# Inelastic Collisions of Slow Atoms: The Two-Level Model

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A two-level model of an atomic system is investigated in order to study the cross section for certain inelastic collision processes. An impact-parameter method is employed. The time-dependent Schrödinger equation has been integrated numerically for some simple interaction potentials. Cross sections for excitation have been determined and are presented as functions of the parameters describing the model. The results are compared with those obtained by certain approximate methods. The effects of inclusion of diagonal matrix elements in the interaction Hamiltonian are found to be large. For a fixed form of the interaction potential, two cross sections, which may differ quite substantially, are obtained, depending on the algebraic sign of the coupling parameters or the energy difference between the states.

## I. INTRODUCTION

In a previous calculation, an approximate method was devised for the calculation of the cross section for electronic excitation in the inelastic collision of slow atoms. The situation considered was the following: Two massive objects, $A$ and $B$ (either atoms or molecules), collide. In this collision $A$ undergoes an electronic transition, either excitation or de-excitation; $B$ does not. Charge exchange and excitation transfer are not considered.

The collision process was described using the impact parameter method. In this approach, the relative motions of $A$ and $B$ are assumed to be classical, and changes in speed or in direction during the collision process are ignored. The interaction producing the transition is described by an effective potential $V_{\text{eff}}$ which acts within a subspace of the Hilbert space of $A$ spanned by the states actually involved in the transition. Let $a_j(t)$ be the amplitude that at time $t$, $A$ is in state $j$. This quantity obeys the differential equation

$$\frac{da_j}{dt}=-\frac{i}{\hbar}\sum_k (j|V_{\text{eff}}|k)a_k(t)\exp(-i\omega_{k,j}t). \quad (1)$$

As was shown in I, we may assume that the matrix $(j|V_{\text{eff}}|k)$ is traceless. The quantity $\omega_{k,j}$ is given by

$$\hbar\omega_{k,j}=E_k-E_j, \quad (2)$$

and it is to be noted that the energies of the states in Eq. (2) are those for $A$ when $B$ is absent.

Let the separation of $A$ and $B$ be denoted by $R$. The interaction matrix elements in Eq. (1) depend on time through their dependence on $R$, which may be a fairly complicated function. The general behavior of the interaction should be the following: When $R$ is very large, we expect $(j|V_{\text{eff}}|k)$ usually to be proportional to some negative power of $R$. Thus, in the case of a van der Waals interaction, the matrix elements will be proportional to $R^{-6}$ for large $R$; while in the case of proton-hydrogen interactions, the elements are proportional to $R^{-2}$ or $R^{-3}$ times a function of angle. As $R$ decreases, exponential terms will enter with the effect that the matrix elements will not continue to increase so rapidly. Finally, for small values of $R$, the matrix elements will probably either vanish, approach some constant limit, or be rather weakly singular (like $1/R$). This behavior is apparent for instance in the interaction between protons and hydrogen atoms in which no singularities occur in the interaction matrix after the trace has been removed.

An approximate method of solving Eq. (1) was proposed in I.[1] We consider the quantities $a_j$ to be components of a vector $\mathbf{a}$ and the elements $(j|V_{\text{eff}}|k)e^{-i\omega_{k,j}t}$ to be elements of a matrix $\mathbf{Q}(t)$ which is just the interaction matrix in the Dirac picture. The approximate solution of (1) is

$$\mathbf{a}(t)=\exp[-i\mathbf{T}(t)]\mathbf{a}(-\infty), \quad (3)$$

in which the matrix $\mathbf{T}(t)$ is given by

$$\mathbf{T}(t)=\int_{-\infty}^{t} Q(t')dt'. \quad (4)$$

Equation (3) is correct only if $Q$ and $T$ commute:

$$[\mathbf{Q}(t),\mathbf{T}(t)]=0; \quad (5)$$

however, it remains as a useful approximation in other situations.

The purpose of this paper is to present some exact numerical solutions of the time dependent Schrödinger equation for a simple model which may be compared with the predictions of the approximate Eq. (3) and with perturbation theory. Some interesting properties of the solutions of Eq. (1) emerge which also may be expected to occur in more realistic models.

The model we will consider here is one in which the matrix elements $(j|V_{\text{eff}}|k)$ are independent of angle and depend only on the distance $R$ according to an inverse power law. This is an oversimplification of the interaction in regard to real reactions, as was mentioned above. However, in the case of reactions with large cross sections, such as the problem of sensitized fluorescence discussed in I, the approximation may not be a bad one. We will also restrict our investigations to a two-level system. We therefore suppose that

$$\begin{aligned}(1|V_{\text{eff}}|1)&=-(2|V_{\text{eff}}|2)=q_2R^{-l},\\ (1|V_{\text{eff}}|2)&=(2|V_{\text{eff}}|1)=q_1R^{-n},\end{aligned} \quad (6)$$

in which $q_1$ and $q_2$ are coupling constants.

