Effect of Mutual Distortion on Phase Shifts of Colliding Systems*

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The box variational principle for scattering phase shifts is extended to one channel collisions of arbitrary angular momentum without exchange, and also to systems with many degrees of freedom, when the energies are nonrelativistic and insufficient to produce inelastic collisions. Under reasonable assumptions of continuity it is proved that the commonly used one state and many state approximations always reduce the scattering phase shift from its correct value, so long as no further approximations have to be made, and thus provide lower bounds to the exact scattering phase shift. The distorted wave approximation is an example. The inclusion of more states into a many state approximation never makes the estimated phase any worse, and generally improves it. Mutual distortion of colliding systems never reduces the phase shift and generally increases it, thus producing an effective attraction between the systems.

I. INTRODUCTION

NONRELATIVISTIC two-body collisions between quantal systems are of great importance in the physics of atoms and nuclei. The partial wave theory of Rayleigh, Faxèn, and Holtsmark has been widely applied and extended in these fields.[1–3] In this theory the collision cross sections are completely determined by a set of scattering phase shifts δ or S matrices which are obtained from the asymptotic form of the time-independent wave functions of the whole system.

For many elastic collisions there is a range of energies and a representation for which the wave functions in the asymptotic region, where the colliding systems are far apart, have a particularly simple form. Such a wave function can be factored into two functions, one representing the internal motion of the colliding systems in their ground states, and the other representing their relative motion. These one channel collisions may be analyzed in terms of phase shifts without recourse to S matrices. In this paper we shall consider only one channel collisions in which the forces between the colliding systems are of short range, and in which there is no exchange of particles.

The scattering phases may be obtained from a solution of the Schrödinger equation, but in nearly all collisions of this type such a solution is too difficult to obtain by direct analytic or numerical methods, and approximations must be made. It has been difficult to estimate the effect of these approximations on the phase shift and it has often been necessary to rely on rough physical evidence to make this estimation.

It would be very desirable to obtain bounds to phase shifts. Such bounds have been obtained and used for scattering phase shifts of spherically symmetric systems with no internal degrees of freedom,[4–6] but the bounds are then of limited value because the Schrödinger equation may be integrated without difficulty by numerical methods. Useful bounds for more complex systems have recently been obtained in the zero-energy limit,[7] and extended to higher energies under certain limiting conditions.

The box variational method proposed by Risberg[5] has been shown by Percival[6] to provide a lower bound to the exact scattering phase when the trial functions are chosen from the same finite linear function space at all energies; that is, when the Rayleigh-Ritz method is used within the box. In this paper we extend the box variational principle to systems with internal degrees of freedom and we are able to show that some widely used approximations also set lower bounds to exact scattering phases. These approximations may be generally described as one state and many state approximations, and include the distorted wave approximation when there is no exchange.

The one state approximation is obtained by neglecting all temporary excitation of the colliding systems, so that they are supposed to remain in their ground states during the collision. In other words the colliding systems are supposed to remain undistorted, although of course the waves which represent the relative motion of the systems are distorted by their interaction. Thus the phase inequality for the one state approximation shows that mutual distortion always increases the scattering phase shift. This may be interpreted as an effective attraction.

We now briefly sketch the proof of the phase inequality.

It is well known[8] that each of the first N eigenvalues of a Hermitian matrix (starting from the least) is

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[1] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Clarendon Press, Oxford, 1949), 2nd ed.
[2] H. S. W. Massey, *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, Göttingen, Heidelberg, 1956), Vol. XXXVI.
[3] J. M. Blatt and V. F. Weisskopf, *Theoretical Nuclear Physics* (John Wiley & Sons, Inc., New York, 1952).
[4] T. Kato, Progr. Theoret. Phys. (Kyoto) **6**, 394 (1951); T. Kikuta, Progr. Theoret. Phys. (Kyoto) **12**, 225 (1953).
[5] V. Risberg, Arch. Math. Naturvidenskab **53**, 1 (1956).
[6] I. C. Percival, Proc. Phys. Soc. (London) **A70**, 494 (1957).
[7] L. Spruch and L. Rosenberg, Phys. Rev. **117**, 143 (1960).
[8] R. Courant and D. Hilbert, *Methoden der Mathematische Physik* (Verlag Julius Springer, Berlin, 1931), Vol. I, p. 28.

smaller than the corresponding eigenvalue of a reduced Hermitian matrix obtained by projecting the original matrix onto a linear subspace. This theorem has been extended by Hylleraas and Undheim[9] to Hamiltonian operators in quantum mechanics. These are reduced to Hermitian matrices of finite order by the Rayleigh-Ritz method. It is not difficult to extend the theorem to the case in which they are reduced to Hermitian operators. This may be considered as an extended Rayleigh-Ritz method.

