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Comparison of Perturbation and Direct-Numerical-Integration Techniques for the Calculation of Phase Shifts for Elastic Scattering*

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The method of Gordon for the solution of the Schrödinger equation for elastic scattering is reformulated. Ordinary Rayleigh-Schrödinger perturbation theory is used to obtain the solution in a succession of intervals of the independent (radial) variable. A criterion for the automatic selection of interval sizes for a requisite accuracy of the phase shift is developed. The perturbation technique (carried to first order, taking the zero-order potential to be constant) is tested against the highly efficient Numerov direct-integration method on the Lennard-Jones (12, 6) potential. It is found that, under the restrictions imposed on the perturbation method, the Numerov procedure is almost always more efficient, except for partial waves of low angular momentum.

I. INTRODUCTION

Several methods have been developed for the accurate determination of phase shifts for elastic scattering. Bernstein [1] has used the Runge-Kutta-Gill method to integrate directly the partial-wave equations for the Lennard-Jones (12, 6) potential. Harris [2], and later Nesbet [3], have applied variational techniques to the attractive exponential potential. More recently Knudson and Kirtman [4] have developed a variation-perturbation approach, which they have tested on attractive exponential and Yukawa potentials. Gordon [5], and later others [6], have employed so called "reference-function" methods to construct the partial-wave

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solutions in piecewise analytic form. Finally, Sams and Kouri [7] have applied a noniterative technique to solve the Volterra integral equation (which is equivalent to the partial-wave equation) for elastic scattering of electrons from hydrogen atoms.

The purpose of the present work is twofold. First, we wish to demonstrate that Gordon's method may be easily derived by a straightforward application of standard Rayleigh-Schrödinger perturbation theory, a fact perhaps not widely known. Second, we wish to compare, for elastic scattering, the computation efficiency and accuracy of our reformulated method with that of the Numerov direct-integration procedure. In this respect, we complement the work of Allison [8] on coupled differential equations for inelastic scattering.

In Section II we present a formal derivation of the perturbation technique, along with the derivation of an interval-length selection formula. The Numerov and perturbation methods are then compared in Section III for the L–J (12–6) Hg–H_2 system considered by Bernstein [1].

II. Derivation of the Perturbation Formalism

From the standard theory of elastic scattering [9] from spherically symmetric potentials, the lth partial wave satisfies the differential equation

$$-\frac{d^2u_l}{dr^2}+\left\{\frac{l(l+1)}{r^2}-\frac{2\mu}{\hbar^2}[E-V(r)]\right\}u_l(r)=0, \tag{1}$$

along with the boundary conditions

$$\lim_{r\to 0} u_l(r)=0, \tag{2a}$$

$$\lim_{r\to\infty} u_l(r)=k^{-1}\sin(kr-l\pi/2+\delta_l), \tag{2b}$$

where

$$k=(2\mu E)^{1/2}/\hbar, \tag{3}$$

μ is the reduced mass, E is the total collision energy, $V(r)$ is the potential energy, and δ_l is the phase shift.

Following Gordon [5], we divide the range of the independent variable r into intervals. Within the ith interval the effective potential $U(r)$ is decomposed into a "reference" potential $U_i^0(r)$ and a remaining potential $\Delta U_i(r)$:

$$\frac{l(l+1)}{r^2}+\frac{2\mu V(r)}{\hbar^2}\equiv U(r)=U_i^0(r)+\Delta U_i(r). \tag{4}$$

This decomposition is specific to each interval. The "reference" (zero-order) potential is chosen according to two criteria: (1) It should be a good representation of the true potential; (2) It should permit known *analytic* linearly independent solutions ϕ_1 and ϕ_2 of the "reference" partial-wave equation

$$\left[-\frac{d^2}{dr^2} + U_i^0(r) - k^2\right]\begin{Bmatrix}\phi_1\\ \phi_2\end{Bmatrix} = 0. \tag{5}$$