[1] J. Callaway and E. Bauer, Phys. Rev. **140**, A1072 (1965). This paper will be referred to as I.

Therefore, we must investigate the pair of differential equations

$$\frac{da_1}{dt}=-\frac{i}{\hbar}[q_2R^{-l}a_1+q_1R^{-n}e^{-i\omega t}a_2],$$
$$\frac{da_2}{dt}=-\frac{i}{\hbar}[q_1R^{-n}e^{i\omega t}a_1-q_2R^{-l}a_2], \tag{7}$$

in which $\omega=\omega_{2,1}=\omega_2-\omega_1$, and $R^2=p^2+v^2t^2$ where $p$ is the impact parameter and $v$ is the speed of $B$ relative to $A$. We will assume that $A$ is in state 1 at $t=-\infty$; thus the cross section for excitation is

$$\sigma=2\pi\int_0^\infty p|a_2(p,\infty)|^2dp, \tag{8}$$

in which $a_2(p,\infty)$ is the limiting value of $a_2(t)$ as $t\to\infty$.

Equation (3) furnishes an exact solution of Eqs. (7) if and only if two conditions are satisfied: (1) $\omega=0$, and (2) $n=l$. In this case, it is possible to evaluate the cross section as given by Eq. (8) in closed form: we give the results for the transition probability and the cross section below for reference:

$$|a_2(p,\infty)|^2=(1+q_2^2/q_1^2)^{-1}\sin^2\Omega,$$

where

$$\Omega=\frac{q_1}{\hbar vp^{n-1}}[\pi(1+q_2^2/q_1^2)]^{1/2}\frac{\Gamma[\frac{1}{2}(n-1)]}{\Gamma(\frac{1}{2}n)}, \tag{9a}$$

$$\sigma=\pi^2q_1^2\{2(n-1)\Gamma(1+2/n-1)\sin[\pi/(n-1)](q_1^2+q_2^2)\}^{-1} \tag{9b}$$

$$\times\{2[\pi(q_1^2+q_2^2)]^{1/2}\Gamma[\tfrac{1}{2}(n-1)]/\hbar v\Gamma[\tfrac{1}{2}(n)]\}^{2/n-1}. \tag{9c}$$

If the conditions mentioned above are not satisfied, the solution of Eq. (7) can only be obtained numerically. Such numerical solutions are reported and analyzed in this paper. Before undertaking a detailed discussion of the calculations, we will summarize the most interesting results. These concern the dependence of the cross section on the sign of the coupling constants, or the sign of the energy difference.

The cross section in the two-level model, if calculated according to Eq. (3), depends on $\omega^2$, $q_1^2$, and $q_2^2$. Thus changing the sign of any or all of $\omega$, $q_1$, and $q_2$ does not affect the answer. The numerical calculations instead show a rather dramatic dependence on the sign of the interaction or the sign of the energy difference. Cross sections for positive and negative values of $\omega$ of the same magnitude (and fixed $q_1$, $q_2$, $v$) may differ by an order of magnitude, or more. These features of the results can be qualitatively explained using second-order perturbation theory. We also find that for fixed $q_1$, $q_2$, $v$, the maximum cross section does not always occur at $\omega=0$, but is slightly displaced from this value. These results will be discussed in more detail below.

The plan of this paper is as follows: In Sec. II, we examine the general properties of the solutions of Eq. (7). Section III contains a discussion of the methods of calculation. The results of the present calculation are presented in Sec. IV, where they are compared with those obtained by the approximate method of I, and with corresponding results obtained from perturbation theory. Finally, Sec. V contains a summary of our conclusions.

## II. GENERAL PROPERTIES OF SOLUTIONS

To facilitate examination of some of the general properties of the solutions of Eq. (7), it is convenient to introduce some dimensionless quantities. We define

$$\begin{aligned} y&=vt/p,\\ p_0&=(|q_1|/\hbar v)^{1/n-1},\\ \beta&=p/p_0\\ x&=\omega p_0/V,\\ k&=q_2p_0^{n-l}/|q_1|,\\ \epsilon(q_1)&=q_1/|q_1|. \end{aligned} \tag{10}$$

With these substitutions, Eqs. (7) become

$$\frac{da_1}{dy}=\frac{-i}{\beta^{n-1}(1+y^2)^{n/2}}[k\beta^{n-l}(1+y^2)^{(n-l)/2}a_1(y)+\epsilon(q_1)e^{-ix\beta y}a_2(y)],$$
$$\frac{da_2}{dy}=\frac{-i}{\beta^{n-1}(1+y^2)^{n/2}}[\epsilon(q_1)e^{ix\beta y}a_1(y)-k\beta^{n-l}(1+y^2)^{(n-l)/2}a_2(y)]. \tag{11}$$

