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Test of a numerical optimization algorithm for obtaining cross sections for multiple collision processes from electron swarm data

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Abstract. A numerical optimization technique is used to obtain low-energy momentum transfer, $j = 0 \rightarrow 2$ rotational and $v = 0 \rightarrow 1$ vibrational, cross sections from measured electron swarm data for parahydrogen. The downhill simplex algorithm is used to find cross sections that represent the best numerical fit to the measured electron drift velocity and characteristic energy over a range of E/N. These results, which are in excellent agreement with published cross sections derived using traditional swarm analysis techniques, demonstrate the feasibility of using automated computational algorithms for swarm analysis involving the estimation of multiple cross sections.

1. Introduction

For nearly a century physicists have been deducing cross sections for electron collisions with atoms and molecules from electron transport measurements. This technique, in which the drift velocity and diffusion coefficient of a swarm of electrons in an electric field are measured and a cross section is deduced using an approximate expression for the electron velocity distribution, was devised by Townsend in 1908. The discipline is still known as swarm physics. Until the invention of quantum mechanics enabled collision cross sections to be computed theoretically, swarm analysis was the only means of obtaining such cross sections.

In the 1950s techniques using electron beams were developed for measuring electron collision cross sections. Theoretical calculations and beam measurements have been greatly improved and refined over the past 20 years. Despite this progress the technique of deducing cross sections from electron swarm data is still very important, especially for low-energy cross sections below several electron-volts. This has become an increasingly active field in recent years due, for example, to the desire for low-energy cross-sectional data on molecules such as CH_4, CF_4 or SiH_4 that are used in semiconductor plasma processing and in switching applications (Morgan 1992). In many ways swarm, beam and theoretical methods complement each other in the process of developing sets of electron collision cross sections for atoms and molecules.

The transport coefficients for electrons moving in a gas under the influence of an externally applied electric field are related in a complicated and highly nonlinear manner to the collision cross sections via Boltzmann's integro-differential equation. The development of techniques for solving Boltzmann's equation for the energy distribution $f(\epsilon)$ of electrons in a gas has enabled us to derive cross sections from measured transport coefficients (Shkarofsky *et al* 1966, Huxley and Crompton 1974). The first sophisticated application of Boltzmann's equation was performed in 1915 by Lorentz for the problem of electron transport in metals. He expanded the velocity distribution function in terms of two spherical harmonics

$$f(v) = f_0(v) + \frac{v}{v} \cdot f_1(v).$$

In 1916 Pidduck applied this technique to solving Boltzmann's equation for the transport of electrons in a gas.

Much progress in measurement technique and in analysis was made in the field from the 1920s to the 1940s by people such as Townsend, Ramsauer, Davydov, Druyvesteyn, Allis and Huxley. Digital computers were developed in the 1940s as was the field of numerical mathematics that enabled the application of computing machines to problems in physics and chemistry. By the early 1960s digital computers had become available to many university and industrial scientists. This was the technology that enabled A V Phelps and his coworkers (Frost and Phelps 1962, Phelps 1968) at the Westinghouse Research Laboratories to make another significant advance in swarm analysis.

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Applying the two-term spherical harmonic approximation to Boltzmann's transport equation, neglecting spatial and temporal effects, and reducing the collision integral to a manageable form yields the following second-order differential equation for $f_0(\epsilon)$ (Shkarofsky *et al* 1966, Huxley and Crompton 1974, Frost and Phelps 1962):

$$\begin{aligned}
&\tfrac{1}{3}(eE/N)^2 \mathrm{d}/\mathrm{d}\epsilon\{\epsilon/\sigma_\mathrm{m} \mathrm{d}f_0/\mathrm{d}\epsilon\} \\
&\quad + \mathrm{d}/\mathrm{d}\epsilon\{(2m\sigma_\mathrm{m}/M)\epsilon^2(f_0(\epsilon) + kT\,\mathrm{d}f_0/\mathrm{d}\epsilon)\} \\
&\quad + \sum_i \delta_0[(\epsilon+\epsilon_i)\sigma_i(\epsilon+\epsilon_i)f_0(\epsilon+\epsilon_i) - \epsilon\sigma_i(\epsilon)f_0(\epsilon)] \\
&\quad - \sum_i \delta_i(g_0/g_i)[(\epsilon-\epsilon_i)\sigma_i(\epsilon-\epsilon_i)f_0(\epsilon-\epsilon_i) \\
&\quad + \epsilon\sigma_i(\epsilon)f_0(\epsilon)]. \qquad (1)
\end{aligned}$$

