AAPT PHYSICS EDUCATION | AMERICAN JOURNAL of PHYSICS

Solution of a simple inelastic scattering problem

Stephen K. Knudson

Citation: American Journal of Physics **43**, 964 (1975); doi: 10.1119/1.10021
View online: http://dx.doi.org/10.1119/1.10021
View Table of Contents: http://scitation.aip.org/content/aapt/journal/ajp/43/11?ver=pdfcov
Published by the American Association of Physics Teachers

Solution of a simple inelastic scattering problem

Stephen K. Knudson
Department of Chemistry
Florida Technological University
Orlando, Florida 32816
(Received 22 January 1974; revised 21 June 1974)

Simple examples of elastic scattering, typically from square wells, serve as important pedagogical tools in discussion of the concepts and processes involved in elastic scattering events. An analytic solution of a model inelastic scattering system is presented here to serve in this role for inelastic events. The model and its solution are simple enough to be of pedagogical utility, but also retain enough of the important physical features to include most of the special characteristics of inelastic systems. The specific model chosen is the collision of an atom with a harmonic oscillator, interacting via a repulsive square well potential. Pedagogically important features of inelastic scattering, including its multistate character, convergence behavior, and dependence on an "inelastic potential" are emphasized as the solution is determined. Results are presented for various energies and strengths of inelastic scattering, which show that the model is capable of providing an elementary representation of vibrationally inelastic scattering.

I. INTRODUCTION

Standard treatments of collision problems motivate the concepts involved in elastic scattering by considering simple examples, usually one-dimensional scattering from square or spherical wells.[1] The behavior of the parameter characterizing the scattering (phase shift, transmission coefficient, or the like) is discussed with reference to the physical nature of the system. Not only does this often clarify particular points for the student, but it also explains the meaning of the numerical or functional results in terms of the physics of the system, which is the point of the exercise. However, for inelastic scattering, typical discussions are purely formal, with no exact solutions of examples provided. Thus, no concrete base is laid for new concepts, nor can the student obtain a proper feeling for the expected magnitude or behavior of the results. As such material appears earlier in the curriculum, it becomes increasingly desirable to present this assistance.

We describe here an inelastic collision system by means of which this basis can be provided. The model system is sufficiently complex that the results display a number of the special features of inelastic systems, but it nonetheless possesses a relatively simple, analytic solution. There are a few other inelastic systems[2] for which analytic solutions are known, but they involve much more severe simplifications. The system used here is not only of tutorial interest, but may also prove valuable as an elementary model for the behavior of inelastic scattering in real systems.

In the next section we describe the inelastic scattering process and begin the solution of the Schroedinger equation for the model system presented here. Points of special pedagogical interest for the inelastic collision process are discussed in detail. In the third section, the specification of the model system is completed and the solution presented. Here emphasis is placed on the interpretation of the particular solution found and on the relation of its behavior to the physical processes occurring during the collision event. The final section summarizes the results of this investigation.

II. DESCRIPTION OF THE INELASTIC SCATTERING PROCESS

The purpose of this section is to provide a physical description of the inelastic scattering process to accompany the formal mathematical development from the Schroedinger equation. The description is given using the scattering of an atom from a nonrotating diatomic molecule as a model. Before and after the collision, the atom and molecule are so well separated that the interaction between them is negligible. During the close encounter portion of the collision, the interaction may be strong enough to change the vibrational state of the diatom. If the molecule does leave the encounter in a new state of different energy, the kinetic energy of the atom will be changed also, to conserve energy; such collisions, resulting in a change in relative speed of the particles, are called inelastic.

To avoid nonessential complications, the specific model for this process is taken to be the collision of a structureless particle (the atom) with a harmonic oscillator (the molecule), with all three particles constrained to lie on a straight line; the rationale is that the collinear configuration is the most effective in promoting vibrational excitation of the molecule. This one-dimensional model is incapable of assigning any angular distribution to the scattering; the results of interest are the inelastic scattering probabilities which specify the distribution of molecules among the possible vibrational states. The model is crude not only in its description of the particles but also in its neglect of all three-dimensional aspects of the real problem. Nonetheless, it proves useful for the vibrational scattering problem,[3] and by so limiting the possible physical processes it focuses attention on the inelastic event itself.