We want to investigate the symmetry properties of the solutions of Eqs. (11). We are principally interested in the **S** matrix, which relates the solutions at $t=-\infty$ to those at $t=\infty$:

$$\mathbf{a}(\infty)=\mathbf{S}\mathbf{a}(-\infty). \tag{12}$$

Equation (12) will be used as a definition of **S** for this problem. It is easy to show that, as a consequence of the vanishing of the trace of the interaction matrix,

$$\det\mathbf{S}=1. \tag{13}$$

For a two-level system **S** is, of course, a $2\times2$ unitary matrix. The requirements of unitarity and unimodularity reduce the number of independent parameters in **S** to three. It is convenient to write the elements of $S$ in the form

$$S_{ij}=s_{ij}e^{i\theta_{ij}}. \tag{14}$$

Then we have the relations

$$\begin{aligned} &s_{11}=s_{22},\\ &s_{11}^2=1-s_{12}^2,\\ &s_{12}=s_{21},\\ &\Theta_{11}=-\Theta_{22},\\ &\Theta_{21}=-\Theta_{12}\pm\pi(\mathrm{mod}2\pi). \end{aligned} \tag{15}$$

From this, we see that the $S$ matrix is specified by the three real numbers $s_{12}$, $\Theta_{12}$, $\Theta_{11}$.

The cross section for the transition $1 \rightarrow 2$ is given from Eqs. (8) and (10):

$$\sigma = 2\pi p_0^2 \int \beta |\, a_2(\beta,x,y=\infty)\,|^2 d\beta$$
$$= 2\pi p_0^2 \int_0^\infty \beta s_{12}^2(\beta,x) d\beta. \quad (16)$$

It will be observed that the scale for the measurement of the cross-section is $p_0^2$. The cross section is proportional to $p_0^2$ times a function of $x$.

We have yet to consider time-reversal symmetry. Changing the direction of time sends $y$ into $-y$ in Eqs. (11). This is seen to be equivalent to taking the complex conjugate of the system of equations. This gives rise to the condition that

$$S^* = S^\dagger \quad \text{or} \quad S = S^T, \quad (17)$$

where $S^*$ is the complex conjugate, $S^\dagger$ the adjoint, and $S^T$ the transpose of $S$. As a result, we see that the off-diagonal elements $S_{12}$, $S_{21}$ must be purely imaginary; that is $\Theta_{12} = \Theta_{21} = \pm\pi/2$. Hence, the $S$ matrix is determined by the quantities $s_{12}$ and $\Theta_{11}$.

We are now ready to study the effect of changing the algebraic signs of the quantities $q_1$, $q_2$, and $\omega$ (or $x$). This will enable us to restrict somewhat the region of values of the parameters which must be investigated. Let us suppose that we have obtained solutions for the situation in which all these quantities are positive (and therefore that $\epsilon = +1$). We denote these solutions as $a_1(+)$ and $a_2(+)$. We will call the cross section calculated with these values $\sigma(+)$. Now let us change the sign of $q_1$. However, this is equivalent to changing the sign of $y$ and interchanging the solutions $a_1$ and $a_2$. The $S$ matrix is unchanged by this, apart from phases, and so the transition probability is unaltered.

The situation is, however, quite different if we change the sign of $q_2$. We can not restore the original equations by the previously mentioned operations. Instead we obtain an entirely different solution set we will call $a_1(-)$ and $a_2(-)$, and a new cross section $\sigma(-)$. Changing the signs of both $q_1$ and $q_2$ yields the same cross section as does retaining the original signs of $q_1$ and $q_2$ and changing that of $\omega$. These conclusions are summarized in Table I. We see that in fact the eight different choices of algebraic sign for the parameters yield only two different cross sections: that is, there are only two independent problems. Of course, if the diagonal elements of the interaction vanish, only a single cross section will be obtained, regardless of the sign of $\omega$.

TABLE I. Effect of changing signs of parameters on the cross section.

| $q_1$ | $q_2$ | $\omega$ | $\sigma$ |
|---|---|---|---|
| + | + | + | $\sigma(+)$ |
| − | + | + | $\sigma(+)$ |
| + | − | + | $\sigma(-)$ |
| − | − | + | $\sigma(-)$ |
| + | + | − | $\sigma(-)$ |
| − | + | − | $\sigma(-)$ |
| + | − | − | $\sigma(+)$ |
| − | − | − | $\sigma(+)$ |

## III. CALCULATIONAL METHODS

We have investigated the solutions of Eqs. (11) for several sets of values of the parameters $q_1$ and $q_2$, and $x$. Since the arguments of the last section indicate that when the eight possible choices of sign of the three parameters are considered, there are only two different results for the cross section, we have chosen to take quantities $q_1$, $q_2$ always to be positive, and have considered both positive and negative values of $x$. If $x>0$, we get the cross section $\sigma(+)$, if $x<0$, we get $\sigma(-)$. We also see from Eq. (12), that if the cross section is measured in units of $p_0^2$, it is then a function of $k(=q_1/q_2)$ and $x$. The values of $k$ and the exponents $n$ and 1 which were investigated are listed in Table II. Our procedure was to obtain the two cross sections $\sigma(+)$, and $\sigma(-)$ as functions of $x$ in the five cases listed in Table II.

