of Krauss and Neumann[20,48] is excellent except for some small and insignificant discrepancies just beyond the maximum. Errors in the collision integrals due to fitting are expected to be negligible.

The only required alteration in the computer code of Ref. 30 is in the subroutine to calculate the potential and its first two derivatives. Collision integrals for potentials with long-range maxima and second minima have been calculated previously,[39] in particular for the $^5\Sigma_g^+$, $^1\Pi_g$, $^3\Delta_u$, and $^1\Sigma_u^-$ states of C_2. However, in those cases, the height of the maximum was at least an order of magnitude less than the depth of the primary minimum, whereas in this case the maximum and minimum are nearly equal in magnitude. The $^5\Sigma_g^+$ state of nitrogen thus provides an exacting test of the numerical methods of Ref. 30. Nevertheless, the computer program succeeded in calculating the collision integrals without difficulty.

The potential function of Ferrante and Stwalley[22] for the $^7\Sigma_u^+$ state of nitrogen can also be fit to an HH potential, but it is more convenient to use their potential directly. In reduced units such that $V^*(1) = 0$ and $V^*_{min} = -1$, their potential function is

$$V^*(r^*) = Ae^{-Br^*} - [C_6 r^{*-6} + C_8 r^{*-8} + C_{10} r^{*-10}]F(r^*) , \tag{6}$$

where

$$F(r^*) \begin{cases} = \exp[-(r_s/r^* - 1)^{1.9}] , & r^* \le r_s , \\ = 1 , & r^* > r_s . \end{cases} \tag{7}$$

The parameters are

$A = 2.2666 \times 10^5$, $B = 10.833$, $C_6 = 2.9089$,

$C_8 = 1.4917$, $C_{10} = 0.9993$, $r_s = 1.4151$,

and the well depth and the effective hard sphere diameter are

$$\epsilon = 8.436 \times 10^{-22} \text{ J} , \quad \sigma = 3.2814 \times 10^{-10} \text{ m} .$$

The potential and its first derivative are continuous, but its second derivative has an infinite discontinuity at $r^* = r_s$. The divergence is quite weak since the second derivative goes as $(r^* - r_s)^{-0.1}$ as $r^* \to r_s$ from below. For the calculation of collision integrals, the normal requirement[30] is that

$$z(r) \equiv V(r) + \tfrac{1}{2} r \frac{dV}{dr}$$

be continuous. The only conceivable computational problem would occur if r_s were close to the "critical

TABLE VI. The diffusion collision integral $\sigma^2\Omega^{(1,1)*}$ and viscosity collision integral $\sigma^2\Omega^{(2,2)*}$ for nitrogen atoms in the ground (^4S) state.

T (K)	$\sigma^2\Omega^{(1,1)*}$ (10^{-20} m^2)	$\sigma^2\Omega^{(2,2)*}$ (10^{-20} m^2)
1 000	6.4576	7.2410
2 000	5.3645	5.9686
3 000	4.8256	5.3556
4 000	4.4763	4.9581
5 000	4.2093	4.7010
6 000	3.9974	4.4604
7 000	3.8249	4.2838
8 000	3.6824	4.1384
9 000	3.5232	4.0104
10 000	3.4348	3.8943
11 000	3.3313	3.7921
12 000	3.2383	3.7017
13 000	3.1490	3.6146
14 000	3.0642	3.5304
15 000	2.9878	3.4539
16 000	2.9184	3.3842
17 000	2.8545	3.3194
18 000	2.7948	3.2561
19 000	2.7376	3.1971
20 000	2.6860	3.1428

distance"[30] r_c, the location of the maximum of $z(r)$. Here, $r_c = 1.3256$ and is sufficiently removed from r_s.

Once again, the only required changes in the computer code of Ref. 30 are in the subroutine to calculate the potential and its derivatives, and the program computed the collision integrals without difficulty. The results are in reasonable agreement with those obtained using the ER potential of Meador.[21]

DISCUSSION

The transport collision integrals for each of the four possible interactions between two ground state nitrogen atoms have been computed. For the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states, Hulburt–Hirschfelder (HH) potentials were obtained from available spectroscopic parameters.[47] For the $^5\Sigma_g^+$ state, the potential of Krauss and Neumann[20] was fitted by a slightly modified HH potential function, and collision integrals for the $^7\Sigma_u^+$ state were calculated directly using the potential obtained by Ferrante and Stwalley.[22]

The novel computational methods of Ref. 30 were important for the successful calculation of the collision integrals for the $^5\Sigma_g^+$ state, since its potential possesses a long-range maximum and a second minimum. The present work contrasts with previous work[23,24] in which potentials were fit to functional forms for which collision integrals had been previously tabulated.[25-28]

Transport collision integrals for nitrogen atoms in the ground electronic state are obtained by averaging the results for each of the four molecular states according to their degeneracies.[49] Results for the diffusion and viscosity collision integrals are given in Table VI. A comparison with the results obtained previously[23,24] for the viscosity collision integral is given

TABLE VII. Comparison of various results for the viscosity collision integral $\sigma^2\Omega^{(2,2)*}$ of nitrogen atoms.