The electron impact cross sections involved are $\sigma_\mathrm{m}(\epsilon)$, the momentum transfer cross section, and $\{\sigma_i(\epsilon)\}$, the set of cross sections for transitions from the ground state to the various excited states $\{i\}$. δ_0 and δ_i are the fractional populations of the ground and excited states and g_0 and g_i are their respective statistical weights, which enter the equation when the principle of detailed balance is used to obtain de-excitation (superelastic) rates in terms of the excitation (inelastic) cross sections. Equation (1), about which much has been written over the years, consists of terms describing electron energy loss due to elastic collisions with gas molecules, energy gain due to the electric field, energy gain due to the gas molecules having temperature T, energy loss due to inelastic collisions which cause transitions to the excited states of the gas molecules and energy gain due to superelastic collisions (also known as collisions of the second kind) which cause de-excitation of excited molecular states.

Frost and Phelps (1962) used a digital computer to numerically solve this equation for an accurate distribution function and were able to develop a set of cross sections for H_2 and N_2 consistent with measured swarm data. Prior to the use of electronic computers the inelastic and superelastic terms were either ignored or dealt with in a very approximate manner. The work of Frost and Phelps began an era that has given us very accurate momentum transfer and lower-energy (rotational and vibrational) inelastic cross sections that have been derived from measurements of the drift and diffusion of electron swarms in gases. There have been a number of refinements and advances in techniques for dealing with Boltzmann's equation, as well as refinement of the measurement techniques to very high accuracy by Crompton, Elford and others at the Australian National University. The methodology for obtaining cross sections from swarm measurements has nevertheless remained the same; this methodology has been reviewed by Phelps (1968, 1987) and by Huxley and Crompton (1974).

The cross sections are fundamental quantities depending only on the energy of the incident electron and the particular initial and final atomic or molecular states. The swarm parameters, such as drift velocity, diffusion coefficients and excitation coefficients, are derived quantities depending on the local environment of the electron swarm. They are integrals over the product of a cross section and the energy distribution $f_0(\epsilon)$ of the electrons, which is the solution to Boltzmann's transport equation. Boltzmann's equation, via the probability density function $f_0(\epsilon)$, is a microscopic description of the behaviour of electrons in a gas and is related via certain integrals to macroscopic transport coefficients that can be measured. The two most commonly measured transport coefficients are the drift velocity, v_d, and the transverse diffusion coefficient, D_T, which are related to $f_0(\epsilon)$ and the momentum transfer cross section, $\sigma_\mathrm{m}(\epsilon)$ by the following:

$$\begin{aligned}
v_\mathrm{d} = &-\tfrac{1}{3}(2e/m)^{1/2}(E/N) \\
&\times \int_0^\infty (\sigma_\mathrm{m}(\epsilon))^{-1}(\mathrm{d}f_0/\mathrm{d}\epsilon)\epsilon\,\mathrm{d}\epsilon \qquad (2a)
\end{aligned}$$

$$D_\mathrm{T} = \tfrac{1}{3}N(2e/m)^{1/2}\int_0^\infty (\sigma_\mathrm{m}(\epsilon))^{-1}f_0(\epsilon)\epsilon\,\mathrm{d}\epsilon. \qquad (2b)$$

The drift velocity and diffusion coefficient sample different aspects of $f_0(\epsilon)$ and, hence, represent two somewhat independent pieces of information. Generally the quantity D_T/μ, the *characteristic energy*, is reported in the literature, rather than D_T itself. For a Maxwellian distribution of electrons, where $f_0(\epsilon) \propto \exp(-\epsilon/kT_\mathrm{e})$ an electron temperature, T_e, can be defined and Einstein's relation $D_\mathrm{T}/\mu = kT_\mathrm{e} = 2\langle\epsilon\rangle/3$ holds. Since the mean electron energy $\langle\epsilon\rangle$ is not a measurable quantity (it is usually computed by solving Boltzmann's equation), the characteristic energy is generally the only measure of electron energy that we have.

