The $v = 0 \to 1$ vibrational cross-section for e–H$_2$ scattering: An unresolved problem with wide implications

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Abstract. Controversy has surrounded the determination of the $v = 0 \to 1$ vibrational cross-section for e–H$_2$ scattering for some thirty years: differences exist between values measured in crossed-beam experiments, which agree well with *ab-initio* quantum mechanical values, and cross sections derived from swarm experiments. These differences are far larger than the estimated errors associated with all three determinations, which will all remain under something of a cloud until the discrepancy is resolved. Following the suggestion of Buckman et al. [1], research on this problem has recently refocused on the transport theory used to determine cross sections from swarm data. This paper will review the results and implications of this recent research and will present new results on the validity of conventional semi-classical transport theory. We consider approximations used in contemporary solutions of the semi-classical Boltzmann equation including steady-state hydrodynamic assumptions. In addition, we address the validity of the semi-classical Boltzmann equation itself with particular reference to conservation of angular momentum and to the importance of taking into account the essentially fermionic nature of electrons in transport theory.

1. Introduction

Understanding the interaction of electrons and positrons with molecules in gaseous systems is important in many areas of science, technology and medicine, e.g., plasma processing for

microchip-etching technology, diagnostics of low-temperature plasmas, the development of Hg-free discharge lamps, high-energy particle detectors [2, 3] and positron emission tomography. Development of these technologies and procedures requires accurate values for electron and positron-molecule cross sections and an understanding of the physical mechanisms responsible for them. Yet, this knowledge is haunted by one of the most vexing problems in atomic and molecular collision physics—a problem that persists in spite of for over 30 years of continuous theoretical and/or experimental effort: the large discrepancy ($\lesssim 50\%$) in the electron-induced $v = 0 \rightarrow 1$ excitation of H_2 as determined from swarm experiments [4, 5, 6, 7, 8], beam experiments [9, 10, 1, 11, 12] and *ab-initio* quantum mechanical calculations [13, 14]. This discrepancy contrasts strikingly with the situation for the momentum transfer cross section, for which all three appraoches are in agreement, and with the rotational excitation cross sections for of H_2, for which agreement between the theoretical and swarm-derived cross-sections is excellent. The contrast with the situation for *atomic* gases in generalis also striking, since by and large the three methods all agree splendidly.

The implications of this controversy are serious indeed. Far more is at stake than the values of the particular low-energy e–H_2 vibrational cross sections that are its focal point. For if our understanding of the physics of non-resonant vibrational excitation for this simplest of electron-neutral molecule systems is in doubt, then what confidence can we place in our understanding of electron scattering from more complicated molecules? Furthermore, what confidence can we place in the accuracy of the huge data base of electron-molecule cross sections that has been used for decades in modelling technological applications e.g. [15, 16]? The very *persistence* of this problem—its resistance to over 30 years of intensive research—may cast doubt on the validity of applying the conventional semi-classical transport theory, based on the Boltzmann equation with the Wang-Chang et al. semi-classical collision operator [17], in other fields, such as the analysis and design of plasma discharges for use in microelectronic device fabrication, the analysis of data from high-energy particle detectors, and future development of lasers. Any flaw in the standard kinetic theory of electrons would also have ramifications for positrons systems, a field of substantial current interest and growth. The present situation is indeed worrying.

The H_2 controversy has been reviewed previously, [18, 19, 20, 21] in light of advances in experimental swarm measurements and analysis [6, 7, 8], crossed-beam experiments [20, 21], and quantum theory [14]. In summary (i) the often overlooked swarm experiments conducted in H_2 mixtures (Ar [6], He [7]) support the initial swarm-derived cross-sections [4, 5] and (ii) new age crossed-beam experiments [1] support the theoretical cross-sections [14]. The most recent papers of Buckman et al. [1] and of Crompton and Morrison [19] suggested that the source of the discrepancy may well lie in the transport theory used to unfold cross sections from measured swarm data. From this suggestion followed the initiation of a new phase of research, a collaboration between James Cook University (JCU), the University of Oklahoma (OU), and the Australian National University (ANU) that focusses on the kinetic theory of electrons and (more recently) positrons in molecular gases.

This paper reviews the current status of this latest phase (see [22, 23]) and presents new results. In Section 2, we address semi-classical transport theory and assess errors associated with approximations and assumptions used in contemporary methods. In Section 3, we turn to the validity of the semi-classical Boltzmann's equation, focussing on the implications of its inability to conserve angular momentum or to properly incorporate the fermionic nature of electrons. In Section 4, we will outline our future plans to resolve this problem.