In deriving the box variational principle for scattering phases the whole system which takes part in the collision is placed in a box with impenetrable walls. The energy spectrum of this bound system is related to a set of scattering phase shifts. It may be proved using the theorem of Hylleraas and Undheim that the approximate phases obtained by using the Rayleigh-Ritz method within the box are always less than the exact phases for the same energy.

The one state and many state approximations to the wave functions for the colliding systems may be obtained by an extended Rayleigh-Ritz method applied to the wave function within a box. The phase inequality characteristic of the box variational principle is therefore valid for these approximations.

II. RAYLEIGH-RITZ APPROXIMATIONS TO DISCRETE SPECTRA

Let $H_{\mu\nu}$ be an $M\times M$ Hermitian matrix with a complete set of M orthonormal eigenvectors $\xi_\mu{}^\lambda$ and eigenvalues E^λ ordered so that

$$E^1\leqslant E^2\leqslant\cdots\leqslant E^M. \tag{1}$$

Let $\eta_\mu{}^m$ be a set of N orthonormal vectors with $N\leqslant M$. Then a new matrix may be formed with elements

$$H_{mn}{}'=\sum_{\mu,\nu=1}^{M}\eta_\mu{}^{m*}H_{\mu\nu}\eta_\nu{}^n \quad (m, n=1, 2, \cdots N), \tag{2}$$

and eigenvalues E'^λ ordered in the same way. The reduced matrix $H_{mn}{}'$ may be considered as a projection of $H_{\mu\nu}$ onto the subspace $\mathfrak{V}'$ of the space $\mathfrak{V}$, where the $\xi_\mu{}^\lambda$ are a set of unit vectors which span $\mathfrak{V}$, and the $\eta_\mu{}^m$ span the space $\mathfrak{V}'$. It is well known[5] that the eigenvalues E^λ and E'^λ obey the inequalities

$$E^\lambda\leqslant E'^\lambda \quad (\lambda=1, \cdots, N). \tag{3}$$

In words: If a Hermitian operator in a finite linear vector space $\mathfrak{V}$ of dimension M is projected onto a linear subspace $\mathfrak{V}'$ of dimension N the values of its first N eigenvalues are all increased.

This theorem is also valid when $\mathfrak{V}$ or both $\mathfrak{V}$ and $\mathfrak{V}'$ are Hilbert spaces and H is a Hermitian operator with a discrete spectrum and a smallest eigenvalue. We prove it when H is a Hamiltonian operator in nonrelativistic quantum mechanics.

[9] E. A. Hylleraas and B. Undheim, Z. Physik **65**, 759 (1930).

Let $\mathfrak{V}$ be a Hilbert space and $\mathfrak{V}'$ a linear space of finite dimension. Let $\mathfrak{V}$ be the space of state vectors of a quantal system confined in a box. In position representation the space $\mathfrak{V}'$ could be spanned by a finite set of N orthonormal functions

$$\varphi_m(X) \quad (m=1, 2, \cdots, N), \tag{4}$$

where X represents all the coordinates of the system and the $\varphi_m(X)$ satisfy the condition that they should be zero at the walls of the box. Let $H(X)$ be the Hamiltonian operator and E^λ its eigenvalues ordered as above. Then the reduced Hamiltonian matrix is

$$H_{mn}{}'^{(N)}=\int dX\ \varphi_m{}^*(X)H(X)\varphi_n(X) \quad (m, n=1, 2, \cdots, N), \tag{5}$$

which is simply a Rayleigh-Ritz approximation.

Suppose that $\varphi_m(X)$ is made into a complete set spanning the space $\mathfrak{V}$ by including the infinite sequence of functions

$$\varphi_m(X) \quad (m=N+1, N+2, N+3, \cdots). \tag{6}$$

Then if $N<M$ and

$$H_{mn}{}'^{(M)}=\int dX\ \varphi_m{}^*(X)H(X)\varphi_n(X) \quad (m, n=1, 2, \cdots, M), \tag{7}$$

$H_{mn}{}'^{(N)}$ is a reduction of the matrix $H_{mn}{}'^{(M)}$, and

$$E'^{(M)\lambda}\leqslant E'^{(N)\lambda} \quad (1\leqslant\lambda\leqslant M). \tag{8}$$

But since the set (4,6) of $\varphi_m(X)$ is complete

$$\lim_{M\to\infty} E'^{(M)\lambda}=E^\lambda. \tag{9}$$

Therefore

$$E^\lambda\leqslant E'^{(N)\lambda}. \tag{10}$$

This was proved by Hylleraas and Undheim.[9]