This inelastic vibration scattering process is, of course, formalized in the Schroedinger equation. For the collision of a particle of mass μ with this oscillator, the Schroedinger equation in atomic (Hartree) units is

$$\left(-\frac{1}{2\mu}\frac{\partial^2}{\partial x^2}+H_I+V(x,y)-E\right)\Psi_t(x,y)=0, \qquad (1)$$

where x is the distance of the atom from the equilibrium position of the molecule, E is the total energy of the system (excluding center-of-mass motion), and Ψ is the wave function describing both the oscillator and the atom, with the subscript i identifying the initial state of the molecule. $V(x,y)$, the interaction between the collision partners, vanishes when x is large (pre- and postcollision regions). H_I is the Hamiltonian for the molecule; it gives the well-known harmonic oscillator result

$$H_I\phi_n(y) = \epsilon_n\phi_n(y) = (n-\tfrac{1}{2})\phi_n(y), \quad n = 1, 2, 3, \ldots, \quad (2)$$

where ϕ_n is the eigenfunction with eigenvalue ϵ_n and y is the oscillator (molecular) coordinate. By way of nomenclature, each state ϕ_n determines a "channel" for the collision: The atom begins the collision in the entrance channel i (the molecule is in state ϕ_i) and departs in some exit channel f (the molecule is in state ϕ_f).

The dependence of the wave function on two independent variables has several important consequences. First, the solution of the equation is difficult to obtain directly. Equally important, even if the solution were found, its interpretation in terms of physical processes would still be difficult. In order to obtain both the solution and its meaning, we expand the wave function in terms of the complete set of bound molecular (oscillator) states:

$$\Psi_i(x, y) = \sum_{n=1}^{N} \psi_{ni}(x)\phi_n(y); \quad (3)$$

this expansion is formally exact if all the molecular states are included ($N \to \infty$). The wave function $\psi_{ni}(x)$ then describes the colliding atom when the molecule is in state n, a function much easier to interpret than the two-dimensional form. It is the necessity[4] to make this expansion of the wave function that in part distinguishes inelastic from elastic scattering. That is, inelastic scattering is inherently a multistate process, in contrast to elastic scattering and most elementary bound-state processes. Inelastic scattering provides a particularly simple demonstration of the behavior of such a system.

We employ the separation of variables suggested by Eq. (3) in the following way. Substitute this equation into the Schroedinger equation (1) and use Eq. (2) to find

$$\sum_n \left(-\frac{1}{2\mu}\frac{\partial^2}{\partial x^2} + V(x, y) - (E - \epsilon_n)\right)\psi_{ni}(x)\phi_n(y) = 0. \quad (4)$$

Now multiply on the left by $\phi_m^*(y)$, integrate over all y, and use the orthonormality of the molecular wave functions; then

$$\left(\frac{d^2}{dx^2} + k_m^2 - 2\mu V_{mm}(x)\right)\psi_{mi}(x) - 2\mu \sum{}' V_{mn}(x)\psi_{ni}(x) = 0. \quad m = 1, 2, 3, \ldots, \quad (5)$$

where

$$V_{mn}(x) = \int \phi_m^*(y)V(x, y)\phi_n(y)\,dy, \quad (6)$$

$$k_m = |2\mu(E - \epsilon_m)|^{1/2}, \quad (7)$$

and the prime on the summation over n in Eq. (5) means that the $n = m$ term is to be omitted. If the off-diagonal elements of V were zero, the summation in Eq. (5) would vanish; the interpretation of the first term would be just that of elastic scattering by the potential $V_{mm}(x)$ at a collision energy $E - \epsilon_m$. It is the second term of the equation that causes the inelastic scattering by coupling all the wave functions together. Thus, initially only ψ_{ii} contains amplitude, but as the collision progresses and x becomes smaller, the $V_{mi}\psi_{ii}$ term in each of the Eqs. (5) pumps amplitude into each of the states ψ_{mi}. The precise nature of the final distribution of amplitude among all the states ψ according to the prescription (5) determines the inelastic scattering probabilities.

