

Calculation of absolute scattering phase shifts

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Use of a simple semiclassical estimate of Bessel function phase for arbitrary argument avoids the modulo π errors which the conventional approach tends to introduce into the calculation of absolute quantal phase shifts for high partial waves. This has significant implications for the direct quantum mechanical calculation of second virial coefficients at high temperatures.

1. Introduction

Scattering phase shifts are central to a quantum mechanical description of scattering cross-sections and a host of dilute gas virial and transport properties which are governed by molecular collision behaviour [1–3]. For an intermolecular collision at energy E with angular momentum quantum number ℓ between two particles with reduced mass μ which interact through the intermolecular potential energy function $V(r)$, the effective radial Schrödinger equation is

$$-\frac{d^2\psi}{dr^2} + \left\{ \frac{2\mu}{\hbar^2} [V(r) - E] + \frac{\ell(\ell+1)}{r^2} \right\} \psi = 0. \quad (1)$$

If the zero of energy is set at the asymptote of the potential energy function, so that $\lim_{r \rightarrow \infty} [V(r)] = 0$, the asymptotic form of the radial wavefunction is

$$\psi(r) \simeq \sin(kr + \eta_\ell - \ell\pi/2) \quad (2)$$

in which $k = (2\mu E/\hbar^2)^{1/2}$ and $\eta_\ell = \eta_\ell(E)$ is the scattering phase shift [4–6].

The quantum mechanical expressions for the cross-sections associated with elastic scattering and most non-ideal gas properties only depend on terms such as $\sin(2\eta_\ell)$ or $\sin^2(\eta_\ell)$, and hence only require an accurate knowledge of phase shifts to within a modulo of π . A noteworthy exception, however, is the interaction second virial coefficient (for non-identical particles),

which is given by the expression [1, 3, 7]

$$B_{12}(T) = -\frac{N_A A^3}{2} \left(\sum_{v,\ell} (2\ell+1) [\exp[-E_{v,\ell}/(k_B T)] - 1] + \frac{1}{\pi} \int_0^\infty dx \exp(-x) \sum_{\ell=0}^\infty (2\ell+1) \eta_\ell(E) \right) \quad (3)$$

in which the double sum over v and ℓ runs over all truly bound vibration-rotation levels (with energies $E_{v,\ell}$) supported by the potential, $x = E/(k_B T)$, N_A [mol⁻¹] is Avogadro's number and $A = [2\pi\hbar^2/(2\mu k_B T)]^{1/2}$ is the thermal de Broglie wavelength of the system. This dependence on the absolute phase shift qualitatively differentiates second virial coefficients from other non-ideal gas properties. This note addresses problems that may arise in accurate quantum mechanical virial coefficient calculations due to modulo π errors which can arise in certain applications of standard broadly accepted procedures for calculating quantal phase shifts.

2. Quantal phase shift calculations

For all positive energies, at distances large enough that the effective interaction potential $(2\mu/\hbar^2)V(r)$ is much smaller than the centrifugal term $\ell(\ell+1)/r^2$, the exact solution to equation (1) takes on the form [4]

$$\psi_\ell(r) \simeq kr [j_\ell(kr) \cos(\eta_\ell) - y_\ell(kr) \sin(\eta_\ell)] \quad (4)$$

in which $j_\ell(z)$ and $y_\ell(z)$ are spherical Bessel functions of the first and second kind, respectively [8].

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The asymptotic form of the spherical Bessel functions means that for the normal case in which $V(r)$ dies off faster than $1/r^2$, as $r \rightarrow \infty$ equation (4) collapses to equation (2). A quantal calculation of $\eta_\ell(k)$ requires one to numerically integrate the radial Schrödinger equation, equation (1), outward from $r = 0$ while using comparisons of that exact numerical solution with equation (4) to determine a converged value for $\eta_\ell(k)$. The conventional procedure for doing this stops the integration each time the wavefunction changes sign and interpolates to determine the precise position $r_{n,\ell} = r_{n,\ell}(E)$ of that node, where n is a node counter. If the potential $V(r)$ were precisely zero for all $r \geq r_{n,\ell}$ then the wavefunction in that region would be given by equation (4) and an associated apparent ‘local’ estimate of the phase shift would be obtained by setting equation (4) equal to zero and solving for η_ℓ :

$$\eta_\ell^{(n),\text{loc}} = \arctan\{j_\ell(kr_{n,\ell})/y_\ell(kr_{n,\ell})\}. \quad (5)$$

If these apparent phase shifts for two or three successive nodes agree to within a given tolerance, the phase shift is assumed to be converged [9].

