

Some fundamental questions concerning the kinetic theory of electrons in molecular gases and the e–H₂ vibrational cross section controversy

R E Robson¹, R D White² and Michael A Morrison³

¹ Research School of Physical Sciences, Australian National University, Canberra 2600, Australia

² School of Mathematical and Physical Sciences, James Cook University, Cairns 4870, Australia

³ Physics Department, University of Oklahoma, Norman, OK 73019, USA

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Abstract

We commence a fundamental re-examination of the kinetic theory of charged particle swarms in molecular gases, focusing on collisional excitation of molecular rotational and ro-vibrational states by electrons. Modern day analysis of electron swarms has been based upon the kinetic equation of Wang-Chang *et al*, which simply treats *all* processes as scalar energy excitations, and ignores angular momentum conservation and the vector dynamics associated with rotational excitation. It is pointed out that there is no alternative, more exact kinetic equation readily available for electrons which enables one to directly ascertain the degree of error introduced by this approximation. Thus in this preliminary study, we approach the problem *indirectly*, from the standpoint of the *neutral molecules*, using the Waldmann–Snider quantum kinetic equation, and insist that an electron–molecule collision must look the same from the perspective of both electron and molecule. We give a formula for quantitatively assessing the importance of scalar versus vectorial treatments of rotational excitation by looking at the post-collisional ‘echo’ produced by an electron swarm as it passes through the gas. It is then pointed out that in order to remedy any deficiency, it will be necessary to introduce a kinetic collisional operator *non-local* in space to properly account for angular momentum conservation, as has long been established in the literature. This is a major exercise and given the preliminary nature of this study, we consider the inclusion of such effects from a formal point of view only. In particular we show how non-local effects lead to a spatially dependent ‘source’ term in the equation of continuity, and hence to corrections for both drift velocity and diffusion coefficients. The magnitude of these corrections has yet to be established.

1. Introduction

Transport processes in molecular gases are generally significantly influenced by collisions involving both rotational and vibrational excitation, and naturally any kinetic equation should treat the corresponding collision dynamics correctly. In particular, for swarms of electrons or ions in molecular gases, it is clear that excitation of rotational states must be coupled with a transfer of orbital to rotational angular momentum, consistent with conservation of total angular momentum. Unfortunately, in the present day kinetic theory of swarms, angular momentum is ignored, and rotational excitation is treated no differently from a simple, scalar process involving energy exchange only, just like vibrational or electronic excitation. By itself, that might appear merely a problem of esoteric significance, but when one also considers the controversy surrounding the (e , H_2) vibrational (including ro-vibrational) cross section, which has prevailed for some thirty years, and defied every attempt to resolve it, further investigation seems called for. A brief summary of the situation is given below.

There is a large ($\lesssim 60\%$) discrepancy in published results between values of the cross section obtained from, on the one hand, swarm experiments [1] and, on the other, those obtained from quantum mechanical theory [2, 3] and beam experiments [4]. In contrast, the situation for rotational excitations is far more satisfactory, with good agreement between theory and swarm derived cross sections. The H_2 controversy has been reviewed over the years [5, 6], and the discrepancy continually highlighted. For other diatomic gases such as N_2 [7] the situation is, however, not so clear cut.

Swarm experiments [1, 8] have traditionally provided the most accurate information about low energy ($\lesssim 1$ eV) ion–atom and ion–molecule interaction potentials, on the one hand, and electron–atom and electron–molecule cross sections, on the other hand. There is a high demand for these cross sections and for transport coefficients in such diverse scientific and technological applications as astrophysics, lasers, microchip etching technology and high energy particle detectors. The swarm measurements at the Australian National University [1, 8] were unparalleled in their accuracy and, when combined with modern kinetic theory (see [9] for a review), enabled a large number of low energy cross sections to be found. Likewise, the process of deduction of interaction potentials from ion swarm data has been considerably refined over the years, due to significant advances in kinetic theoretical calculations, notably by Mason, Viehland and collaborators [10].

In addition to swarm experiments, beam experiments have been independently probing electron–molecule interaction cross sections, recently to energies well below 1 eV. In the case of H_2 , information has been obtained right down to the threshold of the first vibrational excitation, at about 0.5 eV. Quite independently of experiment, quantum theoretical calculations have furnished e – H_2 impact cross sections at low energies [3], which tend to support the beam experimental results.

The discrepancy referred to above has hitherto been taken to imply that there is something wrong with either:

- (i) the swarm experiments or
- (ii) current beam experiments or
- (iii) quantum theoretical analysis.

To this list we add a fourth possibility [4] which is yet to be fully explored and which is the subject of the current investigation:

- (iv) the kinetic theory which has been used to ‘unfold’ the swarm experiments may be deficient.

Whatever the origin, the implications are of concern. This is because H₂ is the simplest of molecular systems and, if there is a problem with it, then a shadow of doubt is cast over *all* electron–molecule cross sections, however obtained. The seriousness of the problem has long been recognized and there has been a considerable effort over the years aimed at its resolution [5, 11], without success. A new tack is clearly required. Of course, if after pursuing the present line of investigation, the conventional theory comes through unscathed, it will throw the spotlight squarely back on (i)–(iii) above.

Before outlining our plan of attack, we should mention that the problem is already being considered elsewhere on three other fronts:

- Using existing kinetic theory, based upon Boltzmann’s equation and associated ‘multiterm’ computer codes [9], incorporating realistic angular anisotropies in the cross sections [11].
- Using Monte Carlo simulation [11].
- Through an examination of possible quantum degeneracy effects [12], especially near the surface of the anode [13].

So to the outline of this paper. Put most simply, it is about the fundamental kinetic theory of charged particle swarms in molecular gases. While H₂ is of special interest, the questions raised are far more general. The premise is that *something* may be seriously wrong somewhere. If it is kinetic theory that is at fault, then could it be because of the flawed treatment of angular momentum? If so, how do we go about correcting things? We begin our task in section 2 with a review of the equations and assumptions of the conventional kinetic theory for electron swarms. In section 3 we take a different tack and focus on the properties of the *neutral* gas. What could it be about the onset of vibrational and ro-vibrational excitation of molecules, as distinct from pure rotations, that traditional kinetic theory analysis might not handle well? To help address this question, we argue that the treatment of the *same* collisions as seen from the perspective of *both* swarm particles and neutral molecules must at least be internally consistent. The measure of this consistency is the anisotropic ‘echo’ left in neutral rotational states as the swarm passes through the gas. In section 4 we broach the subject of non-locality in the collision operator, albeit in a formal way. We also show, again formally, how the non-locality can lead to corrections in both drift velocity and diffusion coefficients, in a manner reminiscent of the origin of explicit corrections due to ‘reactive collisions’ [14].