2. On the use and solution of the semi-classical Boltzmann equation

2.1. The semi-classical Boltzmann equation

The governing equation that describes a swarm of electrons of charge $-e$ drifting and diffusing through a neutral background gas under the influence of an external electric field $\boldsymbol{E}$ is Boltzmann's equation for the phase-space distribution function $f(\boldsymbol{r}, \boldsymbol{c}, t)$:

$$\frac{\partial f}{\partial t} + \boldsymbol{c} \cdot \nabla f - \frac{e\boldsymbol{E}}{m} \cdot \frac{\partial f}{\partial \boldsymbol{c}} = -J(f) \,, \tag{1}$$

where $\boldsymbol{r}$ and $\boldsymbol{c}$ denote the position and velocity variables of an electron in the swarm, respectively, and $J(f)$ is the collision operator. The electron mass is m, the magnitude of the electron charge is $e > 0$, and t denotes time.[1] All prior applications of Boltzmann theory to swarm experiments have assumed that the electron number density $n(\boldsymbol{r}, t)$ is sufficiently small that the following conditions pertain:

(i) the background of neutral molecules remains in thermal equilibrium;

(ii) electron-electron scattering can be neglected;

(iii) the fermionic character of the electrons can be ignored, i.e., one need not take account of the Pauli exclusion principle in the collision integrals.

In swarm experiments the current is varied over several orders of magnitude to minimize these effects [24]. The collision operator $J(f)$ on the right-hand side of Eq. (1) thus represents only electron–neutral molecule interactions. In the present work we employ the original Boltzmann collision operator for elastic processes [25] and its semi-classical generalization for inelastic processes [17]:

$$J(f) = J_{WUD}(f) = \sum_{vj, v'j'} \int \left[f(\boldsymbol{c}) \, f_0^{v,j}(\mathbf{c}_0) - f(\boldsymbol{c}') \, f_0^{v',j'}(\mathbf{c}_0') \right] g \, \sigma^{vj, v'j'}(g, \widehat{\boldsymbol{g}} \cdot \widehat{\boldsymbol{g}}') \, d\widehat{\boldsymbol{g}}' d\mathbf{c}_0 \,, \quad (2)$$

Here (v, j) denote vibrational and rotational quantum numbers of the target in a particular rovibrational state in the ground Born-Oppenheimer electronic state, while $\sigma^{vj, v'j'}(g, \widehat{\boldsymbol{g}} \cdot \widehat{\boldsymbol{g}}')$ is the differential cross section for the collisionally-induced transition $(v, j) \rightarrow (v', j')$. This cross section depends on the electron's incident kinetic energy and on the angle between the incident and post-collision relative velocities, $\mathbf{g}$ and $\mathbf{g}'$ respectively. For a neutral gas with temperature T_0 and number density n_0 the distribution of neutral velocities $\mathbf{c}_0$ and internal states (v, j) is Maxwell-Boltzmann:

$$f_0^{v,j}(\mathbf{c}_0) = \frac{n_0}{Z(T_0)} \exp\left(-\frac{\epsilon_{v,j}}{kT_0} \right) \, w(\alpha_0, \mathbf{c}_0) \,, \quad (3)$$

where $Z(T_0)$ is the partition function, $\epsilon_{v,j}$ the energy of a molecule in rovibrational state (v, j), and

$$w(\alpha_0, \mathbf{c}_0) \equiv \left(\frac{\alpha_0^2}{2\pi} \right)^{3/2} \exp\left(-\alpha_0^2 \, c_0^2 \right) \,, \quad (4)$$

with $\alpha_0^2 = m_0/kT_0$.

2.2. Solution of the semi-classical Boltzmann equation and common approximations

Electron swarm experiments are generally designed and executed under the assumption of the existence of the *steady-state hydrodynamic regime*. This regime exists once the swarm has evolved to the stage where its subsequent space and time evolution are governed entirely by linear functionals of the electron number density $n(\boldsymbol{r}, t)$ [26]. Under these conditions the swarm can be fully characterized by time-independent transport coefficients that are related to the diffusion equation. A representation of Eq. (1) in the hydrodynamic regime is made via two expansions:

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[1] For *positron* swarms, the sign of the charge changes in the left hand side, and the right hand side contains terms describing annihilation and positronium formation, in addition to the Wang-Chang et al prescription accounting for positron-molecule collisions. It is the latter which is the focus of present attention. Note that the kinetic equation for positrons is of the same *form* as (1), and may be solved using the same mathematical and computational techniques described below.

(i) A sufficient representation of the space- and time-dependence of the phase-space distribution function in the hydrodynamic regime is the density gradient expansion [26]:

$$f(\boldsymbol{r}, \boldsymbol{c}, t) = n(\boldsymbol{r}, t) f^{(0)}(\boldsymbol{c}) - \mathbf{f}^{(1)}(\boldsymbol{c}) \cdot \nabla n(\boldsymbol{r}, t) + \cdots ,$$

$$= \sum_{s=0}^{\infty} \sum_{\lambda=0}^{s} \sum_{\mu=-\lambda}^{\lambda} g(s\lambda\mu; \boldsymbol{c}) G_{\mu}^{(s\lambda)} n(\boldsymbol{r}, t) , \tag{5}$$

where $G_{\mu}^{(s\lambda)}$ is the irreducible tensor form of the gradient operator [27].