Gordon [5] uses a mixed-Wronskian approach to obtain an approximate solution to u_l, valid in the ith interval, which is a linear combination of ϕ_1 and ϕ_2 plus correction terms arising from $\Delta U_i(r)$. Alternatively, we can formally solve all the partial-wave equations pertaining to the ith interval by standard Rayleigh-Schrödinger perturbation theory. We expand u_l in a perturbation series as

$$u_l = \sum_{n=0}^{\infty} u^n, \tag{6}$$

where we have suppressed the indices l and i on u^n. Treating $\Delta U_i(r)$ as a perturbation, we can rewrite Eq. (1) over the ith interval as a hierarchy of equations:

$$\left[-\frac{d^2}{dr^2} + U_i^0(r) - k^2\right] u^0 = 0, \tag{7}$$

$$\left[-\frac{d^2}{dr^2} + U_i^0(r) - k^2\right] u^n = -\Delta U_i(r)\, u^{n-1}, \qquad n = 1, 2, 3, \ldots. \tag{8}$$

u^0 is simply a linear combination of the known solutions ϕ_1 and ϕ_2 [see Eq. (5)] while u^n, $n \geqslant 1$, can be found by Duhamel's method [10]. Thus, we have

$$u^0(r) = c_1\phi_1(r) + c_2\phi_2(r), \tag{9a}$$

$$u^n(r) = W^{-1}\int_{r_i}^{r} dr'\, M(r, r')\, \Delta U_i(r')\, u^{n-1}(r'). \tag{9b}$$

The constants c_1 and c_2 are determined by the requirement that the wave function and its derivative be continuous at the endpoints of the interval. r_i is the boundary between the $(i-1)$th and ith intervals. W is the usual Wronskian

$$W \equiv \phi_1 \frac{d\phi_2}{dr} - \phi_2 \frac{d\phi_1}{dr}$$

and $M(r, r')$ is a kernel defined by

$$M(r, r') \equiv \phi_1(r')\,\phi_2(r) - \phi_2(r')\,\phi_1(r).$$

From Eq. (9b) it is clear that each higher-order correction to u is proportional to some average value of $\Delta U_i(r)$ raised to a higher power. Furthermore, it is easy to show that $u^n(r_i) = 0$ for $n > 0$ and that the first nonzero derivative of u^n evaluated at r_i is the $2n$th derivative. Therefore if $\Delta U_i(r)$ is small over the interval each higher-order term will grow more and more slowly from 0 as r increases from r_i. In other words, the perturbation expansion converges, and it will converge to any order if $\Delta U_i(r)$ is small enough over the interval. For any reasonable choice of $U_i^0(r)$, $\Delta U_i(r)$ can always be made small enough by simply taking the interval small enough. Gordon's approximation to u_l, as defined by Eqs. (2.13) through (2.21) in Ref. 5, is identical to the perturbation method carried out to first order.

Since any practical method of solving the partial-wave equations is approximate, there is some error, ρ_i, associated with the solution u_l over the ith interval. If properly defined, ρ_i should be directly related to the size of $\Delta U_i(r)$ over the interval and should be an increasing function of interval length. Gordon [5] proposes a definition of ρ_i, indicates its functional dependence on interval length, and gives a formula whereby the calculated value of ρ_i can be used to select the $(i + 1)$th interval length. We now derive a different definition of ρ_i motivated by our perturbation formalism and we apply the definition to interval selection.

The error associated with a perturbation solution results from the neglect of high-order terms in the perturbation expansion [Eq. (6)] of the solution. If the expansion is convergent, then the terms ignored are negligible if the highest order term included is small compared to the zero-order term. Letting N be the highest order in our expansion of u_l, we should require that u^N be small with respect to u^0. A problem arises because in the classically allowed regions, a good zero-order solution will be oscillatory, thus making any direct comparison of u^0 and u^N unreliable. Over the ith interval, u_l goes roughly as $\sin k_i r$, where k_i is the effective local wavenumber at r_i^0, the interval midpoint:

$$k_i = [k^2 - U(r_i^0)]^{1/2}. \tag{10}$$

However, in this classically allowed region $| u^0 | + | k_i^{-1} u^{0\prime} |$ (where the prime denotes differentiation with respect to r) should behave as $| \sin k_i r | + | \cos k_i r |$, and thus be approximately constant. Furthermore, $| u^N | + | k_i^{-1} u^{N\prime} |$ is zero at r_i and increases with propagation through the interval. Hence, we define ρ_i as

$$\rho_i \equiv \frac{| u^N | + | k_i^{-1} u^{N\prime} |}{| u^0 | + | k_i^{-1} u^{0\prime} |}. \tag{11}$$