2. Brief review of standard kinetic theory of swarms

2.1. The generic kinetic equation

Analysis of swarm experiments to extract cross sections and interaction potentials generally proceeds via a kinetic equation of the form

$$(\partial_t + \mathbf{c} \cdot \nabla + \mathbf{a} \cdot \partial_{\mathbf{c}}) f = -J(f) \quad (1)$$

in which $f(\mathbf{r}, \mathbf{c}, t)$ is the swarm particle distribution function in phase space (\mathbf{r}, \mathbf{c}), $\mathbf{a} = e\mathbf{E}/m$ is the acceleration suffered by a particle of mass m , charge e in an external electric field \mathbf{E} and $J(f)$ is the collision term, i.e., the rate of change of f due to swarm particle–neutral molecule collisions. For the swarm problem, densities are extremely low, electrons do not interact with each other and any Pauli blocking is assumed negligible. Therefore $J(f)$ is linear in f . The best known kinetic equation is due to Boltzmann, who in 1872 formulated an operator $J_B(f)$ describing classical, elastic collisions between point particles. That and various approximations to it, including the differential operator for very light particles, has been successfully applied to study electrons and ion swarms in monatomic gases [8, 14]. For

molecular gases, however, inelastic collisions must generally be accounted for and other forms of collision operator must be used [8–10, 14]. In any case, physically measurable quantities are determined from ‘moments’ of the distribution function, e.g., the number density

$$n = \int f(\mathbf{c}) d\mathbf{c} \quad (2)$$

and average velocity

$$\mathbf{v} = \frac{1}{n} \int \mathbf{c} f(\mathbf{c}) d\mathbf{c}. \quad (3)$$

For quantum systems, f represents a Wigner distribution density matrix and averages involve an additional trace over the relevant indices.

2.2. Electron swarms: semi-classical and quantum collision operators

Present day analysis [8, 9, 14] of *electron* swarm experiments is based largely on the Wang-Chang, Uhlenbeck, de Boer (WUB) collision term J_{WUB} [15, 16]:

$$J_{\text{WUB}}(f) = \sum_{vj,j'} \int [f(\mathbf{c}) f_0^{vj}(\mathbf{c}_0) - f(\mathbf{c}') f_0^{v'j'}(\mathbf{c}'_0)] g \sigma^{vj,v'j'}(g, \hat{\mathbf{g}} \cdot \hat{\mathbf{g}}') d\mathbf{g}' d\mathbf{c}_0, \quad (4)$$

and its approximations for low mass ratios [14]. Here (v, j) denote vibrational and rotational quantum numbers respectively describing an internal state of the neutral molecule, while $\sigma^{vj,v'j'}(g, \hat{\mathbf{g}} \cdot \hat{\mathbf{g}}')$ is the differential cross section for the collisionally induced transition $(v, j) \rightarrow (v', j')$. The latter depends upon energy and the angle between incident and post-collision relative velocities, \mathbf{g} and \mathbf{g}' respectively. If the neutral gas has temperature T_0 and number density n_0 , the distribution of neutral velocities \mathbf{c}_0 and internal states v, j is governed by a Maxwell–Boltzmann distribution

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

where Z is the partition function, ϵ_{vj} the energy of a molecule in vibrational state v , rotational state j and

$$w(\alpha_0, \mathbf{c}_0) \equiv \left(\frac{\alpha_0^2}{2\pi}\right)^{3/2} \exp\left(-\frac{1}{2}\alpha_0^2 c_0^2\right),$$

where $\alpha_0^2 = \frac{m_0}{kT_0}$. In this model, there is no mention of angular momentum orientation or projection quantum numbers m_j . Moreover, the collision operator is *local*, in the sense that it involves the distribution function $f(\mathbf{r}, \mathbf{c}, t)$ only at the point \mathbf{r} in question and otherwise does not depend explicitly upon position. Conservation of particle number follows from the fact that

$$\int J_{\text{WUB}}[f(\mathbf{r}, \mathbf{c}, t)] d\mathbf{c} = 0 \quad (5)$$

and further moments with respect to momentum $m\mathbf{c}$ and kinetic energy $\frac{1}{2}mc^2$ correctly represent the rate of momentum and energy transfer between swarm particles and neutral molecules respectively. On the other hand, taking the moment of equation (4) with the angular momentum vector $\mathbf{r} \times m\mathbf{c}$ yields only $\mathbf{r} \times \int m\mathbf{c} J_{\text{WUB}}(f) d\mathbf{c}$ and produces no information whatever about transfer of orbital angular to rotational angular momentum. This is a point of major concern, and is amplified in what follows.

It is interesting to note that collisions of electrons with molecules, involving rotational excitation of the latter, are generally governed by non-central forces and this holds too of

course for diatomic molecules such as hydrogen [18]. In general, collisional effects enter into $J(f)$ through scattering amplitudes $a_{m_j, m'_j}^{v_j, v'_j}(\mathbf{g}, \mathbf{g}')$, which for non-central forces depend upon \mathbf{g} and \mathbf{g}' separately. However, in J_{WUB} , these appear only as sums of their squares through the cross sections σ (see equation (7) below) and hence only *one* scattering angle χ , defined by $\cos \chi = \hat{\mathbf{g}} \cdot \hat{\mathbf{g}}'$, appears. To this extent, J_{WUB} cannot differentiate between central and non-central forces. Furthermore, J_{WUB} treats rotational excitation, not as a vector process involving exchange of orbital angular momentum of the electron with rotational angular momentum of the molecule, but as simply another scalar excitation process, involving energy exchange only. There is no distinction (apart from in the actual magnitudes of energy exchanges) between rotational, vibrational or even electronic excitation as far as the WUB equation is concerned. Indeed, it is not clear physically how rotational modes can even be excited in collision operators like J_{WUB} which are assumed to act at a point in space only (local operator), given the general problems this class of operators have with angular momentum conservation. The bright point in all this is that J_{WUB} *does* furnish cross sections for pure rotational excitation in H_2 which are in good agreement with theory [1, 5]. For that reason we wish to focus on *ro-vibrational* collisions in what follows and our subsequent remarks on angular momentum should be taken in that context.