(ii) The angular-dependence of $f(\boldsymbol{r}, \boldsymbol{c}, t)$ in velocity space is generally expanded in spherical harmonics as [27]:

$$g(s\lambda\mu; \boldsymbol{c}) = \sum_{\ell=0}^{\ell_{max}} \sum_{m=-\ell}^{\ell} f(lm|s\lambda\mu; c) Y_{\ell m}(\hat{\boldsymbol{c}}) \delta_{\mu m} , \tag{6}$$

where $\hat{\boldsymbol{c}}$ represents the angles of $\boldsymbol{c}$. If we now define the quantities

$$F_{\ell}^{(0)}(c) \equiv i^{\ell} \left[\frac{2\ell+1}{4\pi} \right]^{1/2} f(\ell 0|000; c); \qquad F_{\ell}^{(L)}(c) \equiv i^{l+1} \left[\frac{2\ell+1}{4\pi} \right]^{1/2} f(\ell 0|110; c);$$

$$F_{\ell}^{(T)}(c) \equiv i^{l+1} \left[\frac{2(2\ell+1)}{4\pi\ell(\ell+1)} \right]^{1/2} f(\ell 1|111; c) , \tag{7}$$

then, in the absence of non-particle-conserving collisional processes such as attachment and ionization, the following hierarchy of equations suffices to determine the quantities of interest in the present work [26]:

$$\frac{l}{2l-1} \left(\frac{eE}{m} \right) \left[\frac{d}{dc} - \frac{l-1}{c} \right] F_{\ell-1}^{(0)}(c) + \frac{l+1}{2l+3} \left(\frac{eE}{m} \right) \left[\frac{d}{dc} + \frac{l+2}{c} \right] F_{\ell+1}^{(0)}(c) = -\hat{J}_{\ell} F_{\ell}^{(0)}(c) \tag{8a}$$

$$\frac{l}{2l-1} \left(\frac{eE}{m} \right) \left[\frac{d}{dc} - \frac{l-1}{c} \right] F_{\ell-1}^{(L)}(c) + \frac{l+1}{2l+3} \left(\frac{eE}{m} \right) \left[\frac{d}{dc} + \frac{l+2}{c} \right] F_{\ell+1}^{(L)}(c) = -\hat{J}_{\ell} F_{\ell}^{(L)}(c)$$

$$+ c \left[\frac{l}{2l-1} F_{\ell-1}^{(0)}(c) + \frac{l+1}{2l+3} F_{\ell+1}^{(0)}(c) \right] \tag{8b}$$

$$\frac{l-1}{2l-1} \left(\frac{eE}{m} \right) \left[\frac{d}{dc} + \frac{l-1}{c} \right] F_{\ell-1}^{(T)}(c) + \frac{l+2}{2l+3} \left(\frac{eE}{m} \right) \left[\frac{d}{dc} + \frac{l+2}{c} \right] F_{\ell+1}^{(T)}(c) = -\hat{J}_{\ell} F_{\ell}^{(T)}(c)$$

$$+ c \left[\frac{1}{2l-1} F_{\ell-1}^{(0)}(c) - \frac{1}{2l+3} F_{\ell+1}^{(0)}(c) \right] , \tag{8c}$$

where the superscripts L and T denote longitudinal and transverse to the electric field. The matrix elements of the collision operator are defined as

$$\int Y_{\ell' m'}^{*}(\hat{\boldsymbol{c}}) \, J(f) \, Y_{\ell m}(\hat{\boldsymbol{c}}) \, d\hat{\boldsymbol{c}} \left[\hat{J}_{\ell}^{\ (\text{el})} + \sum_{i} \hat{J}_{\ell}^{\ (\text{inel})}(i) \right] \delta_{ll'} \delta_{mm'} , \tag{9}$$

where the superscripts 'el' and 'inel' refer to the elastic and inelastic processes and the index i denotes an (inelastic) scattering process. Note that the operator $\hat{J}_{\ell}$ in Eqs. (8) is the quantity in square brackets in Eq. (9). It is traditional to refer to the $\ell = 0$ and $\ell = 1$ members of the system (8) as the isotropic and vector equations, respectively.

The treatment of the speed dependence of the coefficients $F_\ell^{(0)}(c)$, $F_\ell^{(L)}(c)$ and $F_\ell^{(T)}(c)$ in (8) is purely a matter of computational efficiency and accuracy; we refer the reader to the review [28] for details.