Equation (1) does a remarkably good job of describing the transport of electrons under the influence of an electric field in most gases. This equation, or a more sophisticated version that goes beyond the two-term expansion (for a summary of the state of the art see Pitchford *et al* (1990)), is repeatedly solved in an iterative process whereby one develops a set of cross sections given a collection of transport coefficients. One inserts model cross sections into the collision terms of Boltzmann's equation, calculates $f(\epsilon)$ and the swarm coefficients, alters the model cross sections and iterates until an acceptable match between measured and computed swarm coefficients is found. Clearly this iterative process is very labour intensive. The experience of the researcher plays an important role comparable to that of the specific computational techniques used.

The use of numerical optimization algorithms has been previously investigated (Morgan 1991a, b) as a means of obtaining cross sections from electron swarm data. The techniques investigated include the downhill *simplex* (Morgan 1991a) and an artificial *neural network* (Morgan 1991b). The numerical technique used in this work is a multidimensional minimization algorithm called a downhill or creeping simplex. This algorithm manipulates the energy dependence of cross sections in order to minimize the difference between computed and measured transport coefficients. The iteration process is as described above, but now a numerical optimization algorithm has replaced the person modifying cross sections by hand. The enabling technology for this approach is the existence of fast workstations, which have the computational speed of supercomputers at a small fraction of the cost.

The simplex algorithm has been applied to the problem of obtaining the momentum transfer, $j = 0 \rightarrow 2$ rotational, and $v = 0 \rightarrow 1$ vibrational cross sections in para-hydrogen. Para-hydrogen was chosen because the $j = 1$ and $j = 3$ rotational levels do not exist leaving $j = 0 \rightarrow 2$ and $v = 0 \rightarrow 1$ as the only accessible collisional channels for electrons of energy less than about 1.5 eV.

Hydrogen, the simplest of the molecular gases, has been the subject of electron collision research for many years. It has been a test subject for theoretical calculations, beam measurements, and swarm techniques that has allowed refinement and comparison of these techniques. The recent history of swarm analysis of electrons in hydrogen has been discussed by Crompton and Morrison (1987), Morrison *et al* (1987) and Buckman *et al* (1990). H_2 has been studied in great depth from a swarm perspective by the research group at the Australian National University. Their most recent fit of the momentum transfer (σ_m), rotational (σ_r), and vibrational (σ_v) cross sections for hydrogen are reported by England *et al* (1988).

H_2 is still of great interest to the atomic and molecular physics community because of the well known discrepancy between the swarm-derived, the beam-measured and the theoretical cross sections for excitation of $H_2(v = 1)$. The cross section as measured by electron beam methods, with which the computed cross section is in agreement, is some 60% larger than the swarm-derived cross section (Buckman *et al* 1990).

This paper is not an attempt to resolve the cross section controversy, but a demonstration of a new computational approach to swarm analysis that also shows that the swarm-derived cross sections of England *et al* (1988) are indeed very close to the best numerical fit to the measured swarm coefficients. It provides no new information with regard to the vibrational cross section issue since the same form of Boltzmann's equation has been solved and the same swarm data used as in previous analyses.

2. The downhill simplex algorithm

The downhill or creeping simplex algorithm (Nelder and Mead 1965, Press *et al* 1986) is a very versatile method for optimization problems of the kind where we desire to find the minimum of a function of n variables, $y = f(x_1, \ldots, x_n)$. A significant advantage of this technique is that the derivatives of the function being minimized are not needed. We can think of the function $f(x_1, \ldots, x_n)$ as defining an n-dimensional surface in a space of $n + 1$ dimensions. $n + 1$ points on this surface then define what is called a *simplex*.