Equation (4) is valid if the gap $\Delta\varepsilon$ between energy levels is sufficiently large that

$$\tau \Delta\varepsilon \gg h,$$

where τ is the average time between collisions. This is certainly true for the vibrational levels alone, but the $2j+1$ degenerate rotational sub-levels $m_j = -j, \dots, j$ do not satisfy this condition and in any case cannot be considered explicitly in the Wang-Chang *et al* formulation. One must go to a quantum description, e.g., the Waldmann–Snider collision operator J_{WS} [19–22], to treat such degenerate states correctly. Although the explicit form of J_{WS} is not needed for the present, we do observe that it is also a local operator, linear in f , and satisfies particle conservation as in (5). In the Waldmann–Snider equation, the Wigner distribution density matrix generally appears, rather than a scalar distribution function f . However, as the electrons are considered to be structureless point particles, their corresponding Wigner matrix is a scalar, while the Wigner matrix for the neutral molecules is diagonal in and independent of the m -indices, since they are assumed to be in overall equilibrium with a Maxwell–Boltzmann distribution. In this case it is straightforward to show that [16, 20, 21]

$$J_{\text{WS}} \rightarrow J_{\text{WUB}}, \quad (6)$$

with the additional result that

$$\sigma^{v_j, v'_j}(\mathbf{g}, \hat{\mathbf{g}} \cdot \hat{\mathbf{g}}') = \frac{1}{2j+1} \sum_{m_j=-j}^j \sum_{m'_j=-j'}^{j'} \frac{g'}{g} |a_{m_j, m'_j}^{v_j, v'_j}(\mathbf{g}, \mathbf{g}')|^2, \quad (7)$$

where $a_{m_j, m'_j}^{v_j, v'_j}(\mathbf{g}, \mathbf{g}')$ are scattering amplitudes. The latter can be calculated from T -matrices in the usual way [2]:

$$a_{m_j, m'_j}^{v_j, v'_j}(\mathbf{g}, \mathbf{g}') = \frac{4\pi}{\sqrt{k k'}} \sum_{l, m, l', m', JM} i^{(l-l')} Y_{lm}^*(\hat{\mathbf{g}})(jm_j lm|JM) T_{v'j'l', vjl}^J(j'm'_j l'm'|JM) Y_{l'm'}(\hat{\mathbf{g}}'), \quad (8)$$

where k, k' are incident and scattered wavenumbers respectively and the summation over l, m (incident orbital angular momentum quantum numbers), l', m' (post-collision orbital angular momentum quantum numbers) and J, M (total angular momentum) goes over all values permitted by the Clebsch–Gordan coefficients, $(jm_j lm|JM)$ and $(j'm'_j l'm'|JM)$.

Equation (7) represents a sum over final states and an average over initial states. This is the same definition of the differential cross section as is used in *ab initio* quantum mechanical calculations [2, 3] and is the same quantity as derived from beam experiments [4]. Hence, if conditions in a swarm experiment correspond to the regime of validity of J_{WUB} , we should expect an inversion of the swarm data to yield directly cross sections $\sigma^{vj,v'j'}$ which are consistent with the *ab initio* calculations and beam experiments. Outside the regime of validity of J_{WUB} , we would have to use a quantum operator such as J_{WS} , or more likely a non-local quantum collision operator, where the scattering amplitudes appear *separately*, rather than in the combination (7). In that case, an unfolding of swarm data using such operators would yield $a_{m_j,m'_j}^{vj,v'j'}$ rather than $\sigma^{vj,v'j'}$. However, we could still regain the latter by substituting in (7). What we must *not* do is apply J_{WUB} outside its regime of validity, extract a cross section from the swarm data and expect it to match the *ab initio* or beam derived cross section. It is quite possible that this mistake has been made and is at the root of the discrepancy. This is precisely the question that we address in the present investigation.

2.3. Ion swarms and classical kinetic theory

The kinetic theory of ion swarms is in stark contrast to the above, with a purely classical analysis of rotational collisions considered acceptable [10]. However, it appears that a hybrid semi-classical form would be needed if vibrational excitations are important, but this has yet to be developed. The situation is also in stark contrast with classical collision operators used in earlier kinetic theory of molecular neutral gases. It is especially interesting to note that unlike J_{WUB} , noncentral forces become manifest through a differential cross section which is a function of *two* angles, i.e., both χ and azimuthal angle ϕ . Also of interest is the way in which earlier researchers approximated inelastic, orientation-dependent collisions to make the problem more tractable. The review by Mason [17] explains these points further.

All in all there is a wealth of information contained in the kinetic theory of both ion swarms and classical neutral gases, but it remains to be seen just how much of this can be brought to bear on the electron swarm problem. For the present we have chosen to pursue a fully quantum line of enquiry and have adapted the collision operator of Waldmann and Snider to pursue another facet of the electron swarm problem.

3. The neutral gas ‘echo’: internal consistency considerations

Given the shortcomings of J_{WUB} and its derivatives [14] used in traditional analysis of swarm experiments, one wonders why it has proved so successful in describing pure rotational excitation [5]. Obviously, the treatment of rotational excitation as a *scalar* process in J_{WUB} , as a kind of a very low threshold electronic or vibrational excitation process, is somehow sufficient. However, in view of the discrepancy that arises between swarm derived and *ab initio* quantum mechanical cross sections when vibrations are excited, one must ask whether it is also sufficient for the case of *ro-vibrational* excitations, i.e., rotations accompanied by vibrations. What, if anything, distinguishes between pure rotational and ro-vibrational excitations *from a kinetic theory point of view*? Note that we expect J_{WUB} to treat *pure* vibrational excitations, a scalar process involving no rotational excitation, correctly.

In this section we attempt to throw some light on this question by taking the perspective of the neutral molecules and look in particular at the effect of the electron swarm as it passes through the gas. We shall refer to this as the ‘echo’ of the swarm. The electric field \mathbf{E} induces anisotropy in the swarm velocity distribution; i.e., there are more swarm particles moving along the field axis than in directions perpendicular to it. In collisions with neutral molecules,

there will thus be a preponderance of orbital angular momentum in a plane perpendicular to \mathbf{E} and one might expect the transfer of angular momentum to rotational states of the molecules to also be predominantly in this plane. Such physical arguments lead us to the conclusion that there should be *some* collisionally induced rotational anisotropy i.e., preferential orientation of post-collisional molecular rotational states of the neutrals in a plane perpendicular to \mathbf{E} . There are two observations which we now make to set the stage for what follows:

- (i) At the level of the Wang-Chang *et al* kinetic equation, *as applied to the neutrals*, no such effects can exist, given that it ignores the angular momentum aspect of rotational excitation entirely. If J_{WUB} is replaced by the Waldmann–Snider collision operator such effects can indeed be generated.
- (ii) From the point of view of *the electrons*, the existence of significant rotational anisotropy in the neutrals may be an indication that angular momentum needs to be treated more carefully in the electron kinetic equation and that the local Wang-Chang *et al* operator (4) must be replaced by some other, non-local collision operator. In contrast to the remedy for the neutrals, there is no such ready candidate—applying the Waldmann–Snider equation does not produce anything new.