The reasons governing the choice of the exponents $n$, $l$ given in Table II were the following: the case $n=l=6$ corresponds to transitions induced by a van der Waals force and is relevant to the problem of sensitized fluorescence discussed in I. The case $l=3$, $n=3$ corresponds to the leading term in the interaction matrix for transitions between levels of the same parity induced by a Coulomb field, neglecting angular factors. Because of its intrinsic importance, and also because the numerical problems are simplest for these values of $n$ and $l$, we obtained cross sections for three different values of $k$. We have also made calculations for the situation roughly characteristic of transitions between states of opposite parity induced by a Coulomb field (only if the angular dependence of the matrix elements is neglected): $n=2$, $l=3$. This case has two features which increase its interest: first even when $x=0$, a closed solution to the differential equations cannot be obtained, but (2) also when $\omega/v=0$, the cross section diverges logarithmically.

The numerical solution of Eqs. (11) can be obtained in several different ways. The functions $a_i(y)$ are complex, so that one approach involves the separation of real and imaginary parts in order to obtain a set of four

TABLE II. Values of the exponents $n$, $l$, and the parameter $k$ for which Eqs. (11) were solved.

| $n$ | $l$ | $k$ |
|---|---|---|
| 2 | 3 | 1 |
| 3 | 3 | 0.2 |
| 3 | 3 | 1 |
| 3 | 3 | 5 |
| 6 | 6 | 1 |

linear first-order equations. Alternatively, if we write the amplitudes in polar form, $a_i=r_i e^{i\varphi}$, it is possible to use the conservation of probability, $r_1^2+r_2^2=1$ for all times, to reduce the problem to the solution of two nonlinear first-order differential equations involving real quantities, plus one quadrature.

In order to insure accuracy in the calculations, both approaches were programmed for numerical computation, also using two different methods for solution of the equations. In one method of calculation, the system of four linear equations obtained by separating real and imaginary parts was integrated using a predictor-corrector method given by Hamming.[2] In the second approach, the fourth-order Runge-Kutta method was used to solve the pair of nonlinear equations discribed above. In both methods the $S$ matrix element $s_{12}$ was determined as a function of $\beta$ for specified values of $x$. Enough values were considered so that the cross-section integral of Eq. (16) could be evaluated with reasonable accuracy. However, for small values of $\beta$, an approximate method had to be employed as will be described below. Values of $s_{12}$ obtained by the two integration schemes were compared for a sufficient selection of values of the parameters to give confidence in the correctness of the programs. A further check on calculations was furnished by the known analytic solution to Eqs. (11) when $\omega=0$ and $n=l$.

Our difficulty was encountered. For small values of $\beta$, the terms of Eqs. (11) are large, and the $S$ matrix element $s_{12}$ is a rapidly oscillating function of $\beta$, with a period which decreases repidly as $\beta\to 0$. This behavior, which is also predicted by the approximate solution, Eq. (3) is shown in Fig. 1 in a specific example. This behavior is a consequence of the singularity of the interaction at $R=0$, and would not be expected to occur in more realistic examples in which the interaction is not singular. To follow the oscillations in careful detail for small values of $\beta$ would have required a very large amount of computer time, so the following procedure was devised: The quantity $s_{12}^2$ was approximated for small $\beta$ by

$$s_{12}^2(\beta)=\tfrac{1}{2}[c_1+\beta c_2]. \tag{18}$$

The quantities $c_1$ and $c_2$ were determined graphically from the maxima of $s_{12}^2$. The factor of $\frac{1}{2}$ takes account of the oscillatory behavior of the true $s_{12}^2$. Because of the factor $\beta$ in Eq. (16), the contribution to the cross section from the region in which extrapolation is necessary was usually of the order of 10%. The extrapolated formula may be expected to give accuracy within 10% itself, so that the uncertainty in the cross section due to this extrapolation would be, in most cases, of the order of 1%. Certain exceptional cases, in which the cross section is small, have a somewhat larger uncertainty, perhaps 5 or 10%.