These probabilities are uniquely specified by the imposition of the boundary conditions for the system. The directness of this procedure in scattering problems stresses the important role of boundary conditions in specifying solutions to the Schroedinger equation. A set of boundary conditions appropriate to the present problem are

$$\lim_{x\to-\infty} \psi_{ni}(x) = 0, \quad (8a)$$

$$\lim_{x\to+\infty} \psi_{ni}(x) = k_n^{-1/2}[\delta_{ni}\sin(k_n x) + R_{ni}\cos(k_n x)], \quad n \leq M \quad (8b)$$

$$= 0, \quad n > M. \quad (8c)$$

Equation (8a) is simply the statement that the atom is not allowed to pass completely through the molecule; the potential $V(x,y)$ must account for this physical constraint on the system, as well as vanishing for large positive x. Now consider Eq. (8c). If the oscillator energy ϵ_n is greater than the total energy E, energy conservation forbids scattering to this state. If M is the molecular state with the highest energy less than E, channels labeled by $n \leq M$ are called open and are accessible to scattering; the remaining channels, with n larger than M, are closed. However, this does not mean that the expansion given in Eq. (3) can be truncated at $n = M$; rather it means that amplitude produced in a closed channel during the course of a collision must leak back out of the channel before the termination of the encounter.

Equation (8b) contains the information which determines the inelastic scattering probabilities. The delta term merely ensures the proper behavior of the wave function in the entrance channel. The numbers R_{ni} for n and i ranging from 1 to N determine an $N \times N$ ($M \times M$ if N is greater than M) matrix $\mathbf{R}$ called the reactance matrix. These boundary conditions are used because they make the solution found in the next section to be real; then the inelastic transition probability is given by

$$P_{fi} = |\sum (\mathbf{R} - i\mathbf{1})_{fn}[(\mathbf{R}^2 + 1)^{-1}]_{nm}(\mathbf{R} - i\mathbf{1})_{mi}|^2. \quad (9)$$

An alternate form[5] for the boundary condition would replace Eq. (8b) with

$$\lim_{x\to\infty}\psi_{ni}(x)=\delta_{ni}\exp(-ik_n x)+T_{ni}\exp(+ik_n x), \quad (8b')$$

for which

$$P_{fi}=|T_{fi}|^2. \quad (9')$$

This set of boundary conditions has the advantage of being directly interpretable in terms of the physical processes involved. Thus, the first term represents the incoming atom as a plane wave moving to the left; the second, the outgoing plane wave moving to the right, having been scattered by the vibrator. The interpretation of the unprimed set of boundary conditions is then that it is a convenient linear combination of the physically more meaningful set.

III. A SOLUBLE MODEL

In this section we complete the specifications of the model system, by defining the interaction potential $V(x,y)$, and discuss the solution obtained. We choose the potential to be separable,

$$V(x,y)=v(x)v(y), \quad (10)$$

and maintain a connection with previous work[3] on vibrational scattering by using an exponential potential in the molecular coordinate:

$$v(y)=\exp(\alpha y). \quad (11)$$

For simplicity, we then choose a square-mound potential in the relative coordinate:

$$\begin{aligned} v(x)&=\infty, \quad x<x_I \text{ (region I)}\\ &=D, \quad x_I<x<x_E \text{ (region II)}\\ &=0, \quad x_E<x \text{ (region III)}. \end{aligned} \quad (12)$$

As in the elastic case, the choice of a square potential has the special advantage that an analytic solution of the Schroedinger equation is possible. The choice of potential in region I prevents the atom from passing through the oscillator, in agreement with Eq. (8a); the choice in region III is fixed by the requirement that the interaction between the collision partners vanish at infinity. Using Eqs. (10)–(12) in Eq. (5) and defining

$$\begin{aligned} U_{mn}(\alpha)&=\int \phi_n^*(y)\exp(\alpha y)\phi_m(y)\,dy\\ &=(2^{m-n}m!/n!)^{1/2}\exp(\alpha^2/4)\\ &\quad\times\alpha^{n-m}L_m^{n-m}(\alpha^2/2), \qquad n>m \end{aligned} \quad (13)$$

where $U_{nm}=U_{mn}$ and L_b^a is an associated Laguerre polynomial,[3] in region II Eq. (5) becomes

$$\left(\frac{d^2}{dx^2}+k_m^2-2\mu DU_{mm}\right)\psi_{mi}(x)-2\mu D\sum{}'U_{mn}\psi_{ni}(x)=0, \quad (14a)$$

and in region III it becomes

$$\frac{d^2}{dx^2}+k_m^2\ \psi_{mi}(x)=0. \quad (14b)$$

The form of Eqs. (14) is similar to one given by Newton,[6] but the explicit solution is not given there. The solution of Eq. (14a) that satisfies the boundary condition (8a) at $x=x_I$ is[7]

$$\psi_{nj}(x)=\sum_{m=1}^{N}A_{mnj}\frac{\sin[\gamma_m(x-x_I)]}{\gamma_m}. \quad (15a)$$