Of course, if collisional production of rotational anisotropy were weak, then one might deduce that the Wang-Chang *et al* analysis should suffice for both electrons and neutrals, but we have no measure of the effect, since no such investigation has ever been carried out. We emphasize that our interest in post-collisional neutrals is *only* to the extent that they may provide *indirect* evidence for any possible flaws in the calculation of electron properties, for it is these which are measured in experiment and which are unfolded to obtain cross sections. This is the essence of the logic and the motivation for the numerical study described below.

The easiest way to begin the analysis is to use the equations of change given by Waldmann [20] or, equivalently, take moments of the Waldmann–Snider equation. Thus, letting \hat{A} denote the operator corresponding to some physical observable pertaining to neutral molecule internal states, diagonal in the m -indices, we can calculate $\frac{\partial}{\partial t}\langle A \rangle|_{\text{coll}}$, the rate of change due to collisions with electrons of the average value of the physical observable, as

$$\frac{\partial}{\partial t}\langle A \rangle|_{\text{coll}} = \sum_{v_j, v'_j; m_j, m'_j} (A_{m'_j}^{j'} - A_{m_j}^j) \int f(\mathbf{c}) \frac{f_0^{v_j}(\mathbf{c}_0)}{2j+1} g \sigma(\mathbf{g})_{m_j m'_j}^{v_j, v'_j} d\mathbf{c} d\mathbf{c}_0, \quad (9)$$

where

$$\sigma(\mathbf{g})_{m_j m'_j}^{v_j, v'_j} \equiv \frac{g'}{g} \int |a_{m_j, m'_j}^{v_j, v'_j}(\mathbf{g}, \mathbf{g}')|^2 d\mathbf{g}'. \quad (10)$$

Examples of such physical observables include J_z , J^2 , J_z^2 . In the right-hand side of (9) we have approximated the neutral molecule Wigner distribution density matrix by a scalar Maxwellian. This is consistent with the basic assumption for swarm conditions whereby the neutral gas acts as an effective heat bath and the probability of an electron colliding with a neutral molecule that has already undergone a collision with an electron is negligibly small. The electrons have been treated as classical point particles. Note that the scattering amplitudes and cross sections appearing here in the equations for neutral molecule change are the same as the quantities appearing in the corresponding electron equations of change.

3.1. Alignment effects I: polarization

Setting $A = J_z$ in (9), where the z -axis is parallel to the external electric field, gives the rate of collisionally induced alignment as

$$\frac{\partial}{\partial t} \langle J_z \rangle|_{\text{coll}} = \sum_{vj, v'j'; m_j, m'_j} (m'_j - m_j) \hbar \int f(\mathbf{c}) \frac{f_0^{vj}(\mathbf{c}_0)}{2j+1} g \sigma(g)_{m_j m'_j}^{vj, v'j'} d\mathbf{c} d\mathbf{c}_0. \quad (11)$$

Simple physical arguments indicate that there can be no *net* rotational angular momentum generated in the neutral gas through collisions with point particles such as electrons; i.e., we should find $\frac{\partial}{\partial t} \langle J_z \rangle|_{\text{coll}} = 0$. This is true for example if $f(\mathbf{c})$ is isotropic, corresponding to zero field. For non-zero fields, other conditions on $\sigma(g)_{m_j m'_j}^{vj, v'j'}$ must come into play, but we do not explore the full implications in the present work.

3.2. Alignment effects II: collisionally induced rotational anisotropy

We have already explained why there should be an anisotropic distribution of post-collisional rotational degrees of freedom, with components of \mathbf{J} lying preferentially in a plane perpendicular to \mathbf{E} . This has also been called ‘alignment’ in the literature and is measured by the symmetric traceless part of tensors such as $\langle \mathbf{J}\mathbf{J} \rangle$; see, e.g. [23]. We prefer the term ‘rotational anisotropy’ to ‘alignment’, but are otherwise happy to adopt effectively the same measure as in the earlier literature. If rotational excitation were isotropic, or could be treated as a scalar energy excitation process, then we would observe an equipartitioning of the respective rates of collisionally induced generation of rotational energies; i.e., for molecules with moments of inertia I ,

$$\frac{\hbar^2}{2I} \frac{\partial}{\partial t} \langle J_x^2 \rangle|_{\text{coll}} = \frac{\hbar^2}{2I} \frac{\partial}{\partial t} \langle J_y^2 \rangle|_{\text{coll}} = \frac{\hbar^2}{2I} \frac{\partial}{\partial t} \langle J_z^2 \rangle|_{\text{coll}}$$

or equivalently

$$\frac{\partial}{\partial t} \langle J_z^2 \rangle|_{\text{coll}} = \frac{1}{3} \frac{\partial}{\partial t} \langle J^2 \rangle|_{\text{coll}}.$$

Therefore, to ascertain the departure from rotational anisotropy we set

$$A = \frac{1}{3} J^2 - J_z^2$$

in (9) and find

$$\begin{aligned} & \frac{1}{3} \frac{\partial}{\partial t} \langle J^2 \rangle|_{\text{coll}} - \frac{\partial}{\partial t} \langle J_z^2 \rangle|_{\text{coll}} \\ &= \sum_{vj, v'j'} \frac{1}{3} [j'(j'+1) - j(j+1)] \hbar^2 \int f(\mathbf{c}) f_0^{vj}(\mathbf{c}_0) g \sigma(g)_{\text{T}}^{vj, v'j'} d\mathbf{c} d\mathbf{c}_0 \\ &\quad - \sum_{vj, v'j'; m_j, m'_j} [(m'_j)^2 - (m_j)^2] \hbar^2 \int f(\mathbf{c}) \frac{f_0^{vj}(\mathbf{c}_0)}{2j+1} g \sigma(g)_{m_j m'_j}^{vj, v'j'} d\mathbf{c} d\mathbf{c}_0, \end{aligned} \quad (12)$$

where the total cross section for the $vj \rightarrow v'j'$ transition is defined by

$$\sigma(g)_{\text{T}}^{vj, v'j'} = \frac{1}{2j+1} \sum_{m_j, m'_j} \sigma_{m_j m'_j}^{vj, v'j'}(\mathbf{g}). \quad (12')$$

Notice that if $\sigma_{m_j m'_j}^{vj, v' j'}$ (or its integral with the distribution functions over all velocities) were independent of the m -indices, then the identity $\sum_{m=-j}^j m^2 = \frac{1}{3}j(j+1)(2j+1)$ would ensure that the right-hand side of (12) vanishes and equipartitioning pertains. This is the situation, for example, when $f(\mathbf{c})$ is isotropic. Otherwise, general arguments (see the appendix) show that only the $l = 2$ term in the spherical harmonics decomposition of the electron distribution function $f(\mathbf{c}) = \sum_{l=0}^{\infty} f^{(l)}(\mathbf{c}) P_l(\hat{\mathbf{c}} \cdot \hat{\mathbf{E}})$ contributes to the right-hand side of (12). The traditional ‘two-term’ kinetic theory ($f^{(l)} = 0, l \geq 2$) therefore gives an expression for the right-hand side of (12) which is identically zero in all circumstances and has no hope of picking up the effects that we are looking for. It is of special interest here to investigate the contribution to (12) from excitation of ro-vibrational states of H_2 , as compared with pure rotational states, as the field is increased.