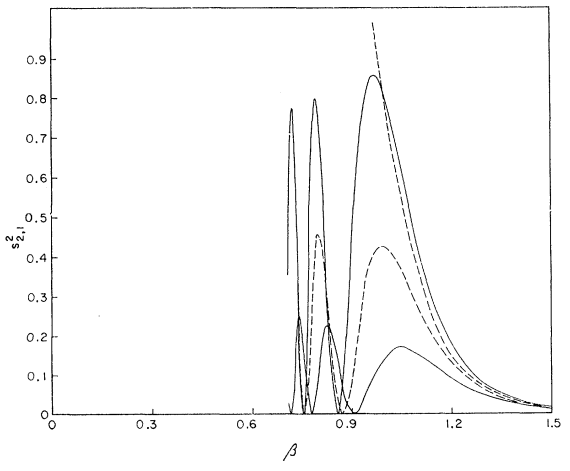


FIG. 1. The transition probability, $s_{12}^2$ is shown as a function of the dimensionless impact parameter $\beta$ for the case $n=6$, $l=6$, $k=1$, $x=\pm 1$. The upper solid curve represents the case in which the parameters $q_2$, $\omega$ are positive $[\sigma(+)]$; the lower solid curve that in which either $q_2$ or $\omega$ is negative $[\sigma(-)]$. The upper dashed curve shows the result of first-order perturbation theory, Eq. (22); the lower dashed curve is that obtained from the approximate solution, Eq. (20).

## IV. RESULTS AND DISCUSSION

In Fig. 1, we show the quantity of $s_{21}^2$ as a function of $\beta$ for the cases $n=6$, $l=6$, $k=1$, $x=\pm 1$. In Fig. 2, the same quantity is shown for $n=3$, $l=3$, $k=1$, $x=\pm 0.1$. These curves are, in most qualitative respects, quite typical of all those we have studied. The following features of the results deserve emphasis:

In the first place, the transition probability is seen to oscillate rapidly as $\beta$ decreases, as was mentioned in the previous section. The origin of these oscillations is easily understood from application of the approximate Eq. (3) to the two level problem. It was shown in I that in this case

$$s_{21}^2=\frac{T_{21}^2}{T_{11}^2+T_{21}^2}\sin^2[T_{11}^2+T_{21}^2]^{1/2}, \tag{19}$$

where $T_{ij}=T_{ij}(t=\infty)$, and the matrix $\mathbf{T}(t)$ was defined in Eq. (4). The elements of $\mathbf{T}$ are rapidly increasing functions of $\beta$ as $\beta$ decreases. Oscillations of the transition probability are to be expected in all cases in which the interaction is sufficiently strong, and such oscillations are in principle experimentally observable, although actual observation might be quite difficult.

Second, we see that there can be a very large difference between the transition probabilities for $x>0$ and $x<0$, corresponding to the two different solutions discussed in Sec. II, except for large values of $\beta$. This difference is not predicted either by perturbation theory or the approximation of Eq. (3). Neither is this behavior predicted by the calculation of Rosen and Zener[3] who found an exact analytic solution of Eq. (1) with $\omega\neq 0$

[2] R. W. Hamming, J. Assoc. Computing Machinery 6, 37 (1959).

[3] N. Rosen and C. Zener, Phys. Rev. 40, 502 (1932).

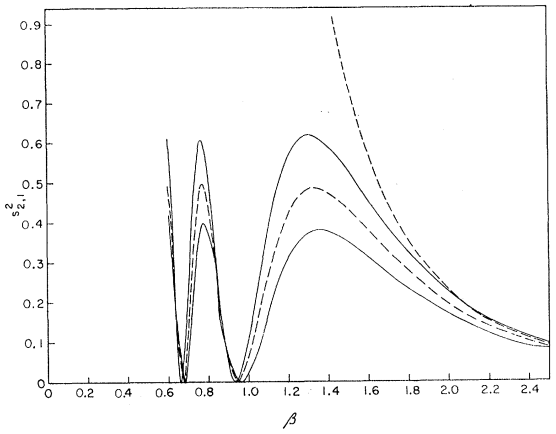


FIG. 2. The transition probability is shown for the case $n=3$, $l=3$, $k=1$, $x=\pm 0.1$. The curves have the same significance as in Fig. 1.

for a special form of the interaction. As will be seen below, their failure to find this feature is presumably due to their neglect of the diagonal elements of the perturbation. Similarly, a comparison of exact and approximate solutions of (1) for certain other interactions reported by Skinner[4] failed to reveal this effect. However, Bates[5] has observed that the diagonal matrix elements should be important.

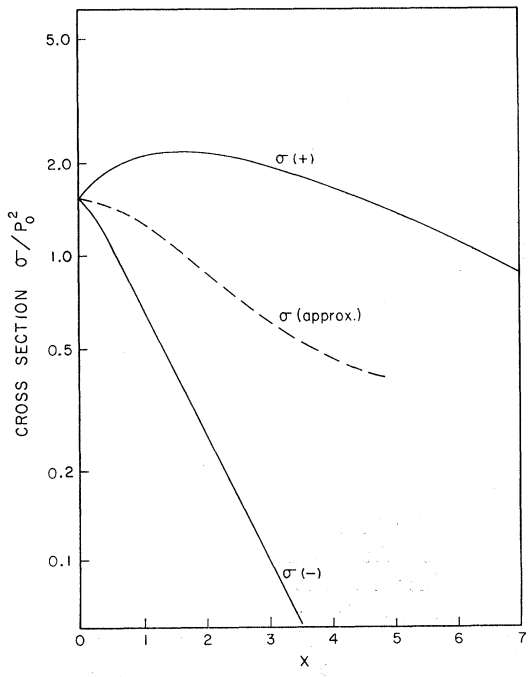


FIG. 3. The dimensionless cross section $\sigma/p_0^2$ is shown as a function of $|x|$ for the case $n=6$, $l=6$, $k=1$. The upper solid curve represents $\sigma(+)$; the lower solid curve shows $\sigma(-)$. The intermediate dashed curve shows the result of the approximate method described in I for this case.