This basic method of calculating quantal phase shifts usually requires the numerical integration of equation (1) to propagate to fairly large distances, which increases the computational expense and amplifies problems arising from cumulative errors in the numerical integration procedure. Munn *et al.* [10] showed that such problems are minimized if these purely quantal local phase shifts were supplemented by a semiclassical estimate of the additional phase correction due to the residual non-zero $V(r)$ function at distances beyond $r_{n,\ell}$. This yields the semiclassically corrected, total (relative) nodal phase shift expression

$$\eta_\ell^{(n),\text{rel}} = \eta_\ell^{(n),\text{loc}} + \int_{r_{n,\ell}}^{\infty} \left(\left[k^2 - \frac{2\mu}{\hbar^2} V(r) - \frac{\ell(\ell+1)}{r^2} \right]^{1/2} - \left[k^2 - \frac{\ell(\ell+1)}{r^2} \right]^{1/2} \right) dr. \quad (6)$$

While Munn *et al.* approximated this semiclassical phase integral by a simple analytic expression based on a single inverse-power-term approximation for the potential [10], it was later shown that a much better approach was to perform a direct numerical quadrature, and that as few as four quadrature points gave greatly accelerated convergence [11]. However, the net effect was the same as that of the basic quantal approach: overall relative phase shifts $\eta_\ell^{(n),\text{rel}}$ are calculated at successive wavefunction nodes until convergence is achieved.

3. Determining absolute phase shifts

The one significant shortcoming of the above procedure is that it only yields *relative* phase shifts defined to within a modulo of π , since the domain of the arctan function is only $(-\pi/2, +\pi/2)$. Equation (3) shows that this can present problems for virial coefficient calculations, since the integrand in the last term of equation (3) depends on the magnitude of η_ℓ , and not merely on $\sin^2(\eta_\ell)$ or $\sin(2\eta_\ell)$. The standard method of determining the multiple of π to add to the converged value of $\eta_\ell^{(n),\text{rel}}$ to give the correct absolute phase shift is to use a comparison of the exact absolute wavefunction phase (of $n\pi$) at node n , with an estimate for the phase in the modulus/phase expression for Bessel functions (see equations (9.2.17)–(9.2.20) of [8]) at that distance, $\Theta_\ell(kr_{n,\ell})$, corrected by the (relative) apparent local phase shift:

$$\eta_\ell^{\text{abs}} = \eta_\ell^{(n),\text{rel}} + \pi \left(n - \text{int} \left\{ \left[\Theta_\ell(kr_{n,\ell}) + \eta_\ell^{(n),\text{loc}} \right] / \pi \right\} \right), \quad (7)$$

where ‘int’ is a function which rounds its argument to the nearest integer.

The conventional way of estimating $\Theta_\ell(kr)$ is to approximate it by the first few terms of an asymptotic series expansion in $1/k$ using equation (9.2.29) of [8], yielding values denoted herein as $\Theta_\ell^{\text{ac}}(kr)$. That approach usually gives satisfactory results. However, in the course of performing calculations of interaction virial and diffusion coefficients for the $\text{D}_2\text{-Xe}$ system [12], we found that for high partial waves this approach can break down. For example, at a collision energy corresponding to a wavenumber of 1645 cm^{-1} , the absolute phase shifts obtained in this way have the behaviour illustrated by the dotted curves in figure 1; the implication of this (mis)behaviour for calculated virial coefficients is shown by the deviation between the solid and dotted curves in figure 2. This misbehaviour was only discovered because efforts to achieve very high precision led the calculations to be pushed to include very high numbers of partial waves; if a less restrictive convergence criterion had been applied, the existence of this problem would not have been evident.

In retrospect, the errors arising from use of the above approximation could have been foreseen by examining the behaviour of the error associated with the finite (to order $1/(kr)^7$) expansion for $\Theta_\ell^{\text{ac}}(kr_{n,\ell})$ of equation (9.2.29) of [8]. For small n and ℓ these errors are very small, but for $\ell > 13$ they are always negative and grow monotonically in magnitude. For a wide range of angular momenta ℓ and node numbers n ,

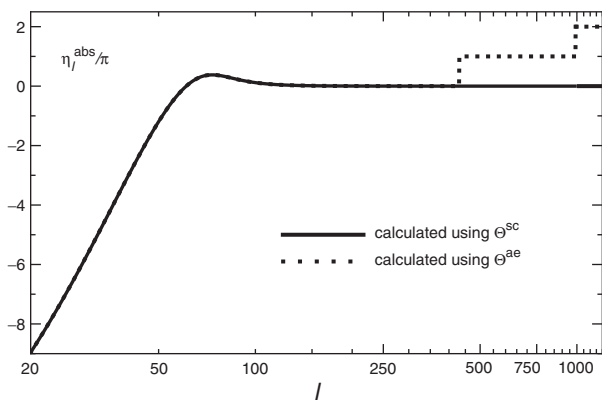


Figure 1. Absolute phase shifts for D_2 -Xe collisions at a collision energy of 1645 cm^{-1} on the isotropic part of the potential energy surface of [12], calculated using two different methods of determining the modulo of π in equation (7).