The transport coefficients of interest in this work can be expressed as

$$W = \left(\frac{4\pi}{3}\right) \int c\, F_1^{(0)}(c)c^2\, dc, \tag{10a}$$

$$D_L = \left(\frac{4\pi}{3}\right) \int c F_1^{(L)}(c)c^2\, dc, \tag{10b}$$

$$D_T = \left(\frac{4\pi}{3}\right) \int c F_1^{(T)}(c)c^2\, dc, \tag{10c}$$

$$\varepsilon = 4\pi \int \frac{1}{2}mc^2 F_0^{(0)}(c)c^2\, dc, \tag{10d}$$

$$R_{vj-v'j'} = 4\pi \int F_0^{(0)}(c)\, g\sigma^{vj,v'j'}(g, \widehat{\boldsymbol{g}} \cdot \widehat{\boldsymbol{g}}')\, \sin\theta\, d\theta\, d\boldsymbol{c}_0\, d\boldsymbol{c}\ , \tag{10e}$$

where W is the drift velocity; D_L and D_T are, respectively, the components of the diffusion tensor parallel and perpendicular to the electric field; ε is the mean energy; and $R_{vj-v'j'}$ is the rate coefficient for the excitation $(v, j) \to (v', j')$. (In the case of positrons, extra terms have to be added to the right hand side of (10 a,b,c) to allow for annihilation and positronium formation [27])

In 2002, using the most accurate available kinetic theory, which was based upon the Wang Chang et al. collision operator, White, Morrison and Mason [22] undertook a comprehensive study of the validity of approximations widely used in contemporary solutions of semi-classical Boltzmann equation to determine cross sections from electron swarm experiments in molecular hydrogen (see e.g., [29, 24]). Of particular note for the current semi-classical kinetic theory are the following points:

 (i) No restrictions were made about the number of spherical harmonics in the expansion (6).

 (ii) No assumptions were made about the action of the various collision-process operators in the spherical harmonic equations. All collision processes for all l-equations in Eqs. (8) were treated as distinct processes.

(iii) Mass-ratio effects for all collision process operators were treated in a consistent manner.

(iv) No restrictions were placed on the angular dependence of the differential cross section. This point distinguishes the assessment of White, Morrison and Mason from contemporary two-term theories, which sample only the total and momentum transfer cross sections.

 (v) No assumptions were made about the relative magnitudes of cross sections for the various collisional processes. Neither was the assumption made that the elastic momentum-transfer cross section, which appears in the elastic collision operator in the isotropic equation, is equal to the total momentum transfer cross section in the vector equation [29, 24].

(vi) The thermal motion of the neutrals was systematically incorporated into all collision-process operators and all spherical-harmonic equations.

The results of this investigation have been detailed in [22]. In brief, all approximations used in contemporary steady-state solutions of the semi-classical Boltzmann equation were found to be valid for the analysis of e-H_2 system.

2.3. The problem

With this background we now turn to the most recent results of this research. We here focus exclusively on the simplest case: electron transport in para-H_2 at $77\,\text{K}$. We restrict the range of E/N to $0.1\,\text{Td} - 10\,\text{Td}$, where $1\,\text{Td} = 1\,\text{Townsend}\,10^{-21}\,\text{Vm}^2$. We employ the full set of the latest theoretical differential cross sections [14]. In contrast to previous work [6], we do not assume that the angular dependence of the differential cross section is energy independent. Furthermore,

we treat rovibrational processes explicitly rather than via a lumped overall vibrational cross section.

In Table 1, we compare experimentally measured transport coefficients [24] with coefficients calculated via the semi-classical Boltzmann equation using the latest theoretical differential cross sections. These comparisons illustrate the disparity between *ab-initio* theory and swarm experiment from a point of view different than the more familiar comparison of theoretical and swarm-derived integral cross sections. The differences in this table appreciably exceed the quoted uncertainty for the experimental coefficients over this range of E/N.

Table 1. Comparison of calculated transport coefficients, based on *ab-initio* theoretical differential cross-sections (A) in conventional Boltzmann theory, with experimental data (B) [24], for electrons in para-H_2 at 77 K.

E/n_o (Td)		ϵ (10^{-2}eV)	W (10^3ms^{-1})	n_oD_T (10^{23}m^{-1}s^{-1})	n_oD_L (10^{23}m^{-1}s^{-1})	D_T/μ (10^{-2}V)
0.01	A	1.0998	0.32374	2.2159	2.4783	0.76552
	B		0.333		2.65	0.761
0.05	A	1.7973	1.1453	2.2263	3.1321	1.3673
	B		1.131		3.19	1.410
0.1	A	2.3002	1.9550	2.4404	3.4733	1.7766
	B		1.913		3.47	1.814
0.5	A	5.5754	5.5732	2.5180	4.7629	4.2730
	B		5.42		4.64	4.28
1.0	A	10.145	7.3664	2.5008	5.7816	7.8486
	B		7.15		5.62	7.86
5	A	37.672	13.441	3.9347	8.4123	31.294
	B		13.04		8.42	32.3
10	A	56.564	19.625	4.6373	9.3170	47.475
	B		18.90			

2.4. On the hydrodynamic and steady-state approximations

Swarm experiments are designed so that steady-state, hydrodynamic conditions prevail throughout the swarm. The data is consequently analysed on this premise, as detailed in Section 2.2. Within the discharge there can be many sources of behaviour that would invalidate these assumptions, which are generally assessed experimentally, e.g., by varying the drift length and/or pressure [24]. Of particular interest in this section is the influence of the electron source as a possible origin of non-steady state or non-hydrodynamic behaviour.