[4] B. G. Skinner, Proc. Phys. Soc. (London) **77**, 551 (1961).
[5] D. R. Bates, Discussions Faraday Soc. **33**, 7 (1962).

It will be observed that as $\beta$ decreases, the first maximum of the transition probability occurs for approximately the same value of $\beta$ in the two cases, ($x>0$ and $x<0$) but the magnitudes of the transition probabilities, at the first maximum differ by a factor of approximately 4 in Fig. 1 and 1.5 in Fig. 2. It is not necessary for the transition probability to attain a large value for oscillations to begin. For larger values of $x$, the difference between the transition probability curves becomes even more striking, and for $x=3$, the difference in the cross sections $\sigma(+)$ and $\sigma(-)$ amounts to nearly two orders of magnitude. For small values of $x$, the transition probability curves for the two solutions

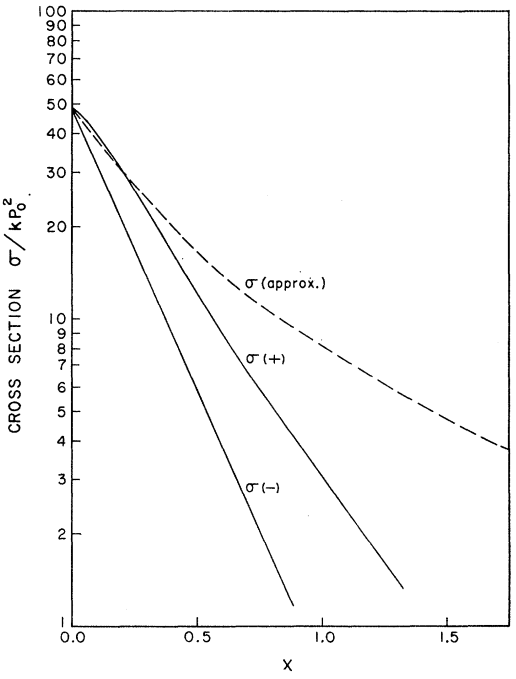


FIG. 4. The dimensionless cross section is shown as a function of $|x|$ for the case $n=3$, $l=3$, $k=.2$. Curves have the same significance as in Fig. 3.

come together. The behavior of the cross section as a function of $x$ is shown in Figs. 3–7 in the cases we have studied (which are summarized in Table II).

Let us compare these results with those of perturbation theory. First-order perturbation theory gives the result

$$s_{21}^2=\hbar^{-2}\left|\int_{-\infty}^{\infty}\langle 1|V_{\text{eff}}|2\rangle e^{-i\omega t}dt\right|^2. \tag{20}$$

For the potential of Eq. (6) this becomes

$$s_{21}^2=\pi\left[\frac{2}{\Gamma(n/2)}\frac{q_1}{\hbar V p^{n-1}}\right]^2\left(\frac{\omega p}{2V}\right)^{n-1}K^2_{(n-1)/2}(\omega p/V)$$

$$=\frac{4\pi}{[\Gamma(n/2)]^2}\left(\frac{x}{2\beta}\right)^{n-1}K^2_{n-1/2}(x\beta), \tag{21}$$

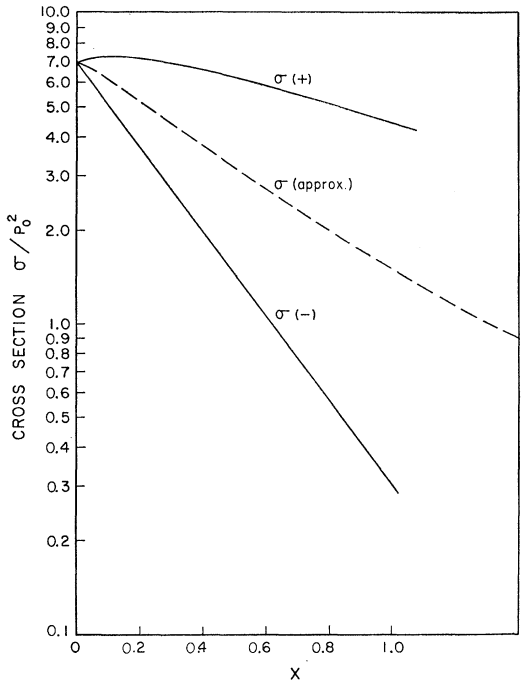


FIG. 5. The dimensionless cross section is shown as a function of $|x|$ for the case $n=3$, $l=3$, $k=1$. Curves are drawn as in Fig. 3.

