Calculation to a prescribed accuracy of the transport cross sections for collisions between structureless particles

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Abstract. Careful analysis of multiple orbiting for collisions in classical mechanics shows that a larger impact parameter does not necessarily result in a larger orbiting separation. To take such possibilities into account, a new computer program has been developed for calculating the transport cross sections when a potential energy curve is supplied as a table of points. It is shown that the new program is superior to those used previously, but that it is not necessary to redo results obtained over the past 25 years in situations where transport cross sections were obtained to the requested accuracy by the previous programs.

1. Introduction
There are several methods [1] for determining gaseous ion transport coefficients over wide ranges of the gas temperature, $T_0$, and the ratio, $E/n_0$, of the electric field strength to the gas number density. Similar methods are involved in determining the transport properties of neutral gases as functions of $T_0$ [2]. All of these methods depend upon calculating a set of transport cross sections, $Q^{(l)}(E)$, over wide ranges of the kinetic energy, $E$, for collisions between two structureless particles and for many $l \geq 1$. The first two cross sections are known as the momentum-transfer (or diffusion) and viscosity (or thermal conductivity) cross sections, respectively, but the others are unnamed because they arise only in corrections to the first-approximation formulas that are dominated by $Q^{(1)}(E)$ and $Q^{(2)}(E)$.

The transport cross sections are defined by the classical-mechanical expression [1]

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

or by an equivalent expression using Legendre polynomials of the cosine rather than powers. Here $b$ is the impact parameter and $\chi$ is the deflection angle defined by the expression [1]

$$\chi(b, E) = \pi - 2b \int_{r_{\text{m}}}^\infty \frac{dr}{r^2 \left[F(r, b, E)\right]^{1/2}}.$$

The lower limit on the integral in eq. (2) is the classical turning point, i.e., the largest, positive, real root of

$$F(r, b, E) = 1 - \frac{b^2}{r^2} - \frac{V(r)}{E} = 1 - \frac{V_{\text{eff}}(r)}{E}.$$

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It is through eq. (3) that the position-dependent interaction potential, \( V(r) \), affects the transport cross sections and hence the transport coefficients.

The \( Q^{(l)}(E) \) are single-valued functions of \( E \) for each integer value of \( l \). Following Smith and coworkers [3, 4], we adopt the condition that we must be able to specify a fractional error, \( \epsilon \), such that the final values of the \( Q^{(l)}(E) \) are known to be correct within this relative accuracy. Calculation difficulties arise because of singularities at or near the endpoints of the intervals of integration in eqs. (1) and (2), particularly when \( E, b \) and \( r \) are such that the colliding particles can orbit about one another indefinitely. These singularities are best understood in terms of the effective potential

\[
V_{\text{eff}}(r) = V(r) + \frac{Eb^2}{r^2}.
\]  

Orbiting can only occur at energies smaller than some critical value, \( E_c \), that depends upon the interaction potential. This is because larger values of \( E \) mean that the \( V(r) \) term in eq. (4) is negligible compared to the other term. Eq. (3) shows that, for orbiting to occur, there are three conditions that must be satisfied by the effective potential at an orbiting energy \( E_o < E_c \), an orbiting separation, \( r_o \), and an orbiting impact parameter, \( b_o \). They are \( V_{\text{eff}}(r_o) = E_o > 0 \), \( V'_{\text{eff}}(r_o) = 0 \), and \( V''_{\text{eff}}(r_o) < 0 \). The second condition can be shown from eq. (4) to mean that \( E_0 b_o^2 = \frac{1}{2} r_o^3 V'(r_o) \). Hence the first and the third conditions become \( E_0 = V(r_o) + \frac{1}{2} r_o V'(r_o) > 0 \) and \( V''(r_o) + 3r_o^{-1}V'(r_o) < 0 \).

Orbiting difficulties are further complicated by the phenomenon of multiple orbiting discovered by Rainwater et al. [5]. Here there are two or more pairs, \( (b_o, r_o) \), for a particular orbiting energy. Multiple orbiting was considered by one of the present authors shortly after its discovery [6, 7], in the context of numerical rather than functional potentials, i.e., in the situation where the interaction potential is supplied as a tabulated set of points, \( (V, r) \). However, it has been assumed in all of the work on multiple orbiting to date that the orbiting impact parameter always increases when the orbiting separation increases. While this is ordinarily the case, we have found situations for numerical potentials where the reverse is true over small regions of orbiting energy. The exceptions can be understood by comparing the derivatives of \( b_o \) and \( E_o \) with respect to \( r_o \): it is found that

\[
\frac{db_o}{dr_o} = \frac{r_o^2 V'(r_o)}{2E_o b_o} \frac{dE_o}{dr_o}.
\]  

When multiple orbiting occurs, \( V(r_o) \) must be negative but it is possible for \( dE_o/dr_o \) to have either sign; hence \( db_o/dr_o \) can be negative in some regions. This possibility seems to have been overlooked in previous discussions of the calculation of the transport cross sections and contradicts the general assertion by Rainwater et al. [5] that "the larger of the two impact parameters [at the same \( E_o \)] is associated with the larger orbiting radius" and similar but more specific claims by Smith and Munn [3].