As a practical measure of rotational anisotropy generation, we work with the dimensionless quantity

$$\begin{aligned} \Delta &= \frac{\frac{1}{3} \frac{\partial}{\partial t} \langle J^2 \rangle|_{\text{coll}} - \frac{\partial}{\partial t} \langle J_z^2 \rangle|_{\text{coll}}}{\frac{1}{3} \frac{\partial}{\partial t} \langle J^2 \rangle|_{\text{coll}}} \\ &= \left\{ \sum_{vj, v' j'} \int f(\mathbf{c}) f_0^{vj}(\mathbf{c}_0) \frac{1}{2j+1} \sum_{m_j, m'_j} \left\{ \frac{1}{3} [j'(j'+1) - j(j+1)] \right. \right. \\ &\quad \left. \left. - [(m'_j)^2 - (m_j)^2] \right\} g\sigma(g)_{mj m'_j}^{vj, v' j'} d\mathbf{c} d\mathbf{c}_0 \right\} \\ &\quad \times \left\{ \frac{1}{3} \sum_{vj, v' j'} [j'(j'+1) - j(j+1)] \int f(\mathbf{c}) f_0^{vj}(\mathbf{c}_0) g\sigma(g)_{\text{T}}^{vj, v' j'} d\mathbf{c} d\mathbf{c}_0 \right\}^{-1} \quad (13) \end{aligned}$$

obtained from (12) by dividing through by $\frac{1}{3} \frac{\partial}{\partial t} \langle J^2 \rangle|_{\text{coll}}$. As in (12), deviations in Δ from 0 indicate the importance of the contributions of rotational angular momentum in electron–molecule collisions. A value $\Delta \sim 1$ would indicate the extreme case where all rotational angular momentum generated in these collisions was in a plane normal to the electric field. Such a situation might be expected to arise, for example, for very heavy ions, but for electrons and light ions generally, and for e– H_2 in particular, smaller values are expected. The interesting thing is to see how Δ varies over a wide range of E/n_0 , as successive inelastic channels are opened, particularly with the onset of ro-vibrational excitations. If Δ is very small in all circumstances, one can be sure that the semi-classical picture is at least internally consistent, that suppressing vector angular momentum properties from the outset is justified and that the continued use of semi-classical kinetic theory for the purposes of unfolding swarm experiments is warranted. If not, and especially if Δ were to show a significant rise during the opening of ro-vibrational channels, then one would begin to suspect that vector angular momentum properties are important, suggesting the need for a complete re-examination of the kinetic equation for electrons, with incorporation of the conservation of total angular momentum. One would then have to look in particular at the assumptions of local, instantaneous collisions, for which conservation of total angular momentum is not possible.

We now perform a numerical calculation along these lines, by making certain simplifying assumptions. Firstly, it is usual to neglect the thermal motion of neutrals in the inelastic electron–molecule collision terms, by setting

$$f_0^{vj}(\mathbf{c}_0) = \frac{n_0}{Z} \exp\left(-\frac{\epsilon_{v,j}}{kT_0}\right) \delta(\mathbf{c}_0)$$

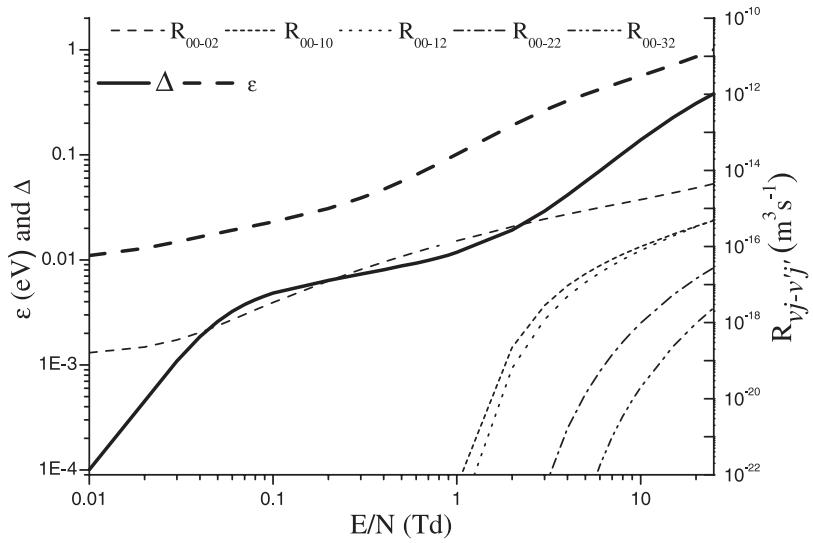


Figure 1. Variation of Δ as defined by equation (3), the mean energy ε and excitation rates $R_{vj-v'j'}$ with E/N for electrons in para- H_2 at 77 K. The indices v and j refer to the vibrational and rotational quantum numbers respectively while the dashes refer to the post-collision states.

in which case (13) simplifies to

$$\begin{aligned} \Delta = & \left\{ \sum_{vj, v'j'} \int f(\mathbf{c}) \exp\left(-\frac{\epsilon_{v,j}}{kT_0}\right) \frac{1}{2j+1} \sum_{m_j, m'_j} \left\{ \frac{1}{3}[j'(j'+1) - j(j+1)] \right. \right. \\ & \left. \left. - [(m'_j)^2 - (m_j)^2] \right\} c\sigma(\mathbf{c})_{m_j m'_j}^{vj, v'j'} d\mathbf{c} \right\} \\ & \times \left\{ \frac{1}{3} \sum_{vj, v'j'} [j'(j'+1) - j(j+1)] \exp\left(-\frac{\epsilon_{v,j}}{kT_0}\right) \int f(\mathbf{c}) c\sigma(\mathbf{c})_{\text{T}}^{vj, v'j'} d\mathbf{c} \right\}^{-1}. \end{aligned} \quad (14)$$

This equation can be expressed in terms of T -matrices, as shown in equation (A.6) of the appendix. In what follows, we show the results of a calculation of Δ for which the following rotationally inelastic channels only:

$$\begin{aligned} j &= 0; & j' &= 2; \\ v &= 0; & v' &= 0, 1; \end{aligned}$$

are considered to contribute to the right-hand side of (14). (Note: rotationally *elastic* channels, for which $j' = j$, do not contribute to Δ in any circumstances.)