The solution of Eq. (14b) that satisfies the boundary conditions (8b) and (8c) at large x is given by

$$\begin{aligned} \psi_{nj}(x)&=k_n^{-1/2}[\delta_{nj}\sin(k_n x)+R_{nj}\cos(k_n x)], \quad n<M\\ &=F_{nj}\exp(-k_n x), \quad n>M. \end{aligned} \quad (15b)$$

The parameters γ_m in Eq. (15) are the eigenvalues of an $N\times N$ matrix W with elements $W_{ij}=k_i\delta_{ij}+2\mu DU_{ij}$. The unknown coefficients A_{mnj}, R_{nj}, and F_{nj} are then found by forcing continuity upon all the wave functions and their first derivatives at $x=x_E$. The numerical procedures of (i) finding the eigenvalues and (ii) solving the algebraic equations resulting from the continuity conditions can both be carried out without great difficulty upon a digital computer. Accurate values for the transition probabilities P_{ij} can then be found by increasing N until the probabilities remain constant.

We now comment on the interpretation of the solutions obtained. The wave function for the open channels beyond the range of the potential is self-explanatory; for the closed channels, the wave function there is a decaying exponential in order to satisfy the boundary condition that they contain no amplitude at infinity. This is, of course, just the behavior of a bound-state function for a particle in a box; in fact, the closed-channel states are most important when a quasibound state of the system exists, but this is a separate topic we cannot discuss here.[8] Inside the square-mound potential, the wave function is more complicated. Basically, the γ_m's are combinations of all the k_m's with the inelastic potentials DU_{nm}. We may define inelastic potential strength parameters as

$$S_{mn}=2\mu DU_{mn}/k_m^2; \quad (16)$$

then with $t=k_m x$, Eq. (14a) may be written

$$\left(\frac{d^2}{dt^2}+1-S_{mm}\right)\psi_{mi}(t)-\sum_n S_{mn}\psi_{ni}(t)=0. \quad (17)$$

Table I. $\alpha = 1.00$.

m:	0	1	2	3	4	
			R_{nm}			n
	−1.0539	−1.4445	−1.3019	−0.7253	−0.1812	0
		−2.9956	−3.0289	−1.7358	−0.4336	1
0	0.6197		−3.8019	−2.4684	−0.6664	2
1	0.2858	0.1981		−2.1256	−0.7764	3
2	0.0709	0.4157	0.1189		−0.5459	4
3	0.0202	0.0846	0.3609	0.3006		
4	0.0034	0.0158	0.0336	0.2337	0.7134	
n			P_{nm}			

When all the S parameters are small, the set of momenta γ will be only weakly shifted (perturbed) from the set of momenta k. As the inelastic potential strengths increase, the shifts become large, and γ_m can no longer be identified with k_m. Under these conditions the states represent more nearly those of the atom–diatom complex than those of the separate species.

We have carried out calculations for a variety of values of E, D, and α with $\mu = 1$, $x_1 = 0$, and $x_E = 1$. Some typical results are given in Table I for $E = 5$, $D = 1$, and $\alpha = 1$, and in Table II with α changed to ¼. The upper right-triangular portion of the tables contains the R-matrix elements; the lower left-triangular portion, the transition probabilities P (both **R** and **P** are symmetric matrices). In these calculations, N was increased until P_{12}, the probability of making a transition from the ground state to the first excited state, appeared to converge to 0.1%. The accuracy of the other elements was not generally monitored, but trial calculations indicate convergence to the accuracy reported in the tables. In Table I, nine states were required for convergence, while for Table II only five states were needed; in both the number of open channels is five. The general trend confirmed these results: for small α, $N \approx M$, but for large α, from five to ten closed channels are necessary to obtain this degree of convergence.