As a preliminary study we consider the time-of-flight experiment [24]. The initial velocity distribution of electrons prior to entering the drift tube is essentially unknown. We assume, as a first approximation, that the velocity distribution is a stationary Maxwellian at a temperature T_{init}. Figure 1 illustrates the temporal relaxation profiles for the electron drift velocity in para-H_2 at 77 K, as calculated using the OU *ab-initio* theoretical cross-sections. For pressures typical of those in swarm experiments, these results indicate that the influence of non-steady state behaviour arising from initial conditions is minimal. This conclusion validates the steady-state analysis of swarm data in this case and supporting the pressure invariance of results [24].
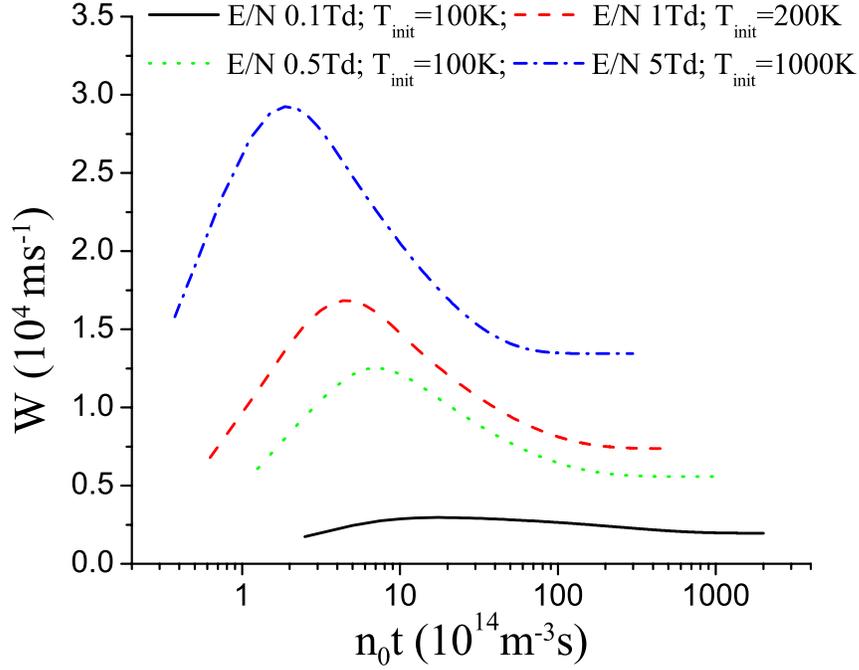
Figure 1. The temporal evolution of the drift velocity of an electron swarm in para-H_2 at $77\,K$ for various applied reduced fields and initial swarm temperatures T_{init}. (The distribution is assumed to be Maxwellian). Note that the results scale as $n_0 t$ where n_0 is the number density of para–H_2.

We have also conducted studies of the spatial relaxation length in the steady-state Townsend experiment. In Figure 2, we display the spatial relaxation of electrons in a 2.892% Ne/H_2 mixture at $293\,K$ and $20\,kPa$ as considered in [8] for an idealised system (see [30, 31] for a schematic). The results demonstrate that the relaxation length for non-hydrodynamic behaviour is much less than the dimensions of the discharge for pressures used in these swarm experiments. These results further validate the steady-state, hydrodynamic prescription outlined in Section 2.2.

3. On the validity of the semi-classical Boltzmann equation

3.1. The fermionic character of electrons

In all previous studies of electron swarms, the fermionic nature of electrons has been ignored on the grounds that the electron number density in these experiments is assumed to be low. To study this effect we need to incorporate the Pauli-exclusion principle for electrons via the following modification to the semi-classical Wang-Chang et al. form of the collision operator:

$$J(f) = J_{UU}(f) = \sum_{vj,v'j'} \int \left[f(\boldsymbol{r},\boldsymbol{c},t) \left\{ 1 - \gamma f(\boldsymbol{r'},\boldsymbol{c'},t) \right\} f_0^{v,j}(\boldsymbol{c}_0) \right.$$
$$\left. - f(\boldsymbol{r'},\boldsymbol{c'},t) \left\{ 1 - \gamma f(\boldsymbol{r},\boldsymbol{c},t) \right\} f_0^{v',j'}(\boldsymbol{c}_0') \right] g\sigma^{vj,v'j'}(g,\widehat{\boldsymbol{g}}\cdot\widehat{\boldsymbol{g}}') \, d\widehat{\boldsymbol{g}}' d\boldsymbol{c}_0 \;, \quad (11)$$