The variable ρ_i is the "error" associated with the solution in the ith interval in the sense that if ρ_i at the end of the interval is small, then Nth order perturbation theory is adequate to propagate the solution to the end of the interval and u^{N+1} and higher-order terms can be ignored. While the motivation for our definition

of ρ_i is specific to classically allowed regions, the definition itself is equally applicable to classically forbidden regions.

The error expression (11) we have developed can now be used to select the largest intervals such that the error for each interval does not exceed some preset maximum tolerable error. By using the largest intervals consistent with a desired accuracy, the perturbation method becomes optimally efficient. In order to select the largest ith interval, we need to know how ρ_i evaluated at the end of the interval varies with the interval length h. We restrict ourselves to first-order perturbation theory as, in effect, does Gordon. We consider first the classically allowed region; later we discuss the classically forbidden region. In the classically allowed region, the denominator of ρ_i is a mildly oscillating function which we approximate as a constant. Then ρ_i evaluated at the end of the interval varies with h as its numerator evaluated at the end of the interval varies with h. Expanding the numerator at the end of the interval in a Taylor series about the beginning of the interval, we obtain

$$|u^1(r_i+h)| + |k_i^{-1}u^{1'}(r_i+h)| = \left|u^1(r_i) + hu^{1'}(r_i) + \frac{h^2}{2}u^{1''}(r_i) + \cdots\right| + \left|k_i^{-1}\left[u^{1'}(r_i) + hu^{1''}(r_i) + \frac{h^2}{2}u^{1'''}(r_i) + \cdots\right]\right|. \tag{12}$$

As discussed above

$$u^1(r_i) = u^{1'}(r_i) = 0. \tag{13}$$

So Eq. (12) becomes

$$|u^1(r_i+h)| + |k_i^{-1}u^{1'}(r_i+h)| \approx \frac{h^2}{2}|u^{1''}(r_i)| + \frac{h}{k_i}|u^{1''}(r_i) + \frac{h}{2}u^{1'''}(r_i)|. \tag{14}$$

From Eq. (8) $u^{1''}(r_i)$ and $u^{1'''}(r_i)$ are known. Making the substitution into Eq. (14), we obtain

$$|u^1(r_i+h)| + |k_i^{-1}u^{1'}(r_i+h)| \approx \frac{h^2}{2}\left\{|\Delta U_i(r_i)\,u^0(r_i)| + \left|\left\{\frac{\Delta U_i(r_i) + (h/2)[\Delta U_i(r_i)]'}{(h/2)\,k_i}\right\}u^0(r_i) + \Delta U_i(r_i)\,k_i^{-1}u^{0'}(r_i)\right|\right\}. \tag{15}$$

The Taylor series expansion in Eq. (15) would be good to second order in h if it were not for the fact that k_i and usually $\Delta U_i(r_i)$ are defined relative to the midpoint of the interval and are therefore not constants but functions of h. To proceed further we must assume some form for $U_i^0(r)$ in order to define the behavior of

$\Delta U_i(r_i)$ as a function of h. As an example, we take $U_i^0(r)$ to be the first m terms in the Taylor series expansion of $U(r)$ about r_i^0, the interval midpoint. Then $\Delta U_i(r)$ consists of the remaining terms of the expansion:

$$\begin{aligned} \Delta U_i(r) &= \frac{(r - r_i^0)^m}{m!} U^m(r_i^0) + \frac{(r - r_i^0)^{m+1}}{(m+1)!} U^{m+1}(r_i^0) + \cdots, \\ [\Delta U_i(r)]' &= \frac{(r - r_i^0)^{m-1}}{(m-1)!} U^m(r_i^0) + \frac{(r - r_i^0)^m}{m!} U^{m+1}(r_i^0) + \cdots. \end{aligned} \tag{16}$$