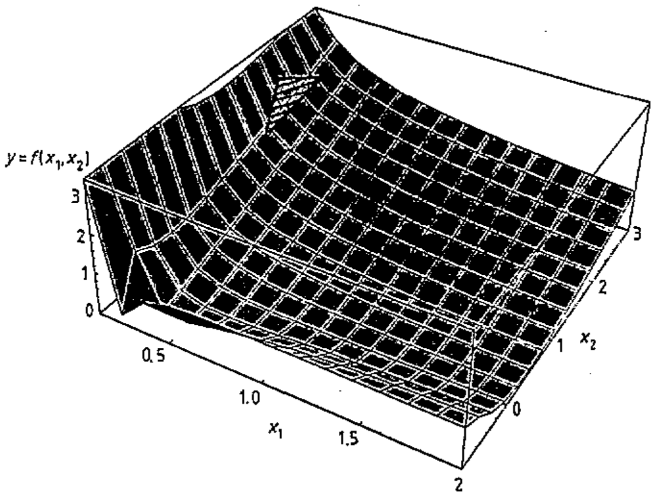

Figure 1. Planar simplex on a three-dimensional surface $y = f(x_1, x_2)$.

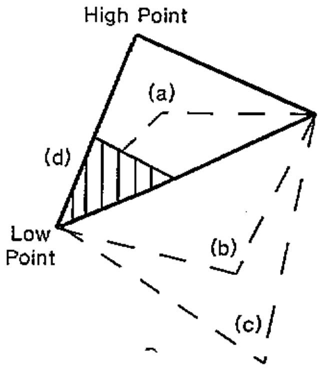

Figure 2. Simplex transformations: (*a*) a contraction away from the high point; (*b*) a reflection; (*c*) a reflection and expansion; (*d*) a contraction in all dimensions toward the low point.

In figure 1 is shown a picture of a surface defined by $y = f(x_1, x_2)$; it is easy to see that this simplex is a triangle, i.e. the three (non-collinear) points (x_1^0, x_2^0, y^0), (x_1^1, x_2^1, y^1) and (x_1^2, x_2^2, y^2) determine two lines that define a plane in three dimensions. This simplex, or n-dimensional plane, is moved around on the surface using several transformation rules Specifically, it can be made to follow the contours of the surface always moving 'downward' toward the lowest point. The transformation rules are depicted in figure 2, which is based on a similar figure in Press *et al* (1986). The possible transformations comprise: (a) a contraction away from the high point; (b) a reflection; (c) a reflection and expansion; (d) a contraction in all dimensions toward the low point. Each iteration typically begins with operation (c), which is followed by operation (d) if successful. Operations (a) and then (d) follow. Linear combinations of the points in the simplex, the best and worst points, and the average of all the points are used in performing the transformations on the simplex. This ensures that initially smooth functions (i.e. the cross sections in our case) remain smooth functions throughout the minimization process. The result of these transformations is that the simplex will creep downhill toward the minimum of the surface. The simplex moves rapidly on steep surfaces. It may take a great number of moves to reach the minimum on a very gentle surface, such as the 'rain gutter' part of the surface shown in figure 1, where x_1 is large and $0 < x_2 < 1$. The surface in figure 1 is actually taken from a test calculation in which I was fitting a cross section of the form $\sigma(\epsilon; x_1, x_2) = x_1\epsilon^{-x_2}$ to drift velocity 'data' computed using $\sigma_{\rm ccf}(\epsilon) = \sigma_0\epsilon^{-1/2}$, the constant collision frequency cross section. It represents the squared difference in drift velocities (equation (2*a*)),

$$y = (v_{\rm d}[\sigma_{\rm ccf}(\epsilon); E/N] - v_{\rm d}[\sigma(\epsilon; x_1, x_2); E/N])^2$$

for one value of E/N. Thus the minimum $y = 0$ in the surface is at $x_1 = \sigma_0$ and $x_2 = -1/2$.

We set up the simplex algorithm by making an initial guess $y^0 = f(x_1^0, x_2^0, \ldots, x_n^0)$ for the minimum and generating n other guesses using a transformation, such as $y^i = y^0 + \lambda_i e_i$ where e_i is a unit vector. This yields an $(n+1)$-dimensional simplex that is then manipulated to minimize $f(x)$. Ideally, the final result (to within machine precision) is $y_{\rm min} = y^0 = y^1 = \ldots = y^n$ and $x_{\rm min} = x^0 = x^1 = \ldots = x^n$. That is, the simplex reduces to a point on the surface.