where γ is the density of translational states. This is the Uehling and Uhlenbeck [32] operator generalized to account for internal states of the background neutral molecules. The additional terms are due to 'Pauli blocking' of collisions: collisions which would normally have scattered an electron into a phase volume that is already occupied are blocked by the Pauli-exclusion
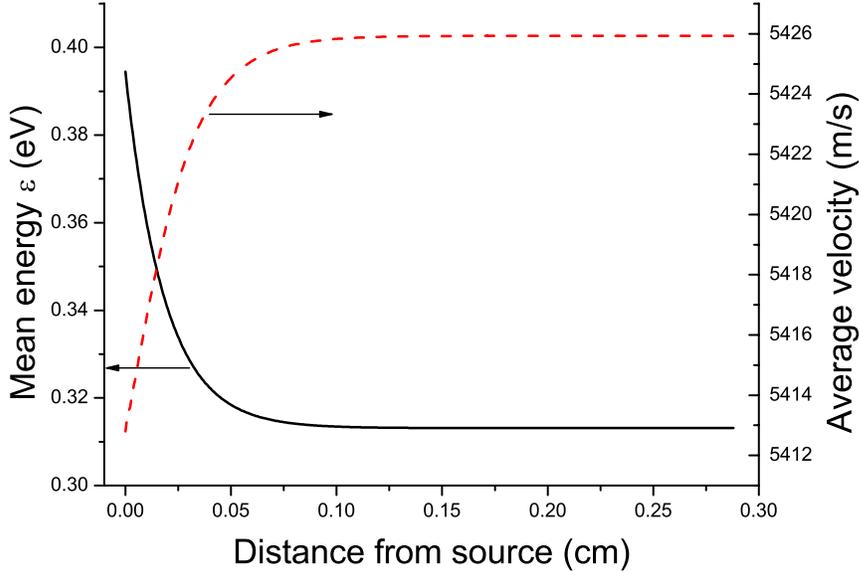
Figure 2. The spatial evolution of the mean energy and average velocity for an idealised steady-state Townsend system where the constant source of electrons has a drifted Maxwellian velocity distribution (temperature: $3500\,\mathrm{K}$ and drift velocity: $5000\,\mathrm{m/s}$) and the background neutral gas is a $\mathrm{Ne/H_2}$ (2.892%) mixture at $293\,\mathrm{K}$ and $20\,\mathrm{kPa}$.

principle. The presence of these additional terms complicates solution of the Boltzmann equation, which now is non-linear in f. Note that we have assumed that the neutral distribution can be accurately described by Maxwell-Boltzmann statistics and hence no 'blocking/affinity' factors are required for the neutral distribution.

We consider elastic collisions only; inelastic collisional processes are treated in [33]. We solved the Boltzmann equation using techniques similar to those used in contemporary solutions of the semi-classical Boltzmann equation outlined and validated in Section 2.2 (see [33] for details). Of particular note are the following assumptions and approximations:

(i) spatially uniform conditions;

(ii) the two-term approximation for the the velocity distribution function;

(iii) truncation of the first-order mass ratio in the $l = 0$ elastic collisional matrix elements $\hat{J}_{\ell}^{\,(\mathrm{el})}$ and truncation at zeroth order otherwise.

Analytically, we were able to benchmark the solutions to the resulting system of equations for a variety of limiting cases. For the field-free case ($E = 0$), we showed that in the limit of low electron densities the solution approaches a Maxwellian speed distribution at the neutral gas temperature. In the limit of high electron densities, the solution approaches the Fermi-Dirac distribution. Under non-equilibrium conditions ($E/N \neq 0$), the distribution function in the limit of low electron density approaches the classical Druyvesteyn distribution [34]. For arbitrary electron densities and electron-neutral cross-sections, the steady-state solution must be obtained numerically. Both the Newton-Raphson and iterative techniques were used, and both were found to be robust and relatively insensitive to the initial estimates of the solution. The details of the derivation of the collision operator and our analytical and numerical solution techniques are given in [33].

Figure 3 shows the variation of the speed distribution function with electron density for a simple model hard-sphere cross-section. These results demonstrate the enhanced influence of Pauli-blocking with increasing electron number density. Interestingly, increasing the electron