Substituting Eq. (16) into Eq. (15) and retaining only the leading term in $\Delta U_i(r_i)$ and $\{\Delta U_i(r_i) + (h/2)[\Delta U_i(r_i)]'\}$, we find

$$\begin{aligned} &| u^1(r_i + h)| + | k_i^{-1} u^{1'}(r_i + h)| \\ &\approx \begin{cases} \dfrac{h^3}{8} \{| 2U'(r_i^0)\, u^0(r_i)| + | U''(r_i^0)\, k_i^{-1} u^0(r_i) + 2U'(r_i^0)\, k_i^{-1} u^{0'}(r_i)|\}, & m = 1; \\ \dfrac{h^{m+1}}{2} \left| \dfrac{U^m(r_i^0)}{m!} \right| \{| hu^0(r_i) + 2(m-1)\, k_i^{-1} u^0(r_i) - hk_i^{-1} u^{0'}(r_i)|\}, & m \geqslant 2. \end{cases} \end{aligned} \tag{17}$$

In this expression k_i^{-1}, $U'(r_i^0)$, $U''(r_i^0)$, and $U^m(r_i^0)$ are all functions of interval length through their dependence on r_i^0. However, the leading terms of the Taylor series expansions of each of these functions about r_i are independent of interval length. Therefore, from Eq. (17) we see that, if $U_i^0(r)$ is taken to be the first m terms of the Taylor series expansion of $U(r)$ about r_i^0, then ρ_i evaluated at the end of the interval varies with interval length as

$$\rho_i \alpha \begin{cases} h^3, & m = 1; \\ h^{m+1}, & m \geqslant 2. \end{cases} \tag{18}$$

The proportionality constant in this expression could be determined from Eq. (17). However a more practical approach is to assume the constant is approximately the same for adjacent intervals. Then, taking our criterion for accuracy to be that ρ_i never exceed a given upper limit ρ_0, we arrive at the following formula for predicting successive interval lengths:

$$h_{i+1} = \begin{cases} h_i \left(\dfrac{\rho_0}{\rho_i}\right)^{1/3}, & m = 1, \\ h_i \left(\dfrac{\rho_0}{\rho_i}\right)^{1/(m+1)}, & m \geqslant 2, \end{cases} \tag{19}$$

where h_{i+1} is the predicted $(i+1)$th interval length given the error ρ_i over the ith interval of length h_i. If ρ_i exceeds ρ_0, then h_{i+1} is made suitably smaller than h_i;

if ρ_i is less than ρ_0, then h_{i+1} is made suitably larger than h_i. Hence by Eq. (19) appropriate interval sizes are *automatically* selected as the integration proceeds.

Equation (19) is rigorously valid only in the classically allowed region, because we have assumed that the denominator in ρ_i is approximately constant. For propagation out of classically forbidden regions, the denominator of ρ_i increases exponentially with interval length. Therefore, the dependence of ρ_i on h is overestimated by Eq. (18) and consequently h_{i+1} is underestimated by Eq. (19). For propagation into classically forbidden regions, the denominator of ρ_i decreases exponentially with interval length. Hence the dependence on h is underestimated by Eq. (18) and h_{i+1} is overestimated by Eq. (19). These difficulties with Eq. (19) in the classically forbidden regions are not serious for two reasons. First, when the wavefunction is small relative to its asymptotic amplitude, large relative errors in its calculation have negligible effect on the ultimate accuracy of the phase shift. This means that for most of the strongly forbidden region about $r = 0$, the very small value of the wavefunction can be approximated by zero with no loss in accuracy. This also means that while the wavefunction is small, yet not small enough to be approximated by 0, we can tolerate unusually large relative errors [such as those measured by ρ_{i+1} if h_{i+1} were to be overestimated by Eq. (19)] without sacrificing accuracy. In other words, little of the classically forbidden region need be included in the calculation and the part of the region that is included can support, with no loss of accuracy in the phase shift, a wavefunction with unusually high relative error. A second reason that the difficulties of Eq. (19) are not serious is that the proportionality constant used in deriving the equation is based upon the success of predicting the error for the previous interval. In an empirical way, Eq. (19) will compensate for the fact that in the classically forbidden region ρ_i does not vary with h exactly in accordance with Eq. (18). Hence, for both of these reasons, Eq. (19) would seem to be an acceptable interval-selection formula in the classically forbidden region. In our experience, the equation has always proven adequate.