In figure 1 we show the variation of Δ over a range of E/n_0 for electrons in para-hydrogen at 77 K for which first the rotational and then the ro-vibrational channels open. Also shown are the electron mean energy ε and the excitation rates $R_{vj-v'j'}$. For the latter we have shown for comparison the rotationally elastic situation $j = j' = 0$; $v = 0$, $v' = 1$, plus higher order vibrational excitation ($v = 0$, $v' = 2$; $v = 0$, $v' = 3$) cases. Note that the evaluation of Δ , like the calculation of the electron velocity distribution function $f(\mathbf{c})$ from (1) and (4), uses cross sections calculated from T -matrices calculated as in [2]. Our observations are as follows:

- (i) For E/n_0 below about 1 Td = 10^{-21} V m², we observe that $\Delta \lesssim 2\%$ and can conclude that collisionally induced rotational anisotropy is weak. We also observe that below

1 Td vibrationally inelastic collisions are very infrequent compared with pure rotational excitations, which are characterized by the rate R_{00-02} . Thus there are grounds for having every confidence in using the traditional kinetic theory analysis for extracting pure rotational excitation cross sections from swarm data at lower E/n_0 . It is significant that there is indeed good agreement between swarm derived and *ab initio* quantum mechanical pure rotation cross sections—one would not expect anything else on the basis of the present analysis.

- (ii) Above 1 Td it is a different story: ro-vibrational and pure vibrational excitation, as measured by R_{00-12} and R_{00-10} respectively, increase dramatically and Δ grows to around 40% at 10 Td. The onset of vibrational excitations is accompanied by strong rotational anisotropy, indicating that one simply cannot neglect angular momentum considerations in the analysis. It is also in this region where the swarm derived vibrational cross section deviates so markedly from both the beam and quantum mechanically derived results, as discussed in the introduction.

Could it be that the latter observation indicates some remarkable coincidence or does it, albeit indirectly, imply a breakdown in the traditional kinetic theory, based on the Wang-Chang *et al* collision operator, by virtue of its inability to account correctly for angular momentum? Following the recent extensive, but inconclusive investigations of [11] in a number of other directions, it seems that this is the only remaining possibility, *if* there is to be any flaw in the kinetic theory *per se*. The analysis in the following section indicates how a more general, non-local collision operator does indeed lead to corrections in transport properties.

4. Non-local collisional effects

4.1. General remarks on conservation of angular momentum, non-locality

It has long been recognized in the literature [24, 25] that only a *non-local* collision operator can provide coupling between the orbital angular momentum $\mathbf{I} = \mathbf{r} \times \mathbf{p}$ of the electron and the rotational angular momentum \mathbf{j} of the molecule, such that the total angular momentum

$$\mathbf{J} = \mathbf{j} + \mathbf{I} \quad (15)$$

is properly conserved. The non-central forces operating in electron–diatomic molecule collisions exert a torque on the electron, i.e., cause a change in \mathbf{I} which in turn causes the rotational angular momentum \mathbf{j} of the molecule to change by an equal and opposite amount. This (semi-classically speaking) is how rotational excitation takes place. Rotational excitation of molecules by electron impact therefore cannot be described in even a *qualitatively* correct way through central forces or a local collision operator. Orbital and rotational angular momentum would be separately conserved under a central force and, if a molecule were in a particular rotational state, it would remain in that state forever, according to this straightforward dynamical argument!

4.2. Formal construction of the non-local kinetic equation

Thomas and Snider [25] derived a non-local quantum collision term for a pure gas and represented corrections to the usual Waldmann–Snider expression by the first terms of a Taylor series expansion. Adaptation of their expression to the electron–molecule swarm situation appears not to be straightforward. For now, we therefore focus on the formal structure of the equations to deduce as much general information as we can without doing specific

calculations. Thus, to account for non-local effects to a first approximation, we introduce a gradient correction $\delta J(f)$ to the right-hand side of (1) of the form

$$\delta J(f) = \mathbf{c} \cdot \nabla J_{11}(f) + \nabla \cdot J_{12}(\mathbf{c} f). \quad (16)$$

We observe that this is the most general way of constructing a scalar from the two vectors \mathbf{c} and ∇ without the need to specify further details of the spherically symmetric operators J_{11} and J_{12} .

For simplicity, we now approximate the distribution function through the first two terms of a spherical harmonic expansion,

$$f(\mathbf{c}) = f^{(0)}(c) + \hat{\mathbf{c}} \cdot \mathbf{f}^{(1)}(c) + \dots \quad (17)$$

and resolve the non-local Boltzmann equation into $l = 0, 1, \dots$ components. For $l = 0$, we have

$$\partial_t f^{(0)} + \frac{1}{3} c \nabla \cdot \mathbf{f}^{(1)} + \frac{\mathbf{a}}{3c^2} \cdot \partial_c (c^2 \mathbf{f}^{(1)}) = -J_{\text{WUB}}^{(0)}(f^{(0)}) - \nabla \cdot (A^{(0)} \mathbf{f}^{(1)}) \quad (18)$$

and for $l = 1$, we have

$$\partial_t \mathbf{f}^{(1)} + c \nabla f^{(0)} + \mathbf{a} \partial_c f^{(0)} = -J_{\text{WUB}}^{(1)}(\mathbf{f}^{(1)}) - \nabla \cdot (A^{(1)} f^{(0)}), \quad (19)$$

where

$$A^{(0)} \equiv \frac{1}{3} (c J_{11}^{(1)} + J_{12}^{(1)} c), \quad (20)$$

$$A^{(1)} \equiv \frac{1}{3} (c J_{11}^{(0)} + J_{12}^{(0)} c). \quad (21)$$

The quantities $J^{(l)}$ are operators in c -space. For example, in the limit of small swarm particle to molecule mass ratio m/m_0 , $J_{\text{WUB}}^{(0)}$ is effectively the well known combined Davydov and differential Frost–Phelps finite difference operator [23] used widely in electron swarm kinetic theory, while $J_{\text{WUB}}^{(1)}$ is simply the momentum transfer collision frequency [8]. The remaining operators remain unspecified at present.