density forces electrons to higher energies because of the enhanced Pauli-blocking effect. We observe a significant extension of the speed distribution function into the high energy region before this function rapidly falls off above the (non-equilibrium) 'Fermi-energy'. Most importantly, electron densities of greater than $10^{26}\mathrm{m}^{-3}$ are required for blocking effects to become significant. Throughout most of the time-of-flight drift tube, such effects can safely be disregarded—although near the gates these effect may be important.
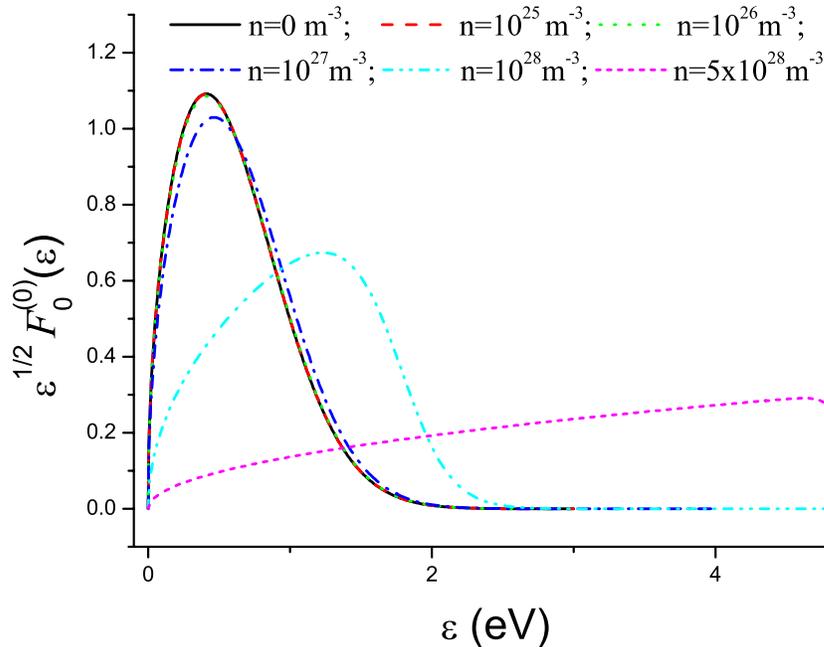
Figure 3. Variation of the speed distribution of electrons with electron density. Electrons are in a model gas of hard spheres of mass $4\,\mathrm{amu}$ at a temperature of $293\,\mathrm{K}$. The elastic cross-section for electron-hard sphere collisions is $6\,\text{Å}^2$. Note, the $n = 0$ plot represents the case where there is no Pauli-blocking.

3.2. Angular momentum conservation

In the Wang-Chang et al. semi-classical formulation [17], rotational excitation is treated as a simple scalar process involving energy exchange only, like pure vibrational or electronic excitation. Therein lies a problem: this formulation does not conserve angular momentum. Trying to solve this problem via the full quantum description afforded by the Waldmann-Snider collision operator [35] does no good, for this operator is also local [36]. That such a local collision operator fails to conserve angular momentum has long been known—see, for example, the classical text by Chapman and Cowling ([37] p. 203). But until now this defect has been considered a problem of principle not of substance. The discrepancy concerning vibrational excitation in molecular hydrogen, however, reveals that this defect is potentially of great substance indeed.

We have explored quantitatively the significance of this problem, that is, we have assessed the validity of the description by a local collision operator of collisionally-induced rotational excitations. To consider the practical importance of angular-momentum conservation in this context, we changed the focus from the electron swarm to the background neutral gas. We devised a quantitative measure of the internal consistency of the Wang-Chang et al. collision operator: the so-called anisotropic echo left in the rotational states of the neutral molecules as

result of the electron swarm [23]. This measure, Δ, is defined by

$$\Delta = \frac{\frac{1}{3}\frac{\partial}{\partial t}\langle J^2\rangle\rangle_{coll} - \frac{\partial}{\partial t}\langle J_z^2\rangle\rangle_{coll}}{\frac{1}{3}\frac{\partial}{\partial t}\langle J^2\rangle\rangle_{coll}}, \qquad (12)$$

where $\boldsymbol{J}$ is the angular momentum of the background molecules and the subscript *coll* indicates generation by collisions. The physical nature of this measure can be understood as follows: the electric field in a swarm experiment induces an anisotropy and a displacement in the velocity distribution function of the electron swarm. In electron collisions with neutral molecules, therefore, there will be a preponderance of orbital angular momentum in the plane perpendicular to the electric field. The transfer of angular momentum to rotational states of molecules should also take place predominantly in this plane. Hence, one expects a preferential orientation of post-collision rotational states of the neutral molecules in a plane perpendicular to the electric field—an 'anisotropic echo' in the rotational states of the neutral gas. The existence of such an echo would signal the need for a new, more accurate treatment of angular momentum in the kinetic transport equations that govern the electron swarm.
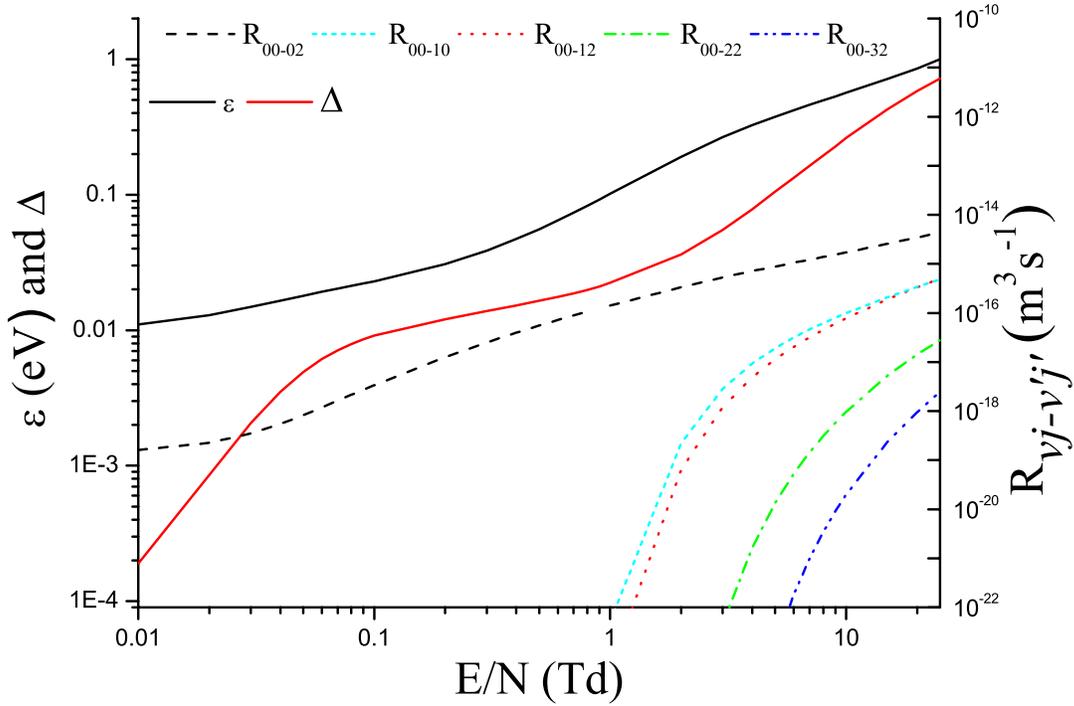