When both $\mathfrak{V}$ and $\mathfrak{V}'$ are Hilbert spaces the projection of the Hamiltonian H onto $\mathfrak{V}'$ is an extension of the Rayleigh-Ritz approximation to the case in which the trial functions in the variational formulation form an infinite linear set. The proof of the inequality is the same up to Eq. (8) except that the infinite sequence

$$\varphi_m(X) \quad (m=1, 2, 3, \cdots) \tag{11}$$

is chosen to be a complete set for the *reduced space* $\mathfrak{V}'$. Then $E^\lambda\leqslant E'^{(N)\lambda}$ is still valid for all N, since the functions $\varphi_1(X)\cdots\varphi_N(X)$ are contained in the space $\mathfrak{V}$. Let E'^λ be the eigenvalues of the reduced Hamiltonian formed by projecting H onto $\mathfrak{V}'$. Then

$$\lim_{N\to\infty} E'^{(N)\lambda}=E'^\lambda. \tag{12}$$

Therefore

$$E^\lambda\leqslant E'^\lambda. \tag{13}$$

The extended Rayleigh-Ritz approximation may be used to reduce the dimension of a Schrödinger equation. Suppose that the Hamiltonian is $H(X,Y)$ and the wave function for energy E^λ is $\Psi_{E^\lambda}(X,Y)$, where X and Y may each represent many variables. A reduced Hamiltonian may be obtained by projecting onto the Hilbert space defined by the functions

$$\sum_{\gamma^0=0}^{\Gamma-1} \varphi_{\gamma^0}(X)F_{\gamma^0}(Y), \tag{14}$$

for which φ_{γ^0} and F_{γ^0} obey the required boundary conditions, and $\varphi_{\gamma^0}(X)$ are a fixed orthonormal set of functions. The reduced Schrödinger equation for the functions $F_{E'^\lambda\gamma}(Y)$ is of the form;

$$\sum_{\gamma^0} H_{\gamma\gamma^{0\prime}}(Y)F_{E'^\lambda\gamma^0}(Y)-E'^\lambda F_{E'^\lambda\gamma}(Y)=0,$$

$$(\gamma, \gamma_0=0, 1, \cdots, \Gamma-1), \tag{15}$$

where the approximate energies E'^λ are determined by Eq. (15) and by the boundary conditions. The reduced Hamiltonian is

$$H_{\gamma\gamma^{0\prime}}(Y)=\int dX\ \varphi_\gamma{}^*(X)H(X,Y)\varphi_{\gamma^0}(X). \tag{16}$$

The reduced or approximate wave function $\Psi_{E'^{\lambda'}}(X,Y)$ may be found by substituting the $F_{E'^\lambda\gamma}(Y)$ into Eq. (14).

For this extension of the Rayleigh-Ritz approximation the matrix equation becomes an operator equation, which may be a differential equation or an integral equation.

III. COLLISION OF A PARTICLE WITH A HEAVY SYSTEM

Consider firstly the collision of a particle of mass m and no internal degrees of freedom with a system of effectively infinite mass whose center of mass is at the origin of the coordinates. For instance the particle might be an electron and the system might be an atom; to be specific we shall use "electron" and "atom" to denote the colliding systems. Spin and exchange will be neglected, and the atom supposed to have zero angular momentum. More complicated collisions will be considered in Sec. VII.

Let r be the distance of the electron from the origin and X represent all other coordinates, including the angular coordinates of the electron. Let $\Psi(X,r)$ be the wave function for the whole system of atom and electron. By the usual partial wave theory this may be chosen an eigenfunction of the angular momentum of the whole system, with orbital quantum number l. When the electron is far from the atom l defines the angular momentum of the electron. l also defines the scattering channel, and will be held constant throughout. We suppose the total energy E of the whole system is so low that the electron cannot leave the atom in any other level than the ground level, which we suppose has no accidental degeneracies.

Then $\Psi=\Psi_E$ has the asymptotic form

$$\Psi_E(X,r) \underset{r\to\infty}{\sim} \psi(X)F_E(r)/r, \tag{17}$$

where $\psi(X)$ represents the state of the atom and the angular momentum of the electron. It is a solution of the equations

$$\begin{gathered}[H_{\text{atom}}-E_0]\psi(X)=0\\ [\mathfrak{L}^2-l(l+1)]\psi(X)=0,\\ [\mathfrak{L}_z-m^l]\psi(X)=0\end{gathered} \tag{18}$$

where H_{atom} is the Hamiltonian of the atom, E_0 its energy, and m^l, $\mathfrak{L}^2$, and $\mathfrak{L}_z$ have their usual meanings.