The interesting features of equations (18) and (19) are:

- Inclusion of non-local interaction and noncentral forces mixes the contributions of $f^{(0)}$ and $f^{(1)}$ in the collision terms on the right-hand side and introduces additional coupling between the equations.
- The extra collision terms appear as *gradients* in space, but nevertheless influence both drift velocity and diffusion coefficients, as we show next.
- The correction terms involving the operators $A^{(i)}$, $i = 0, 1$ in (19) and (18) respectively, arise explicitly because of excitation of rotations, whether occurring alone or in company with vibrational excitation. Vibrational excitational alone will not contribute to these terms. Further, since the $A^{(i)}$ are $\sim c$, we might expect that these terms would become more important at higher energies, although it is difficult to be definite about this without having explicit expressions available. However, if it is true, it means that the correction terms are small at low energies, when only rotational states are excited.

4.3. Corrections to drift velocity and diffusion coefficients

Unlike local collision operators, such as J_{WUB} , the non-local contribution $\delta J(f)$ does *not* integrate to zero as in (5). The collision term of Thomas and Snider [25] has this property for example [26]. Thus scattering takes place into and out of different volume elements separated by a finite range. Put another way, electrons generally enter and leave a region of interaction

at two different points. This will lead in general to an effective source term in the equation of continuity, which is obtained from (1) by an integration over all velocities \mathbf{c} :

$$\partial_t n + \nabla \cdot \Gamma = S, \quad (22)$$

where $\Gamma = n\mathbf{v}$ and S is the net number of electrons entering unit volume in unit time at position \mathbf{r} . Naturally the total number of electrons remains constant in the volume V under consideration; i.e.,

$$\int_V S(\mathbf{r}, t) d\mathbf{r} = 0. \quad (23)$$

In the *hydrodynamic regime*, the space-time dependence of all quantities is assumed to be projected onto $n(\mathbf{r}, t)$ and one uses the familiar density gradient expansion [14] to represent this situation:

$$\Gamma = n\mathbf{W} - \mathbf{D} : \nabla n \quad (24)$$

$$S = \mathbf{S}^{(1)} \cdot \nabla n + \mathbf{S}^{(2)} : \nabla \nabla n, \quad (25)$$

where \mathbf{W} and \mathbf{D} are drift velocity and diffusion tensor respectively and $S^{(i)}$ represents a tensor coefficient of rank i . Substitution of (24) and (25) into (22) yields the diffusion equation

$$\partial_t n + \mathbf{W}^* \cdot \nabla n + \mathbf{D}^* : \nabla \nabla n = 0, \quad (26)$$

where

$$\mathbf{W}^* = \mathbf{W} - \mathbf{S}^{(1)}, \quad (27)$$

$$\mathbf{D}^* = \mathbf{D} + \mathbf{S}^{(2)} \quad (28)$$

are the effective drift velocity and diffusion tensor respectively. Since the diffusion equation is used to interpret swarm experiments, it is the latter transport coefficients which are determined, *not* \mathbf{W} and \mathbf{D} . This points to correction terms, non-local in origin, which must be applied to calculate drift velocity and diffusion coefficients in order to make a fair comparison with experiment. The situation is reminiscent of the ‘reactive’ corrections to transport coefficients which arise, for example, due to ionizing and attaching collisions [9, 14]. However, if remarks made in the literature [24, 25] in connection with neutral gas transport are any guide, numerical values of the non-local corrections might be expected to be very small for the very low densities encountered in swarms.

5. Concluding remarks

In this preliminary study we have followed the suggestion of Buckman and collaborators [4] and taken the view that the source of discrepancy in the vibrational cross section of H_2 could lie in the kinetic theory analysis. We have identified an area of fundamental concern associated with the treatment of angular momentum and rotational excitation in the semi-classical WUB kinetic equation (and its variants), used in modern day analysis of electron swarm experiments. Our line of enquiry has taken us to an investigation of the Waldmann–Snider quantum kinetic equation. Taking the perspective of the neutral molecules and considering post-collisional effects, we have derived an expression (14) measuring the importance of including angular momentum considerations in rotational and ro-vibrational excitations. Nonlocal effects were then considered in a formal way and we have derived corrections to both drift velocity and diffusion coefficients.

A line of enquiry parallel to that of the present paper has been followed by White *et al* [11], who subject the traditional approximations and techniques of solution of the semi-classical kinetic equation to minute scrutiny and find nothing untoward. The present paper on the other

hand is far more radical in scope and questions the very integrity of this kinetic equation. Before any definitive statement can be made, however, estimates of the magnitude of the non-local correction terms must be carried out, but this is a long term project.

Finally it is worth looking back three decades or so, when controversy similar to the present one concerning H₂ surrounded the momentum transfer cross section for He. That this was eventually resolved in favour of the swarm derived values can, in the context of this paper, be taken as confirmation of the validity of applying a kinetic theory based upon Boltzmann's classical elastic collision operator to monatomic systems. Further investigation, whether along the lines suggested in this paper or otherwise, is required to confirm that the Wang-Chang *et al* operator (4) enjoys similar validity for molecular systems.

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Appendix. Expression of the anisotropy factor in terms of T-matrices

In order to compute numerical values of the rotational anisotropy parameter Δ as defined by equation (14) we must evaluate certain integrals of squares of scattering amplitudes over scattering angles. However, scattering amplitudes are not normally calculated directly in *ab initio* calculations and for practical purposes it is necessary to express these quantities in terms of *T*-matrices [2]. The following gives the derivation in outline form and focuses on the special case of the transition $J = 0 \rightarrow 2$ only. Further details, including the expression for the more general case, can be found elsewhere [27].

The starting point is the expression for scattering amplitude in terms of *T*-matrices, equation (8) and the familiar spherical harmonic representation of the electron velocity distribution function:

$$f(\mathbf{c}) = \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{\lambda} f_{\mu}^{(\lambda)}(c) Y_{\lambda\mu}(\hat{\mathbf{c}}). \quad (\text{A.1})$$