Figure 4. Variation of Δ as defined by Equation (12), the mean energy ε, and the excitation rates $R_{vj-v'j'}$ with E/N for electrons in para-H$_2$ at $77\,\mathrm{K}$. The indices v and j are the vibrational and rotational quantum numbers respectively, while the dashes refer to the post collision states.

Our preliminary study considered electrons in para-hydrogen at $77\,\mathrm{K}$. The variation of Δ with E/N is displayed in Figure 4 along with the mean electron energy and rates coefficients for various excitations. The details of the evaluation of Δ are complicated and involve integrals over angles of the squares of theoretical quantities that are not normally calculated directly in ab-initio scattering calculations. For practical purposes it was necessary to express these quantities in terms of T-matrices [23]. The results show that over the range of reduced electric fields where pure rotational excitations are the dominant inelastic energy-loss mechanism the echo is weak ($\leq 2\%$). Most importantly, these studies showed that for reduced fields where

vibrational and rovibrational excitation are important, the echo is very strong ($\sim 40\%$) due to the larger energy losses characteristic of these processes. These results shed light on the e-H_2 vibrational cross section controversy: "The weak echo in the regime of pure rotational transitions indicates that conventional local kinetic theory is sufficiently accurate to extract pure rotational-excitation cross sections from swarm data at lower reduced fields. This finding informs the excellent agreement between the swarm derived and theoretical/beam pure rotational cross sections" [23]. The strong echo in the regime of pure vibrational and rovibrational excitation indicates that conventional local kinetic theory fails to accurately determine cross sections for these excitations from swarm data because this theory fails to conserve angular momentum. In light of this discovery, the severe disagreement between the cross sections derived from swarm data using conventional kinetic theory and from theoretical/beam results in this energy region is no longer surprising.

4. Concluding remarks

We have reviewed recent research into the use of semi-classical transport theory to indirectly determine e–H_2 cross-sections by deconvoluting experimental swarm data. Our initial studies focused on the accuracy of the solution of the conventional semi-classical Boltzmann equation, identifying assumptions and approximations used in this solution, and testing their validity. Our results support the validity of other contemporary applications of conventional theory. For the first time, we have proposed a semi-classical transport theory which accounts for the fermionic nature of electrons. Although solution of this new transport equation did not resolve the controversy, the theory and techniques developed and results obtained in this work may find application in other fields where non-equilibrium degenerate electron-gas conditions obtain.

At present we consider the most promising line of research to resolve this long-standing disparity from the standpoint of kinetic theory is to ensure conservation of angular-momentum in the background H_2 molecules. As discussed above, current semi-classical transport theory is local and does not conserve angular momentum. We found that this failure does not affect the results of conventional transport analysis until energy loss in the rovibrational channels becomes important. These results are consistent with the excellent agreement of swarm-derived and theoretical pure-rotational cross sections and with the severe disagreement for summed pure and rovibrational cross-sections. Our future goal is to develop a new non-local transport theory that accurately conserves angular momentum. An approach to doing so has been outlined in [23], which also discusses corrections to measured transport properties due to non-locality in the collision operator.

It is, of course, possible that our new transport theory will produce essentially the same cross sections as the conventional local theory. This outcome would validate the use in prior calculations of an approximate local collision operator, verify the accuracy of the aforementioned large data base of swarm-derived cross sections, and the return the focus to the beam experiments and *ab-initio* quantum calculations. Alternatively, our new kinetic theory may produce cross sections that agree well with those measured in beam experiments and calculated using quantum theory. This outcome would imply that non-local collision operators must be used to describe transport in molecular gases and would have wide-ranging ramifications for a host of fields that now use conventional local kinetic theories, fields such as modelling of low-temperature plasma discharges in the fabrication of microelectronic devices and high-energy charged particle detectors.

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