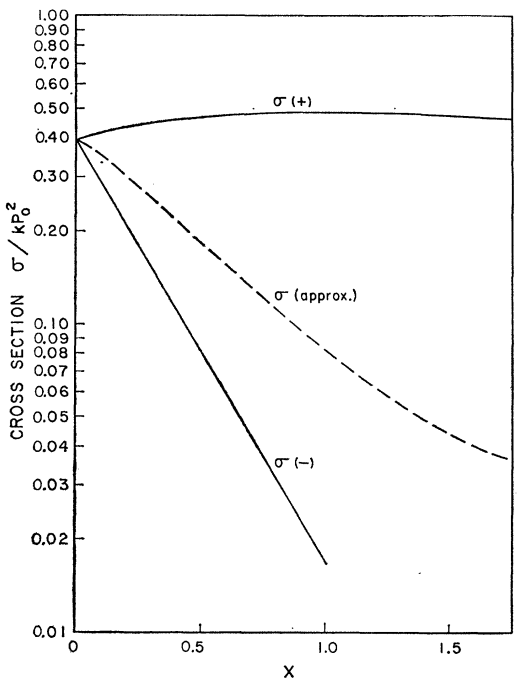


FIG. 6. The dimensionless cross section is shown as a function of $|x|$ for the case $n=3$, $l=3$, $k=5$. Curves are drawn as in Fig. 3.

in which $K$ represents a modified Bessel function of the third kind. A finite cross section can not be obtained from Eq. (20) unless a lower cutoff is imposed.

The results of first-order perturbation theory are also shown in Figs. 1 and 2 for the parameters considered. It is seen that the agreement between the Eq. (21) and the exact calculation is good nearly up to the first maximum in the case $x>0$, but very poor for $x<0$. Of course, for sufficiently large $\beta$, the difference between the two transition probability curves goes to zero, and Eq. (20) is a good approximation. The results of the approximate calculation of I which leads to Eq. (19) are also shown in Figs. 1 and 2. It is seen that this approximation leads to results intermediate between those of perturbation theory and the exact calculations. When $\omega=0$, Eq. (19) is exact, as has already been observed. The cross sections computed using the results of I are also shown in Figs. 3–7. The approximate method of I gives a reasonably good representation of the average of the two cross sections when $x$ is small.

It is quite helpful in understanding the difference between the two transition-probability curves shown in Figs. 1 and 2 to consider the second-order terms in the perturbation expansion in a simple example. From general perturbation theory,[6] we have the $S$-matrix expansion

$$S=1-\frac{i}{\hbar}\int_{-\infty}^{\infty}dt\,H_I(t)+\left(\frac{-i}{\hbar}\right)^2\times\int_{-\infty}^{\infty}dt\int_{-\infty}^{t}dt_1H_I(t)H_I(t_1)+\cdots, \quad (22)$$

where we may take for the interaction-picture Hamiltonian $H_I(t)$ the matrix $\mathbf{Q}$ mentioned in the introduction. We want to look at the second-order terms in the expansion. The second-order calculation is rather difficult with an interaction proportioned to $R^{-n}$, unless it is done numerically. For illustrative purposes we have chosen instead

$$Q_{jk}=(H_I)_{jk}=V_{jk}\exp[-(i\omega_{kj}t+\alpha|t|)], \quad (23)$$

since in this example the $S$-matrix elements can be obtained easily in terms of elementary functions. In Eq. (23) we take $V_{jk}$ independent of time, and, as usual, consider a two-level system. We suppose $Q$ is traceless, so that $V_{11}=-V_{22}$. However in contrast to the procedure of formal scattering theory, we do not let $\alpha\to 0$ or even suppose that it is small. We are interested in $s_{12}$ as a function of $\alpha$. After a straightforward calculation we obtain the second-order $S$-matrix element:

$$S_{12}=-\frac{i}{\hbar}\frac{2\alpha V_{12}}{\alpha^2+\omega^2}\left[1+\frac{6V_{11}\omega}{\hbar(4\alpha^2+\omega^2)}\right] \quad (24)$$

[6] See, for instance, S. S. Schweber, *An Introduction of Relativistic Quantum Field Theory* (Harper and Row, New York, 1962), Chap. 11.