It proves convenient in the analysis to use the identity

$$(jm_j 20 | jm_j) = \frac{3m_j^2 - j(j+1)}{N_j},$$

where $N_j = \sqrt{j(j+1)(2j-1)(2j+3)}$. Then the numerator of the right-hand side of (14) takes the form

$$\begin{aligned} & \frac{1}{3} \sum_{v_j, v'_j} \frac{\exp(-\frac{\epsilon_{v,j}}{kT_0})}{2j+1} \sum_{\lambda, \mu, m_j m'_j} \{ N_j (jm_j 20 | jm_j) \\ & \quad - N_{j'} (j'm'_j 20 | j'm'_j) \} \int_0^\infty f_{\mu}^{(\lambda)}(c) \sigma_{\mu}^{(\lambda)} A_{m_j, m'_j}^{v_j, v'_j}(c) c^3 dc, \end{aligned} \quad (\text{A.2})$$

where

$$\sigma_{\mu}^{(\lambda)} A_{m_j, m'_j}^{v_j, v'_j} = \int d\hat{\mathbf{c}} Y_{\lambda\mu}(\hat{\mathbf{c}}) \sigma(\mathbf{c})_{m_j m'_j}^{v_j, v'_j} \quad (\text{A.3})$$

and $\sigma(\mathbf{g})_{m_j m'_j}^{v_j, v'_j}$ is given by (10). Upon substituting in scattering amplitudes as given by (8) and using the result

$$\int d\hat{\mathbf{c}} Y_{\lambda\mu}(\hat{\mathbf{c}}) Y_{lm}(\hat{\mathbf{c}}) Y_{l'm'}^*(\hat{\mathbf{c}}) = \omega(\lambda ll')(\lambda\mu lm|l'm'),$$

where $\omega(\lambda ll') = \sqrt{\frac{(2\lambda+1)(2l+1)}{4\pi(2l'+1)}}(\lambda 0 l0|l'0)$ is a parity coefficient, we find that (A.3) becomes

$$\begin{aligned} {}^{(\lambda)}\mu A_{m_j, m'_j}^{v_j, v'_j} &= \frac{16\pi^2}{k^2} \sum_{l'm', \bar{l}\bar{m}, JM, \bar{JM}} i^{(l-\bar{l})} \omega(\lambda \bar{l}l)(\lambda\mu \bar{l}\bar{m}|lm) T_{v'_j l', vjl}^J T_{v'_j l', vj\bar{l}}^{*\bar{J}} \\ &\times (jm_j lm|JM)(jm_j \bar{l}\bar{m}|\bar{JM})(j'm'_j l'm'|JM)(j'm'_j l'm'|\bar{JM}). \end{aligned} \quad (\text{A.4})$$

This is as far as we wish to go with the most general situation, and we now limit the discussion to the special case where the transitions are restricted to excitations from the ground state:

$$\begin{aligned} j &= 0 = m_j; & j' &= 2; \\ v &= 0; & v' &= 0, 1; \end{aligned}$$

with $\epsilon_{0,0} = 0$. Then expression (A.4) simplifies to

$$\begin{aligned} {}^{(\lambda)}\mu A_{0, m'_j}^{00, v'2} &= \frac{16\pi^2}{k^2} \sum_{l'm', JM, \bar{JM}} i^{(J-\bar{J})} \omega(\lambda \bar{J}J)(\lambda\mu \bar{J}\bar{M}|JM) T_{v'2l', 00J}^J T_{v'2l', 00\bar{J}}^{*\bar{J}} \\ &\times (2m'_j l'm'|JM)(2m'_j l'm'|\bar{JM}), \end{aligned} \quad (\text{A.5})$$

where we have used the Clebsch–Gordan coefficient property

$$(00 lm|JM) = \delta_{IJ} \delta_{mM}$$

to reduce the number of summations. The sum over the remaining m -indices can then be expressed in terms of a Racah coefficient:

$$\begin{aligned} \sum_{M, \bar{M}, m'} (2m'_j l'm'|JM)(2m'_j l'm'|\bar{JM}) &(\lambda\mu \bar{J}\bar{M}|JM) \\ &= (-1)^\lambda (2J+1) \sqrt{\frac{2\bar{J}+1}{5}} W(\lambda \bar{J} 2l'; J2)(\lambda 0 2m'_j | 2m'_j) \delta_{\mu 0}. \end{aligned} \quad (\text{A.6})$$

Therefore in (A.2), we have the term

$$\begin{aligned} \sum_{m'_j} {}^{(\lambda)}\mu A_{0, m'_j}^{00, v'2} (2m'_j 20|2m'_j) &= \frac{16\pi^2}{kk'} \sum_{J, \bar{J}, l'} i^{(J-\bar{J})} \omega(2\bar{J}J) T_{v'2l', 00J}^J T_{v'2l', 00\bar{J}}^{*\bar{J}} (2J+1) \\ &\times \sqrt{\frac{2\bar{J}+1}{5}} W(2\bar{J} 2l'; J2) \delta_{\lambda 2} \delta_{\mu 0}. \end{aligned} \quad (\text{A.7})$$

where we have used the orthogonality property

$$\sum_{m'_j} (2m'_j 20|2m'_j) (\lambda 0 2m'_j | 2m'_j) = \delta_{\lambda 2}.$$

For this special case, the numerator of (14) as given by (A.2) is thus

$$\begin{aligned} -\frac{16\pi^2}{3} N_2 \sum_{v'=0}^1 \sum_{J, \bar{J}, l'} i^{(J-\bar{J})} \omega(2\bar{J}J) (2J+1) \sqrt{\frac{(2\bar{J}+1)}{5}} W(2\bar{J} 2l'; J2) \\ \times \int_0^\infty f_0^{(2)}(c) T_{v'2l', 00J}^J T_{v'2l', 00\bar{J}}^{*\bar{J}} \frac{c^3}{kk'} dc, \end{aligned} \quad (\text{A.8})$$

where the sum goes over all values of J, \bar{J}, l' permitted by the Clebsch–Gordan and Racah coefficients. The denominator can be readily evaluated and, after some algebra, we find the following expression for the anisotropy factor (14) in terms of T -matrices:

$$\begin{aligned} \Delta = & \left\{ -\sqrt{\frac{7}{2}} \int_0^\infty f_0^{(2)}(c) \sum_{v'=0}^1 \sum_{J, \bar{J}, l'} i^{(J-\bar{J})} (2\bar{J}+1) \right. \\ & \times \sqrt{(2J+1)(20\bar{J}0|J0)} W(2\bar{J}2l'; J2) T_{v'2l', 00J}^J T_{v'2l', 00\bar{J}}^{*\bar{J}} \frac{c^3}{kk'} dc \Big\} \\ & \times \left\{ \int_0^\infty f_0^{(0)}(c) \sum_{v'=0}^1 \sum_{J, l'} (2J+1) |T_{v'2l', 00J}^J|^2 \frac{c^3}{kk'} dc \right\}^{-1} \end{aligned} \quad (\text{A.9})$$

for the special case of transitions for which $J = 0, J' = 2$ and $v = 0, v' = 0$ or 1, in the cold gas approximation. The more general expression for arbitrary J and J' can also be derived, but the details are lengthy, and are to be discussed in another publication.

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