In this section, our analysis has been exclusively directed to the single differential equation of elastic scattering. However, the entire analysis can be readily extended to the coupled differential equations of inelastic scattering in a manner similar to that of Gordon [5]. All the formulas developed in this section for elastic scattering have a direct analogue in inelastic scattering.

III. Comparison of Numerov and Perturbation Methods

To determine whether the perturbation method is competitive with better known so-called "direct" methods of numerical integration, we consider now the parallel application of the perturbation and direct methods to the system treated by Bernstein [1], namely Hg scattering from H_2 via an L–J (12–6) interaction. We take

three different sets of parameters (A and B in Bernstein's reduced units) corresponding roughly to collision energies equal to 1/10 the well depth, the well depth, and 10 times the well depth. For each set of parameters phase shifts for selected partial waves from $l = 0$ to $l = 50$ are computed.

For our comparison we use the most efficient direct integration method, that of Numerov [11]. The particular version of the perturbation method we use is as follows:

(1) The perturbation expansion, Eq. (6), is carried out only to first order;

(2) $U_i^0(r)$ is taken to be the effective potential at the interval midpoint;

(3) $\Delta U_i(r)$ is approximated by the linear and quadratic (but *not* the higher order) terms of Taylor series expansion of the effective potential about the interval midpoint.

By using only first-order perturbation theory, we need do only relatively simple integrals [Eq. (9b)]. By taking $U_i^0(r)$ to be constant throughout the interval, the integrals can be substantially simplified by virtue of symmetry (see the appendix). Finally approximating $\Delta U_i(r)$ eliminates the need to evaluate very small integrals that contribute little to the solution.

In both methods, a starting and a stopping point for the integration must be specified for each l. To ensure a fair comparison, we use the same starting and stopping points for both methods. For each l the starting point is fixed by a preliminary computation and is taken to be where the wavefunction is less than 10^{-3} of its value at the classical turning point. For all l the stopping point is taken to be where the potential falls below $10^{-5}E$.

In both methods the phase shift δ_l is determined at the end of the integration by comparing the numerical solution to the asymptotic spherical-Bessel-function form of the wavefunction [1]. For the perturbation method, the wavefunction and its derivative at the stopping point are sufficient to determine δ_l. For the Numerov method, only the wavefunction, and not its derivative, is available at the stopping point and δ_l cannot be directly determined. Instead, the nearest zero in the numerical solution is found by interpolation. The position of the zero is sufficient to determine δ_l. The accuracy of the computed phase shifts are determined by a single input parameter for each method: ρ_0, defined by Eq. (19), for the pertubation method and h, the grid size for the Numerov method.

All computations were done in Fortran IV on the CDC 6500 computer in the Purdue University Computer Center. The computer programs for both methods were written with care to maximize their efficiency. The results of our calculations are collected in Tables I through III.