More general properties of the transition probabilities can be found in Figs. 1 and 2, in which P_{12} (solid curve) and $1 - P_{11}$, the total inelastic transition probability (dashed curve), are plotted. Figure 1 plots these functions against the parameter α; Fig. 2, against the energy for several values of α. In Fig. 1 the rapid increase of the inelastic transition probability comes as no surprise, since

Table II. $\alpha = 0.25$.

m:	0	1	2	3	4	
			R_{nm}			n
	−0.4458	−0.1104	−0.0210	−0.0030	−0.0002	0
		−0.5770	−0.1758	−0.0290	−0.0021	1
0	0.9705		−0.6601	−0.1874	−0.0182	2
1	0.0287	0.9107		−0.6109	−0.1277	3
2	0.0008	0.0591	0.8740		−0.3963	4
3	0.0000	0.0014	0.0653	0.8946		
4	0.0000	0.0000	0.0008	0.0387	0.9605	
n			P_{nm}			

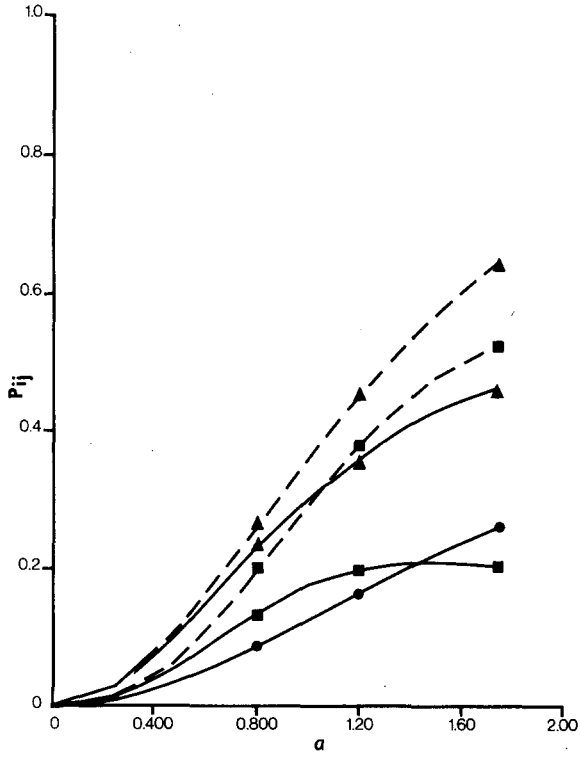

Fig. 1. Excitation probability P_{01} (solid line) and total inelastic excitation probability $1 - P_{00}$ (dashed line) at $D = 1$ for $E = 2$ (●), $E = 4$ (▲), and $E = 7$ (■). The two curves are not resolved for $E = 2$ at this scale.

the coupling strength S_{12} increases with α. The term U_{nm} is proportional to a polynomial of order $(\alpha^2)_{n-m}$, so the off-diagonal (inelastic) rapidly dominates as α increases. At the largest values for S_{12}, there is a tendency for P_{12} to decrease; the corresponding increase in $1 - P_{11}$ provides the interpretation that the rapid increase in the higher excitations occurs in part at the expense of the lower excited states, and emphasizes the dynamical nature of the coupling in Eq. (17).

The plots with the incident energy in Fig. 2 display some other interesting features of the inelastic scattering in this system. For two of the sets of choices of parameters the barrier height is $D = 5$, larger than the incident energy for a long range. This appears to have an important effect at small S_{12}, since the transition probability remains small until the energy exceeds the barrier height; it then increases rapidly. For larger S_{12}, the excitation inside the barrier is appreciable; presumably, even in the classically inaccessible region inside the barrier, the extent of inelastic coupling is large. In addition, at intermediate energies P_{12} decreases as the energy increases, without a large decrease in $1 - P_{11}$; again this implies that the higher excited states are taking amplitude from the less excited as the energy increases. However, here this is occurring as the inelastic potential strengths S_{12} decrease; what is happening is that, as each new channel reverts from closed to open as the energy increases, it steadily begins to acquire its share of the scattering. Eventually, the transition probabilities fall off at high energy, as the decrease in S finally makes itself felt; the total inelastic transition probability peaks at a larger energy than P_{12} because of the increase in S with increasing excitation.