When this method is applied to the many-dimensional problem of obtaining cross sections from swarm data, what we minimize is the squared difference between measured transport coefficients and those computed using the cross sections that define the simplex being manipulated. If $v_{\rm d}$ and $D_{\rm T}/\mu$ are the measured electron drift velocity and characteristic energy, respectively, and w and $\epsilon_{\rm k}$ are their computed counterparts for a range of values of E/N, the function to be minimized is:

$$\chi^2 = \sum_j \left[\left(\frac{w[(E/N)_j] - v_{\rm d}[(E/N)_j]}{v_{\rm d}[(E/N)_j]} \right)^2 + \left(\frac{\epsilon_{\rm k}[(E/N)_j] - D_{\rm T}/\mu[(E/N)_j]}{D_{\rm T}/\mu[(E/N)_j]} \right)^2 \right]. \qquad (3)$$

There are $n + 1$ values of χ^2, each corresponding to one of the $n + 1$ sets of cross sections being manipulated and each being a vertex of the simplex. The set $\{\chi_i^2\}$ corresponds to the set $\{y^i\}$ above and each set of cross sections $\sigma^i = (\sigma_1^i, \sigma_2^i, \ldots, \sigma_n^i) = (\sigma^i(\epsilon_1), \sigma^i(\epsilon_2), \ldots, \sigma^i(\epsilon_n))$ corresponds to an x^i belonging to the set $\{x^i\}$ with $1 \leqslant i \leqslant n + 1$.

The initial simplex is defined by choosing $n + 1$ trial cross section sets. Each cross section set is then used to compute a distribution function $f_0(\epsilon)$, a set of drift velocities $w[(E/N)_j]$, and characteristic energies $\epsilon_k[(E/N)_j]$ for a number of values of $(E/N)_j$. The function χ^2 is then minimized as described above. The final result is the cross section set $\{\sigma(\epsilon_i)\}$, $1 \leqslant i \leqslant n$, associated with the final simplex.

3. Calculations

Calculations have been performed using the technique described above for $\sigma_{\rm m}(\epsilon)$, $\sigma_{\rm r}$ ($j = 0 \rightarrow 2$), and $\sigma_{\rm v}$ ($v = 0 \rightarrow 1$) in para-hydrogen over the energy range from 0 to 1.5 eV. The swarm coefficients, which cover a range of E/N from 0.002 Td to 6 Td, have been measured at a temperature of 77 K by Robertson (1971) ($v_{\rm d}$) and Crompton and McIntosh (1968) ($D_{\rm T}/\mu$). For $E/N < 0.008$ Td we have only characteristic energy data. In all 46 values of E/N were used in these calculations. Boltzmann's equation was used in the two-term form given in equation (1) including $j = 2 \rightarrow 0$ superelastic collisions. The solution technique is that described by Rockwood (1973) (see also Morgan and Penetrante 1990). The finite differencing of equation (1) was performed on a 200-point energy grid. Further discussion of aspects of solving Boltzmann's equation will appear below.

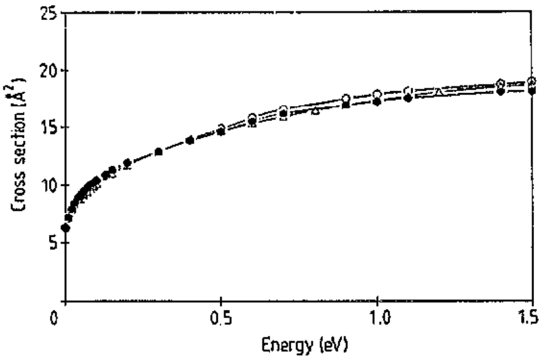

Figure 3. H_2 momentum transfer cross section: ○, present simplex results; ●, results from swarm analysis by England *et al* (1988); Δ, theory (Morrison *et al* 1987).