In Tables I and II we give results for the intermediate case $A = 10$, $B = 125$. In Table I we list phase shifts, along with CPU time and number of intervals

TABLE I

Phase shift, number of intervals, and computation time as a function of l and ρ_0, for the perturbation method. $A = 10, B = 125$.[a] Upper entries are phase shifts; lower entries are number of intervals/CPU time (sec).

	l					
ρ_0	1	10	20	30	40	50
1	−6.7258 11/.018	3.2649 10/.019	0.1405 9/.016	−0.2169 8/.016	−0.3223 8/.017	−0.2009 8/.017
10^{-1}	−6.7198 18/.028	3.4002 16/.027	0.3598 17/.029	−0.0473 14/.024	−0.0505 16/.034	−0.0826 14/.027
10^{-2}	−6.7161 34/.054	3.4935 31/.052	0.4446 36/.057	0.0448 34/.057	0.0047 37/.060	−0.0023 32/.052
10^{-3}	−6.7144 70/.102	3.5169 76/.112	0.4632 89/.133	0.0547 81/.133	0.0120 81/.121	0.0032 69/.107
10^{-4}	−6.7143 148/.218	3.5188 172/.251	0.4653 193/.282	0.0562 174/.257	0.0132 174/.260	0.0042 147/.219
10^{-5}	−6.7143 317/.453	3.5193 369/.548	0.4658 414/.603	0.0565 373/.547	0.0134 372/.542	0.0044 315/.462
10^{-6}	−6.7143 684/.980	3.5194 790/1.15	0.4659 889/1.29	0.0566 800/1.16	0.0135 799/1.16	0.0044 676/.986

[a] Reduced units defined in Ref. 1.

required, as a function of ρ_0 and l for the pertubation method. Table II shows phase shifts, CPU time, and the number of intervals required as a function of h and l for the Numerov method. The CPU time is taken to be the time required to integrate the partial-wave equation from the starting point to the stopping point plus the time to calculate the phase shift. There are obvious trends in Tables I and II. For a given partial wave l, decreasing ρ_0 increases the number of intervals required and hence increases the CPU time for the perturbation method. Likewise, decreasing the grid size increases the number of intervals and consequently the CPU time for the Numerov method.

To compare quantitatively the efficiency of the Numerov and perturbation methods we list in Table III the CPU time as a function of the absolute accuracy demanded in the phase shift. We find these times by linear interpolation using Tables I and II for the case $A = 10$, $B = 125$ and similar tables for the remaining cases. The true phase shift is assumed to be the converged perturbation value, which differs by no more than 10^{-4} from the converged Numerov value. Table III

TABLE II

Phase shifts, number of intervals, and computation times as a function of l and the interval length, h, for the Numerov method. $A = 10$, $B = 125$.[a] Upper entries are phase shifts; lower entries are number of intervals/CPU time (sec)

	l					
h	0	10	20	30	40	50
.09	−6.6489	3.6190	0.5572	0.0893	0.0491	0.0227
	83/.034	82.039	82/.039	80/.036	61/.034	49/.035
.07	−6.6482	3.5659	0.4931	0.0745	0.0189	0.0085
	105/.042	105/.047	103/.045	87/.046	78/.044	63/.039
.05	−6.7025	3.5308	0.4723	0.0615	0.0169	0.0064
	148/.069	148/.064	145/.068	121/.064	110/.062	88/.058
.04	−6.7087	3.5243	0.4687	0.0588	0.0152	0.0047
	185/.079	184/.085	181/.081	153/.074	137/.072	110/.965
.03	−6.7125	3.5210	0.4669	0.0572	0.0139	0.0045
	247/.106	246/.115	241/.113	203/.105	182/.092	146/.080
.02	−6.7139	3.5198	0.4661	0.0567	0.0136	0.0045
	371/.144	369/.154	361/.151	304/.142	273/.127	219/.122
.01	−6.7142	3.5195	0.4659	0.0566	0.0136	0.0045
	742/.290	737/.304	722/.295	610/.261	546/.263	437/.214
.005	−6.7143	3.5194	0.4659	0.0566	0.0135	0.0045
	1483/.569	1474/.623	1444/.596	1219/.518	1091/.474	873/.421
.001	−6.7142	3.5194	0.4659	0.0566	0.0135	0.0045
	7411/2.83	7372/2.92	7219/2.76	6091/2.54	5455/2.34	4364/2.03

[a] Reduced units are defined in Ref. 1.

has several features we describe first before drawing our conclusions on the relative efficiency of the two methods.