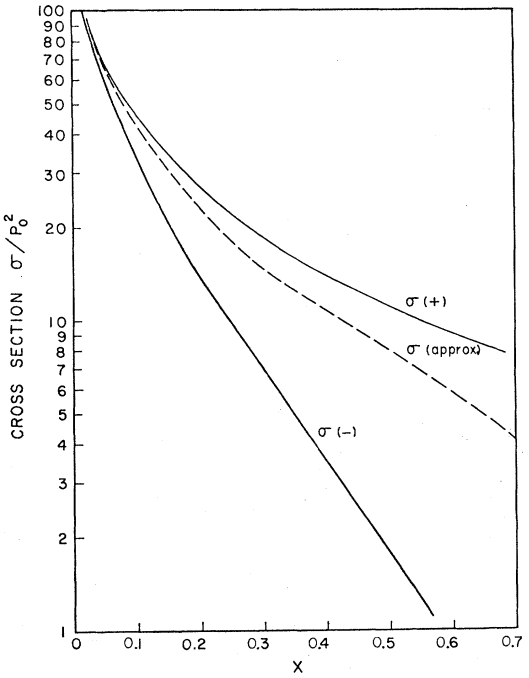


FIG. 7. The dimensionless cross section is shown as a function of $|x|$ for the case $n=2$, $l=3$, $k=1$. Curves are drawn as in Fig. 3.

in which $\omega=\omega_{21}$. We see that (in conformity with the previous discussion) $S_{12}$ is purely imaginary. This guarantees unitarity to this order. The quantity in front of the square brackets is the first-order expression for $S_{12}$. We see that the effect of second-order corrections is to multiply the first-order formula by a factor which is greater than 1 if $\omega V_{11}$ is positive and less than 1 if $\omega$ is negative. Of course, for perturbation theory to be meaningful, the second-order correction must be relatively small. Then we see that the transition probability is independent of the algebraic sign of $V_{12}$, but is greater than that predicted by first-order perturbation theory if $\omega V_{11}>0$ and smaller if $\omega V_{11}<0$. These conclusions are in accord with the results of the machine calculations, and with the statements of Table I concerning the effects of changing signs of the parameters. Finally, we note that if $\omega=0$, Eq. (3) is valid; and the second-order correction vanishes as is predicted by the results of I.

The over-all behavior of the cross section as a function of $x=(\omega p_0/V)$ may be summarized as follows: For small values of $x$ the cross sections vary linearly with $x$. However the two cross sections $\sigma(+)$ and $\sigma(-)$ may exhibit radically different behavior. The cross section $\sigma(-)$ is a decreasing function of $x$, and is well approximated by a decreasing exponential: $\sigma\propto\exp(-bx)$, with $b$ a function of $n$ and $k$. The other cross section, $\sigma(+)$, varies more slowly, and, at least in some cases, begins by increasing initially with $x$. For large $x$, $\sigma(+)$ also appears to approach exponential decrease.

The dependence of the cross section on $x$ is influenced by the parameter $k$, which determines the relative importance of the off-diagonal and diagonal elements of the interaction. This can be seen from inspection of Figs. 4–6. When $k$ is small, the off-diagonal elements of the interaction are large compared to the diagonal, and we see that the cross sections $\sigma(+)$ and $\sigma(-)$ do not differ greatly. The maximum of $\sigma(+)$ occurs either at, or close to, $x=0$. However, when $k$ is large, so that the diagonal elements are large, not only is the cross section reduced in magnitude, but the difference between $\sigma(+)$ and $\sigma(-)$ is greatly enhanced.

These results disagree with some of the predictions made on the basis of the approximate analysis of I. The treatment given there did not reveal the substantial difference between $\sigma(+)$ and $\sigma(-)$; nor did it predict exponential decrease of the cross section for large values of $x$.

Let us finally consider the dependence of the cross section on the range of the interaction which, in the present examples, is characterized by the exponents $n$ and $l$. It is apparent that $\sigma/p_0^2$ increases with decreasing $n$ when $x$ is small. This is in accord with the predictions of I. However, the cross sections decay more rapidly with increasing $x$ for the smaller values of $n$, so that the $\sigma/p_0^2$ increases with increasing $n$ when $x$ is large. The rather special case in which $n=2$ warrants special comment. In this situation the cross section diverges logarithmically as $x\rightarrow 0$. The reason for this is apparent from perturbation theory: in that case the quantity $s_{12}$ is proportional to $1/\beta$ when $\beta$ is large and $x=0$.

Consideration of the results of the numerical calculations reported here leads to the following conclusions. The approximate solution of the time-dependent Schrödinger equation proposed in Eq. (3) furnishes a convenient method of enforcing the requirements of conservation of probability. In several respects, it is in substantial agreement with the exact calculations, particularly in regard to the prediction of an oscillatory transition probability when the interaction is strong. This may be its principal merit. Other methods of insuring unitarity, such as that in which we divide $\mathbf{a}(t)$ as computed from perturbation theory by its norm may not (and the example does not) exhibit this feature. For small values of the quantity $x$, it gives a reasonable approximation to the average of the two cross-sections $\sigma(+)$ and $\sigma(-)$. Its worst defect is that it cannot predict the substantial difference between the two cross sections $\sigma(+)$ and $\sigma(-)$ which the numerical calculations show to exist when $x$ is not zero and the diagonal elements of the interaction matrix do not vanish.