The number of energy points used in the cross section determination was 25 for momentum transfer, 26 for rotation and 13 for vibration between zero or the inelastic threshold and 1.5 eV; 64 points in all. The simplex then consists of the function χ^2 of equation (3) at $n + 1 = 65$ independent points. The initial simplex was generated by randomizing the H_2 cross sections published by England *et al* (1988). The cross sections $\sigma_{\rm m}(\epsilon)$, $\sigma_{\rm r}(\epsilon)$ and $\sigma_{\rm v}(\epsilon)$ were multiplied by a quadratic function $\alpha\epsilon^2 + \beta\epsilon + \gamma$ having random coefficients α, β and γ. In this way 65 independent sets of smooth cross sections were generated. The calculation then proceeded with the 65 cross section vectors being manipulated as described above in order to shrink the 64-dimensional hyperplane defined by the values of χ^2 to a point at the minimum of the hypersurface. The criterion for stopping the calculation was that the difference between the maximum and minimum χ^2 be less than one part in 10^5. The results of this minimization procedure are shown in figures 3–5.

In figure 3 the momentum transfer cross section determined by the simplex algorithm along with the England *et al* (1988) swarm-derived cross section and the cross section computed by Morrison *et al* (1987) are plotted. The three results are nearly indistinguishable. Figure 4 shows the $j = 0 \rightarrow 2$ rotational excitation cross sections as in figure 1. Above the 0.52 eV threshold for $v = 0 \rightarrow 1$ excitation England *et al* used the theoretical rotational cross section computed by Morrison *et al*, so those curves are identical. The simplex algorithm, which is unconstrained, yields a somewhat

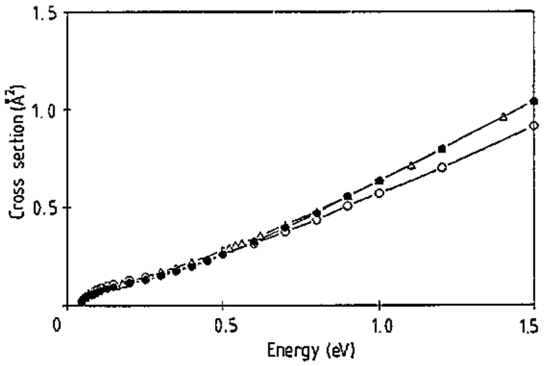

Figure 4. $H_2(j = 0 \to 2)$ rotational excitation cross section: ○, present simplex results; ●, results from swarm analysis by England *et al* (1988); △, theory (Morrison *et al* 1987).

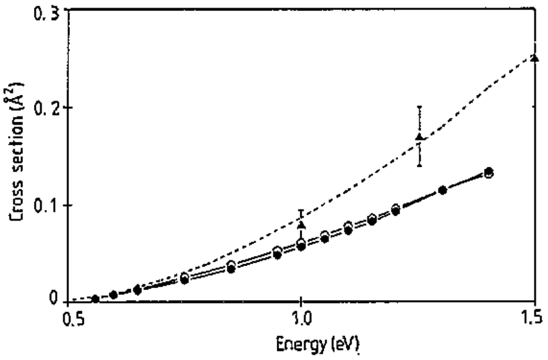

Figure 5. $H_2(v = 0 \to 1)$ vibrational excitation cross section: ○, present simplex results; ●, results from swarm analysis by England *et al* (1988); – – –, theory (Buckman *et al* 1990); △, beam measurements (Buckman *et al* 1990).

smaller cross section although the effects of the difference on the computed swarm coefficients is very small. Figure 5 shows the $v = 0 \to 1$ vibrational cross sections determined by the simplex algorithm, derived from swarm data by England *et al*, measured by Buckman *et al* (1990) and computed theoretically (Buckman *et al* 1990). We see extremely good agreement between the two swarm determinations; the difference between these and the results obtained in beam measurements and by theory is large by comparison.