In Table III the CPU time required for a given accuracy in δ_l has a dependency on l that is different for the two methods. For the perturbation method, the CPU time is not a monotonic function of l but peaks at intermediate l, and then decreases as l increases. This behavior is not unexpected since the contribution of the centrifugal barrier at intermediate l causes the effective potential to vary rapidly as a function of r. At other values of l the effective potential is smoother, either because the centrifugal barrier is smaller (low value of l) or because the outer side of the centrifugal barrier dominates (large value of l). The more sharply varying the effective potential, the shorter each interval must be in order that $\Delta U_l(r)$ be sufficiently small over the interval. The more intervals required, the longer the

TABLE III

Computation times as a function of l, A^a, and the absolute accuracy required of the phase shift. $B = 125$.[a] Upper entries are perturbation results; lower entries are Numerov results. CPU time is given in seconds.

A^a	Absolute Accuracy	l = 0	10	20	30	40	50
	0.01	.03	.10	.06			
		.10	.04	.04			
3	0.005	.03	.12	.08			
		.11	.06	.05			
	0.001	.06	.24	.16			
		.14	.07	.06			
	0.01	.02	.09	.10	.07	.06	.05
		.07	.07	.06	.06	.04	.04
10	0.005	.03	.11	.12	.11	.09	.07
		.08	.08	.07	.06	.05	.04
	0.001	.08	.22	.25	.21	.18	.13
		.13	.13	.11	.10	.08	.06
	0.01	.01	.07	.09	.10	.08	.06
		.08	.09	.08	.06	.06	.06
30	0.005	.03	.09	.10	.12	.11	.09
		.09	.09	.09	.09	.08	.06
	0.001	.10	.18	.12	.19	.20	.16
		.86	.17	.19	.15	.15	.15

[a] Reduced units defined in Ref. 1.

calculation takes. For the Numerov method, the CPU time for a given accuracy in δ_l is almost always a monotonically decreasing function of l. Since increasing l increases the effective potential and hence decreases the local wavenumber (see Eq. 10), the wavefunction oscillates less rapidly for larger l. Since the Numerov method computes the wavefunction directly, as l increases a coarser grid (i.e. larger intervals) is needed to represent the wave function with the same accuracy. The larger the intervals, the quicker the calculation.

In Table III the CPU time required for a given accuracy in δ_l has a dependency on collision energy (proportional to the square root of A in Table III) that is different for the two methods. For the Numerov method, the CPU time, with few exceptions, increases monotonically with A for a given value of l. Increasing A

increases the local wavenumber, implying a more rapidly oscillating wavefunction requiring smaller intervals and hence longer times for accurate calculation. For the perturbation method, the CPU time as a function of A has a complicated behavior due to opposing trends. For a given l, increasing A alters the range of the integration, i.e. the starting and stopping points for the integration move in. This change has little effect on the Numerov method. However, it can strongly affect the perturbation method because the part of the effective potential curve that is newly exposed is very rapidly varying while the part of the curve that is dropped is very slowly varying. Hence more intervals are required to describe the potential and consequently the calculation time increases. Opposing this effect is the general trend that with increasing collision energy the phase shift becomes less sensitive to the details of the potential. In other words as A increases, k^2 begins to dominate Eqs. (7) and (8) for u^0 and u^N even if $\Delta U_i(r)$ is fairly large. So as A increases, the potential need not be described so accurately; this leads to larger intervals and shorter times. These two trends, a more rapidly varying effective potential but less need to describe it accurately, conflict to produce a complicated dependency of CPU times as a function of A for the perturbation method.

The general features of Table III that we have discussed emphasize that the number of intervals required for the perturbation method depends on the effective potential while the number of intervals required for the Numerov method depends on the wave function. Since the effective potential is less "oscillatory" than the wave function, the perturbation method requires far fewer intervals than the Numerov method. However, the Numerov method requires far fewer arithmetic operations per interval than does the perturbation method. The results in Table III indicate that except for values of l near 0, the Numerov method is as fast or considerably faster than the perturbation method. Evidently, the Numerov method's greater efficiency per interval outweights the requirement of a larger number of intervals.