T (K)	$\dfrac{\sigma^2\Omega^{(2,2)*} \text{ [Yun (Ref. 23)]}}{\sigma^2\Omega^{(2,2)*} \text{ (this work)}}$	$\dfrac{\sigma^2\Omega^{(2,2)*} \text{ [Capitelli (Ref. 24)]}}{\sigma^2\Omega^{(2,2)} \text{ (this work)}}$
1 000	0.972	
3 000	0.968	
5 000	0.955	1.02
8 000	0.942	1.01
10 000	0.936	1.01
13 000	0.928	0.969
15 000	0.928	0.988
18 000		0.972
20 000		0.968

TABLE IX. Comparison of the HH and MP results for the transport collision integrals for the $^5\Sigma_g^+$ state of N_2.

T (K)	$\dfrac{\sigma^2\Omega^{(1,1)*} \text{ (MP)}}{\sigma^2\Omega^{(1,1)*} \text{ (HH)}}$	$\dfrac{\sigma^2\Omega^{(2,2)*} \text{ (MP)}}{\sigma^2\Omega^{(2,2)*} \text{ (HH)}}$
1 000	0.742	0.649
2 000	0.888	0.801
3 000	0.952	0.881
5 000	1.02	0.964
10 000	1.08	1.03
15 000	1.11	1.06
20 000	1.11	1.07

in Table VII. The agreement is very good in spite of the fact that the potentials used in this work are generally quite different than those used previously, especially by Yun and Mason.[23] There are evidently two reasons for this. First, the transport collision integrals are relatively insensitive to the details of the potential; there is a rule of thumb that an error of a factor of 2 in the potential leads ot an error of 20%–40% in the collision integrals.[50]

Second, there appears to be a pattern of compensating discrepancies among the cross sections for individual states, which are in considerably poorer agreement than the final degeneracy averaged cross sections. The agreement in Table VII, therefore, may be somewhat fortuitous. In particular, the contribution of the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states alone is consistently at least 15% smaller with the HH potential than with the MP and the contribution of the $^5\Sigma_g^+$ state is considerably higher with the HH potential than with the MP. This is illustrated in Table VIII. The more detailed calculations presented here thus provide greater confidence in the theoretical transport properties of nitrogen atoms.

The calculations for the $^5\Sigma_g^+$ potential (an example of a potential with large multiple extrema) provide a significant test of a method proposed by Hirschfelder and Eliason.[51] A single MP, of course, cannot fit the potential in Fig. 1, but Hirschfelder and Eliason[51] recommend using different MP parameters for different temperatures; here six different sets are used since the multiple extrema are not reproduced by any single set of MP parameters. Table IX gives a comparison of the MP results using the Hirschfelder–Eliason method with the collision integrals calculated directly from the modified HH potential.

Agreement is relatively good for $T \geq 3000$ K, but breaks down for lower temperatures. This trend was also observed in previous work.[39] At low reduced temperatures, the effective barrier for binary collisions is the outer maximum rather than the inner core, and an anomalously large effective cross section results. Such behavior persists to some degree for intermediate temperatures as well. The method of Hirschfelder and Eliason[51] is seen to accommodate the large increase in the cross section with decreasing temperature, but only up to a point for potentials with multiple extrema; these contribute significantly to the collision integrals at low and intermediate temperatures.

The accuracy of the averaged collision integrals for ground state atomic nitrogen depends on both the accuracy of the potentials used as input for each of the states and the relative contribution of the states according to their degeneracies. While the HH potentials for the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states should be very accurate (except at large r^{36}), the large well depths and consequent low reduced temperatures for these states increases the error in the collision integrals with decreasing temperature.[36] The $^5\Sigma_g^+$ and $^7\Sigma_u^+$ states make the largest contribution to the collision integrals because of their higher degeneracies. For these states, the results depend on the accuracy of the theoretical potentials used as input.[20,22] Assuming these potentials are in error by 20% or less, the averaged collision integrals given in Table VI should be in error by less than 10%, with the error decreasing somewhat at higher temperatures.

TABLE VIII. The ratio $\sigma^2\Omega^{(2,2)*}$ (Capitelli and Devoto[a])/$\sigma^2\Omega^{(2,2)*}$ [b] for the N_2 molecular states.

T(K)	$\tfrac{1}{4}\,^1\Sigma_g^+ + \tfrac{3}{4}\,^3\Sigma_u^+$	$^5\Sigma_g^+$	$^7\Sigma_u^+$
5 000	1.19	0.73	1.02
8 000	1.16	0.78	0.99
10 000	1.19	0.80	0.96
13 000	1.17	0.83	0.94
15 000	1.18	0.84	0.93
18 000	1.16	0.86	0.91
20 000	1.16	0.87	0.89

[a]Reference 24.   [b]This work.

ACKNOWLEDGMENTS

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