The fractional differences between the computed values of drift velocity and characteristic energy and the measurements are shown in figures 6(*a*) and 6(*b*). The absolute error bars claimed for these data are 1% for v_d and 2% for D_T/μ. The point is made that the relative errors among the v_d points and among the D_T/μ points are much smaller. We see that, except at the lowest values of E/N, the swarm coefficients lie within one or two per cent of the measurements. The final RMS difference between the calculations and the measurements was 1.71%. At the smallest E/N the optimization algorithm tends to adjust the cross sections in such a way that all the drift velocities are somewhat high and the characteristic energies are somewhat small. In the simplex calculations χ^2 was computed with drift velocities and characteristic energies weighted equally, as shown in equation (3). Since we have an estimate of the experimental uncertainties it may be a reasonable procedure in future calculations to weight the contributions of the swarm coefficients by the reciprocals of their uncertainties.

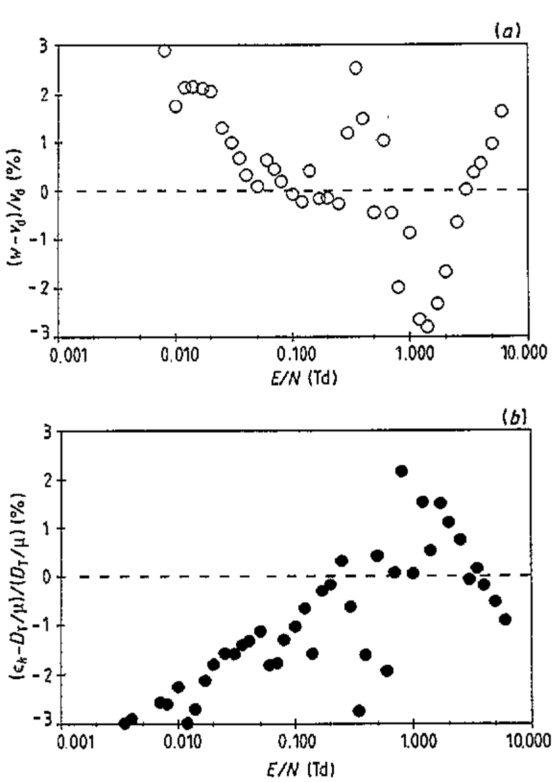

Figure 6. Fractional differences (*a*) between drift velocities and (*b*) between characteristic energies computed using simplex derived cross sections and swarm measurements.

4. Discussion

These computational results demonstrate that a numerical optimization algorithm, coupled with an appropriate routine to solve Boltzmann's equation, can yield accurate cross sections for multiple inelastic processes. That it can give very accurate momentum transfer cross sections when elastic scattering is the only process has been shown elsewhere for argon (Brennan and Morgan 1992). The potential and limitations of this technique are still being explored.

Because a calculation may entail numerically solving Boltzmann's equation thousands and even tens of thousands of times, that is the part of the calculation that determines the computing time needed. Where superelastic collisions do not need to be included in the calculation, and where the two-term approximation is adequate, we can perform a direct numerical integration of Boltzmann's equation using the backward prolongation technique (Frost and Phelps 1962). This is quite fast and very accurate. Superelastic collisions are more problematical. The method used in these calculations is a matrix formulation devised by Rockwood (1973). Most of the time spent in such a calculation is in computing the matrix coefficients that arises from the finite differencing of Boltzmann's equation. Consequently the computational time is proportional to the square of the number of points on the energy grid. Since the numerical errors diminish as we add more points to the energy grid, the choice of grid size is determined by balancing the acceptable accuracy against the acceptable calculational time. An additional factor is the speed of the computer being used. Small calculations using backward prolongation or direct integration can be performed in hours to tens of hours on a fast personal computer. Calculations with very accurate solutions of Boltzmann's equations (several thousand energy points) and multiple cross sections take hours to tens of hours on a workstation. The calculations presented here took a total of about 50 hours of processor time on two different workstations. The first 20 hours were run on an HP-730 and the last 30 on a DEC-5000, the latter being about 40% as fast as the former. The limiting time was the time required to solve Boltzmann's equation. The advantage of not having to include superelastic collisions can be seen from the following comparison: a 500-point solution of Boltzmann's equation on the HP-730 takes 0.1 s per value of E/N using backward prolongation and 3 s per E/N using the matrix solution. It is possible that an iterative solution of Boltzmann's equation, such as that devised by Gibson (1970), which can treat superelastic collisions, may be faster than the matrix solution.