We have written a new computer program, PC, that uses the Clenshaw-Curtis method [8, 9, 10, 11, 12] for evaluating well-behaved integrals; this is the method introduced by O’Hara and Smith [4] for evaluating eqs. (1)-(3). Compared to program QVALUES [6, 7], it more carefully handles multiple orbiting for tabulated potentials. Another improvement is that it uses cubic splines to interpolate between the tabulated points on the potential energy curve, rather than a variable-point Lagrangian interpolation. The latter method was highly effective years ago, when only a limited number of potential energy values were tabulated and when the values often had rather large fluctuations in going from one separation to another. The present state of the art, however, is to obtain the potential energies at a large number of separations by CCSD(T) techniques [13] that use large basis sets extrapolated to the complete-basis-set limit, to correct the calculated energies for basis set superposition error, and to include spin-orbit coupling.
when appropriate. Consequently, it is now better to use cubic-spline interpolation among the tabulated potential values than to use Lagrangian interpolation. Direct comparisons with a recent potential for Cl\textsuperscript{−} interacting with He [15] has shown that there is excellent agreement (within 1 ppm) in most of the tabulated range of separations, but that the use of a clamped cubic spline gives better results near the ends.

2. Calculation and Comparison

It is possible to compute derivatives of a function by differentiating the Lagrangian interpolation function. For numerical potentials, however, this can lead to unphysical oscillations, due to small errors in the tabulated potential points or to use of a higher-order Lagrangian than is warranted by the precision and number of points. Hence program PC computes potential derivatives in a different manner that is more efficient and more accurate. For separations above the last tabulated value, which is assumed to lie on the known long-range potential, it uses analytical derivatives of this asymptotically-correct function. For separations below the first tabulated value, which must lie on the repulsive wall of the potential, it uses the derivative of an inverse-power potential that matches the first two tabulated points. For intermediate separations, it uses the coefficients computed by the cubic spline to evaluate the first (and, when necessary, second) derivative in a manner [14] similar to that used to evaluate the potential at intermediate separations. The cubic spline is clamped so that it matches the derivatives at separations smaller and larger than the tabulated points. The potential and first derivative are forced by the cubic spline to be smooth and continuous at each tabulated separation, while the second derivative is only continuous.

We have used program PC to obtain the orbiting parameters for Cl\textsuperscript{−} colliding with He, using an as-yet unpublished potential [15]. The results are compared in Figs. 1-3 with those obtained from the same potential using program QVALUES [7]. Fig. 1 shows that the differences in the interpolations used in PC and QVALUES lead to slight differences in the orbiting energies at small \(r_o\), i.e. for energies near \(E_c\). More significant is the occasional abrupt rise or fall shown by the QVALUES results at certain separations; such abrupt changes are also shown by the \(b_0\) values in Fig. 2. Abrupt changes have long been observed [4], and special techniques have been employed in previous programs to make small changes to \(r_o\) to avoid them; such techniques are unnecessary in PC. Fig. 3 shows that for this potential for Cl\textsuperscript{−} in He, \(E_o\) is very nearly a single-valued function of \(b_0\). Multiple orbiting occurs only between \(6.64 \times 10^{-5}\) and \(7.27 \times 10^{-5}\) hartree (Fig. 4) and between \(0.96 \times 10^{-5}\) and \(1.00 \times 10^{-5}\) hartree (not shown).

![Figure 1](image1.png)  
**Figure 1.** Orbiting energy, \(E_0\) in hartree, as a function of the orbiting separation, \(r_0\) in bohr, for Cl\textsuperscript{−} collisions with He as computed using the new program, PC, and the older program, QVALUES [7].

![Figure 2](image2.png)  
**Figure 2.** Orbiting impact parameter, \(b_0\) in bohr, as a function of the orbiting separation, \(r_0\) in bohr, for Cl\textsuperscript{−} collisions with He as computed using the new program, PC, and the older program, QVALUES[7].
Figure 3. Orbiting impact parameter, $b_0$ in bohr, as a function of the orbiting energy, $E_0$ in hartree for Cl$^-$ collisions with He as computed using the new program, PC, and the older program, QVALUES [7].

Figure 4. The orbiting parameters obtained by program QVALUES do not show multiple orbiting, following the PC results in multiple orbiting in the energy range between $6.64 \times 10^{-6}$ to $7.27 \times 10^{-6}$ hartree.

As can be seen in Fig. 4, multiple orbiting for Cl$^-$ in He was detected by PC but not by QVALUES. This is a result of more careful and more consistent treatment of the potential and its derivatives in PC. We note, however, that the fact that multiple orbiting occurs here only over two small energies regions implies that it makes only a small effect on the cross sections, which involve integrations over wide ranges of impact parameter, and an even smaller effect on the transport properties, which involve energy averages of the cross sections. Hence it is not necessary to redo results obtained over the past 25 years with QVALUES in situations where transport cross sections were obtained to the requested accuracy.

Finally, program PC is designed to work with tabulated potentials for neutral systems, where the long-range potential varies as the inverse-sixth power of the separation, and for atomic ion-atom systems, where it varies as the inverse fourth power. It also works with potentials that vary as the inverse-third power and where there is both a minimum and a long-range maximum; such potentials represent molecular ion-neutral systems where all of the angles are fixed. In further work we will investigate the latter situation more extensively, in the context of the Monchick-Mason approximation [16].

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