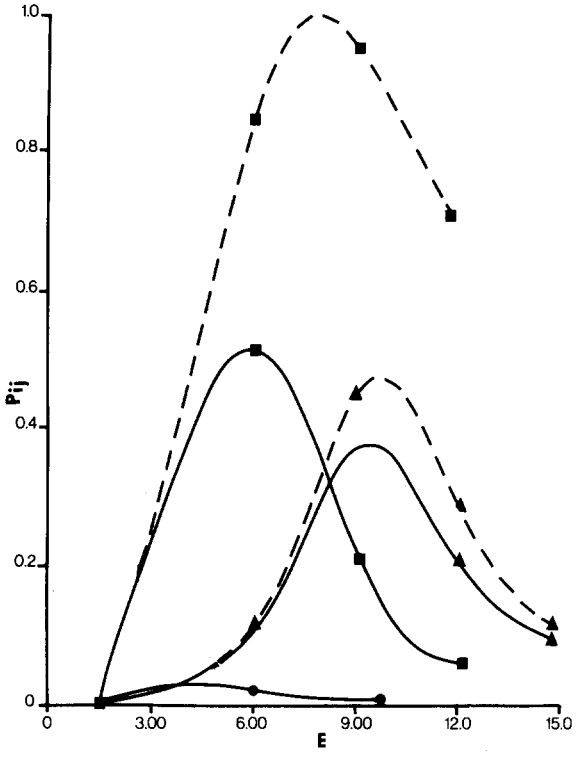

Fig. 2. Excitation probability P_{01} (solid line) and total inelastic excitation probability $1 - P_{00}$ (dashed line) for $\alpha = 0.25$, $D = 1$ (●), $\alpha = 0.25$, $D = 5$ (▲), and $\alpha = 1$, $D = 5$ (■). The two curves are not resolved for $\alpha = 0.25$, $D = 1$ at this scale.

Finally, we note that the calculations also show that the other inelastic transition probabilities display generally the same type of behavior as shown by P_{12}. At small α, P_{12} remains the dominant term, but as this parameter increases, a more excited transition may eventually dominate. Note that this is not entirely a "ladder" effect, since Eq. (14) supports direct excitation to all states.

IV. CONCLUSIONS

An analytic solution for an inelastic model scattering system analogous to simple models of elastic scattering has been presented. Sample calculations have shown that the properties of the system are similar to those of inelastic systems with more realistic potentials.[9] The model is thus a valid one from which the characteristic features of inelastic systems can be deduced. In addition to possible use as an elementary type of inelastic system, the model and its solution are simple enough to possess pedagogical utility in discussions of inelastic scattering. Not only can certain formal aspects of inelastic systems, such as their multistate nature, be explicitly seen, but the behavior of results upon changes of the relevant parameters can be investigated. Because the system is collinear, no information about the angular dependence of inelastic scattering probabilities can be determined; this is a regrettable aspect of the model, since such behavior is often of considerable interest.

ACKNOWLEDGMENT

The author is grateful to Computer Services at Florida Technological University for access to the IBM 360/65 computer used in this research.

[1]D. Bohm [*Quantum Theory* (Prentice-Hall, Englewood Cliffs, NJ, 1951)], for instance, also discusses inverse-power and Gaussian types.

[2]R. J. Huck, Proc. Phys. Soc. Lond. A **70,** 369 (1957); K. E. Shuler and R. Zwanzig [J. Chem. Phys. **33,** 1778 (1960)] numerically solve a simple inelastic system.

[3]See D. Rapp and T. Kassel, Chem. Rev. **69,** 61 (1969), for a recent review.

[4]The Schroedinger equation may be solved without recourse to Eq. (3), but the imposition of the boundary conditions requires the expansion.

[5]See any elementary text on scattering theory, for instance, L. S. Rodberg and R. M. Thaler, *Introduction to the Quantum Theory of Scattering* (Academic, New York, 1967).

[6]R. Newton, *Scattering Theory of Waves and Particles* (McGraw-Hill, New York, 1966).

[7]The factor of γ_m^{-1} appears for convenience for those cases where $\gamma_m^2 < 0$.

[8]R. D. Levine, Acc. Chem. Res. **3,** 273 (1970).

[9]The results here are characteristic of systems with "soft" interactions; see Ref. 3 and D. Secrest and B. Johnson, J. Chem. Phys. **45,** 4556 (1966).