In addition to the downhill simplex the use of other optimization algorithms for obtaining cross sections from swarm data has been explored. These include simulated annealing (Kirkpatrick *et al* 1983, Kirkpatrick 1984, Press, *et al* 1986), which is based on the celebrated Metropolis algorithm for Monte Carlo simulation of a canonical ensemble, and artificial neural networks (Hertz *et al* 1991, Morgan 1991b). Simulated annealing is, in principle, capable of solving any minimization problem but is frequently quite slow, as has been found for this type of problem. Neural networks, specifically feed-forward, back-propagation networks, are machine learning algorithms based on notions of how human brains work. They are frequently finding use in pattern recognition problems. The relationship between transport coefficients and cross sections can be cast as such a problem (Morgan 1991b). Such networks can be trained to recognize the relationship between $\sigma(\epsilon)$ and the pair of $v_d(E/N)$ and $D_T/\mu(E/N)$ for a number of different cross section functional forms and a range of E/N so that when presented with swarm data not in the training set they can give a reasonable estimate of the energy-dependent cross section. This technique has only been tested on some very simple cases and requires much more research. At present the downhill simplex is the most highly developed, robust and fastest of the optimization algorithms that might be applied to this problem.

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References

Brennan M J and Morgan W L 1992 in preparation

Buckman S J, Brunger M J, Newman D S, Snitchler G, Alston S, Norcross D W, Morrison M A, Saha B C, Danby G and Trail W K 1990 *Phys. Rev. Lett.* **65** 3253–6

Crompton R W and McIntosh A I 1968 *Aust. J. Phys.* **21** 637–47

Crompton R W and Morrison M A 1987 *Swarm Studies and Inelastic Electron–Molecule Collisions* ed L C Pitchford *et al* (New York: Springer) pp 143–66

England J P, Elford M T and Crompton R W 1988 *Aust. J. Phys.* **41** 573–86

Frost L S and Phelps A V 1962 *Phys. Rev.* **127** 1621–33

Gibson D K 1970 *Aust. J. Phys.* **23** 683–96

Hertz J, Krogh A and Palmer R G 1991 *Introduction to the Theory of Neural Computation* (Redwood City, CA: Addison-Wesley)

Huxley L G H and Crompton R W 1974 *The Diffusion and Drift of Electrons in Gases* (New York: Wiley)

Kirkpatrick C D 1984 *J. Stat. Phys.* **34** 975–86

Kirkpatrick C D, Gelatt C D and Vecchi M P 1983 *Science* **220** 671–80

Morgan W L 1991a *Phys. Rev.* A **44** 1677–81

—— 1991b *IEEE Trans. Plasma Sci.* **19** 250–5

Morgan W L 1992 *Plasma Chemistry and Plasma Processing* in press; also 1991 *JILA Data Center Report* No 34 University of Colorado

Morgan W L and Penetrante B 1990 *Comput. Phys. Commun.* **58** 127–52

Morrison M A, Crompton R W, Saha B C and Petrović Z Lj 1987 *Aust. J. Phys.* **40** 239–81

Nelder J A and Mead R 1965 *Comput. J.* **7** 308–13

Phelps A V 1968 *Rev. Mod. Phys.* **40** 399–410

—— 1987 *Swarm Studies and Inelastic Electron–Molecule Collisions* ed L C Pitchford *et al* (New York: Springer) pp 127–41

Pitchford L C, Boeuf J P, Segur P and Marode E 1990 *Nonequilibrium Effects in Ion and Electron Transport* ed J W Gallagher *et al* (New York: Plenum) pp 1–9

Press W H, Flannery B P, Teukolsky S A and Vetterling W T 1986 *Numerical Recipes* (Cambridge: Cambridge University Press) pp 288–93

Robertson A G 1971 *Aust. J. Phys.* **24** 445–9

Rockwood S D 1973 *Phys. Rev.* A **8** 2348–58

Shkarofsky I P, Johnston T W and Bachynski M P 1966 *The Particle Kinetics of Plasmas* (Reading, MA: Addison-Wesley)