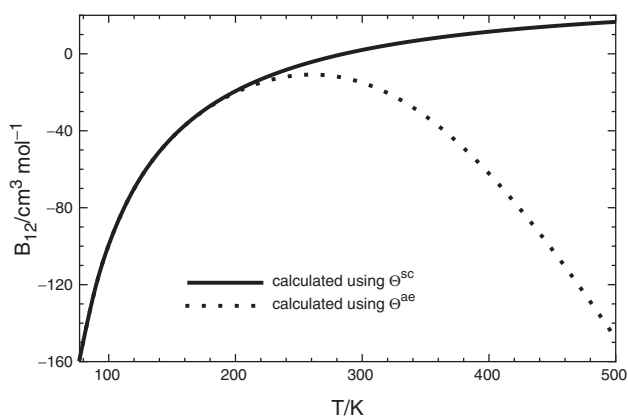


Figure 2. Virial coefficients for D_2 -Xe implied by the isotropic part of the potential energy surface of [12], as calculated from equation (3) using two different methods of determining the modulo of π in the absolute phase shifts of equation (7).

the dotted curves in figure 3 plot the magnitude of the errors in this approximation at a number of Bessel function nodes. The (dimensionless) values of $kr_{n,\ell}$ defining the exact positions of these nodes were determined by solving the Bessel differential equation numerically. When values of these errors $|\text{err}\{\Theta_\ell^{\text{ae}}(kr_{n,\ell})\}|$ become greater than $\pi/2$, the 'int' function in equation (7) will introduce an incorrect multiple of π into the resulting absolute phase shift. Figure 3 shows that this always occurs at high values of ℓ , so the type of problem illustrated by figures 1 and 2 would only be avoided if the partial wave sum in equation (3) were truncated before the onset of this breakdown.

To address this problem, the present work examined the efficacy of an alternate method of estimating the Bessel function phase. Using standard semiclassical methods [13] it is readily shown that the first-order

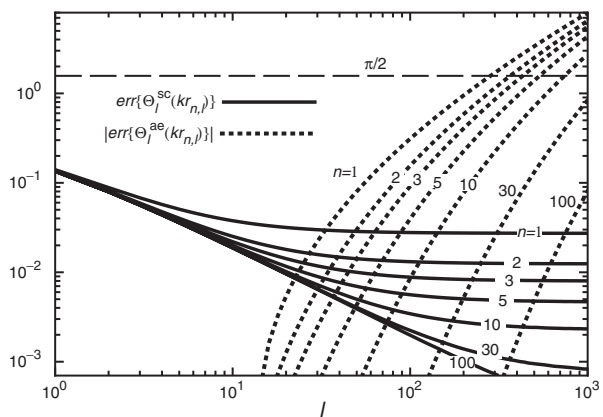


Figure 3. Error (in radians) in approximate estimates of Bessel function phase at the node number n : $\text{err}\{\Theta_\ell^{\text{sc}}(kr_{n,\ell})\}$ shown as solid curves, $\text{err}\{\Theta_\ell^{\text{ae}}(kr_{n,\ell})\}$ as dashed curves.

semiclassical expression for the phase of a spherical Bessel function at a distance r is

$$\Theta_\ell^{\text{sc}}(kr) = \frac{\pi}{4} + \int_{r_{0,\ell}}^r k_\ell(r') dr' = \frac{\pi}{4} + \int_{kr_0}^{kr} (1 - \ell(\ell+1)/z^2)^{1/2} dz \quad (8)$$

in which $k_\ell(r) = [k^2 - \ell(\ell+1)/r^2]^{1/2}$, $r_{0,\ell} = [\ell(\ell+1)]^{1/2}/k$ is the location of the zero of $k_\ell(r)$ and $r > r_{0,\ell}$. The integral in equation (8) may be evaluated in closed form, yielding the expression (for $\ell > 0$)

$$\Theta_\ell^{\text{sc}}(kr) = (\pi/4) + [(kr)^2 - \ell(\ell+1)]^{1/2} - [\ell(\ell+1)]^{1/2} \arccos\{[\ell(\ell+1)]^{1/2}/(kr)\}. \quad (9)$$

For the special case of $\ell = 0$, we of course have the trivial (exact) result that $\Theta_0(kr) = kr$.

Differences between the predictions of equation (9) and the exact Bessel function phase of $n\pi$ at the n th node are shown as solid curves in figure 3 for a range of n values. The errors yielded by this semiclassical approximation are always positive, monotonically decrease as $\ell \rightarrow \infty$ or n increases, and are always less than the value of 0.141 rad which all the solid curves approach as $\ell \rightarrow 1$. Since these errors are always much less than $\pi/2$, it is clear that use of this approximation for $\Theta_\ell(kr_{n,\ell})$ in equation (7) can never give rise to modulo π errors in the determination of the absolute phase shift.

4. Conclusions

We have seen that a problem associated with the conventional way of estimating the phase of a spherical Bessel function of a given argument can give rise

to anomalous errors of multiples of π in numerically calculated absolute quantal phase shifts, and that these in turn can give rise to massive errors in predictions for second virial coefficients. The present work shows that use of a simple first-order semiclassical estimate of that phase completely removes such problems. A robust FORTRAN subroutine for calculating quantal phase shifts which implements the above procedure may be downloaded from the 'computer programs' link on the www site <http://leroy.uwaterloo.ca>. The result reported herein is a small further illustration of the essential role of semiclassical methods in providing insight and methodology for understanding and predicting molecular phenomena, a field in which Mark Child and his collaborators have been leading innovators for the past four decades [13–15].

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