Allison has made a similar comparison of Numerov and perturbation methods for rotationally inelastic scattering. In this case *coupled* differential equations must be solved to obtain an S matrix. Only one collision system at one energy and one total angular momentum was studied. Requiring an accuracy of about 0.005 in the square of magnitude of each S matrix element, Allison concludes in part that the Numerov method is substantially faster unless the number of coupled equations is quite large (larger than 16). However, Allison also concludes that the perturbation approach is much faster if calculations for several different energies are to be performed on the same collision system. The reason for this is that in problems involving coupled equations, the determination of the reference potential matrix $\mathbf{U}_i^0$ requires a matrix diagonalization which takes up much of the time of a calculation at one energy. However, once determined $\mathbf{U}_i^0$ can be saved and reused in calculations at other energies. No such advantage has been developed for the

Numerov method. For the elastic scattering calculations described in this paper, it is *not* true that the perturbation method is much faster than the Numerov method if calculations at several energies must be performed. For elastic scattering, the determination of U_i^0 takes little of the total time of calculation and saving it for use at other energies would provide essentially no advantage over the Numerov method.

To be comprehensive, our work and that of Allison should be extended to other systems over a wider range of energies. Different versions of the perturbation method should be investigated along with automatic procedures for varying the interval length during the Numerov direct integration. We feel our results are demonstrative of the general behavior of the perturbation and Numerov methods for elastic scattering and we leave the comprehensive study to those planning extensive calculations.

APPENDIX. Simplification of Perturbation Integrals by Symmetry

We expand $U_i(r)$ about the midpoint, r_i^0, of the ith interval as

$$U_i(r) = U(r_i^0) + (r - r_i^0)\frac{dU}{dr}\Big|_{r=r_i^0} + \frac{1}{2}(r - r_i^0)^2\frac{d^2U}{dr^2}\Big|_{r=r_i^0} + \cdots. \quad \text{(A1)}$$

We define a new variable x_i

$$x_i = r - r_i^0, \quad \text{(A2)}$$

and express $U(r)$ in the ith interval according to Eq. (4) as

$$U_i(r) = U_i^0(r) + \Delta U_i(r), \quad \text{(A3)}$$

where we implicitly take U_i^0, the zero-order potential, to be constant. Identifying the corresponding terms in (A1) and (A3) and introducing the definition (A2), we have explicitly

$$U_i^0(r) = U(r_i^0), \quad \text{(A4)}$$

$$\Delta U_i(r) = x_i\frac{dU}{dr}\Big|_{r=r_i^0} + \frac{1}{2}x_i^2\frac{d^2U}{dr^2}\Big|_{r=r_i^0} + \cdots \quad \text{(A5)}$$

$$\equiv a_i x_i + b_i x_i^2 + \cdots.$$

In this case the linearly independent solutions of Eq. (7) are

$$\phi_1 = A_i \sin k_i x_i\,,$$
$$\phi_2 = B_i \cos k_i x_i\,, \qquad k_i \equiv [k^2 - U(r_i^0)]^{1/2},$$

in classically allowed regions and

$$\phi_1 = A_i \sinh \bar{k}_i x_i ,$$
$$\phi_2 = B_i \cosh \bar{k}_i x_i , \qquad \bar{k}_i \equiv [-k_i]^{1/2},$$

in classically forbidden regions. From Eq. (9b) the first-order perturbation correction is then (in the classically allowed regions)

$$u^1 = k_i^{-1} \int_{-h_{i/2}}^{h_{i/2}} dx_i' \{\sin k_i x_i' \cos k_i x_i - \cos k_i x_i' \sin k_i x_i\}$$
$$\times \{a_i x_i' + b_i x_i'^2\} \cdot \{A_i \sin k_i x_i' + B_i \cos k_i x_i'\}.$$

Hence the total correction is a sum of eight integrals, whose integrands are either even or odd with respect to reflection about the midpoint of the interval. In fact, four of these integrands are odd and thus vanish. The same considerations hold for the classically forbidden regions.

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