The Hamiltonian of the whole system is

$$H(X,r)=H_{\text{atom}}+\alpha V(X,r)-(\hbar^2/2m)\nabla_r{}^2, \tag{19}$$

where $V(X,r)$ is a Hermitian operator, which in the case of electrons and atoms is a potential function, but may in other cases include an integral operator. α is a parameter which is unity for this Hamiltonian but will be allowed to vary between 0 and 1. If $V(X,r)$ tends to zero sufficiently rapidly as r tends to infinity, then

$$F(r) \underset{r\to\infty}{\sim} A\ \sin[kr-\tfrac{1}{2}l\pi+\delta(E)], \tag{20}$$

where $\delta(E)=\delta$ is a scattering phase shift and A is an arbitrary nonzero constant. $k/2\pi$ is the wave number of the electron, so that

$$\hbar^2k^2=2m(E-E_0). \tag{21}$$

The partial cross section for elastic scattering of electrons with orbital angular momentum l is

$$Q_l=4\pi(2l+1)k^{-2}\sin^2\delta, \tag{22}$$

and the total cross section for elastic scattering is $Q=\sum_l Q_l$.

IV. PHASE SHIFT AND ENERGY SPECTRUM

Let R_0 be a distance from the origin beyond which the wave function $\psi(X)$ is negligible. The particles which constitute the atom have a negligible chance of being found at a distance greater than R_0. Let R_1 be a distance beyond which $F(r)$ attains its asymptotic form with negligible error for all k greater than some arbitrarily small positive $k_{\min}$.

Let $\mathcal{S}_1$ be the whole system of atom and colliding electron which has states represented by $\Psi_E(X,r)$; let $\mathcal{S}_2$ be a system identical with the first except that it is placed within a large perfectly reflecting spherical box centered at the origin and of radius R, where

$$R>R_0 \qquad R>R_1, \tag{23}$$

$$R>-\partial\delta/\partial k \quad (\text{all } k^2>0). \tag{24}$$

The last inequality is discussed in reference 6.

If $\mathcal{S}_1$ has bound states then it has a discrete spectrum,

but when $E>E_0$, $k^2>0$ and the spectrum is continuous. The spectrum of S_2 is entirely discrete, and where the energy levels of S_2 lie in the continuous spectrum of S_1, the two systems may be represented within the box by the same wave function $\Psi(X,r)$, apart from a possible constant factor.

Let $E^1<E^2<E^2<\cdots$ be the successive energy levels E^λ of S_2 and $k_\lambda/2\pi$ the corresponding electron wave numbers of S_1. In the range of energies that interest us there can be no degeneracy in the spectrum of S_2, since for the λth energy level E^λ the wave function $\Psi_{E^\lambda}(X,r)$ within the box can in principle be obtained directly by integrating the Schrödinger equation inwards from $r=R$ where its form is specified by (17) and (20).

It may easily be shown by perturbation theory that for the system S_2, E^λ is a continuous function of α for fixed λ. We shall also make the reasonable assumption that for $k^2>k_{\min}^2$, δ is a continuous function of E (or k) and α. This is not necessarily true for $k^2=0$.

The relation between the energies E^λ and the set of scattering phases follows from the boundary condition at the box. When the scattering system has energy E^λ

$$\sin[k_\lambda R-\tfrac{1}{2}l\pi+\delta(E^\lambda)]=0,$$
$$k_\lambda R-\tfrac{1}{2}l\pi+\delta(E^\lambda)=\mu\pi, \tag{25}$$

where μ is an integer which is not yet uniquely defined. μ may be defined uniquely by invoking the continuity of δ as a function of α and of E. When $\alpha=0$ there is no interaction and $\delta=0$ without ambiguity for all $k_\lambda>k_{\min}$. For $l=0$, $k_\lambda R=\lambda\pi$ and $\mu=\lambda$. In fact when $\alpha=0$, $k_\lambda R-\frac{1}{2}l\pi=\lambda\pi$ and $\mu=\lambda$ for all real positive l. This follows from the asymptotic form of the Bessel functions and the continuity of k_λ as a function of l when R and λ are kept fixed. The value of μ at $l=0$ determines its value for all l.

Now keeping R fixed, keeping l fixed at an integral value and varying α from 0 to 1, it follows from the continutiy of δ as a function of α and E, and k_λ as a function of α, that $\mu=\lambda$ for $\alpha=1$ and

$$\delta(E^\lambda)=(\lambda+\tfrac{1}{2}l)\pi-k_\lambda R. \tag{26}$$

The phase shift $\delta(E^\lambda)$ may be obtained from the boundary condition at the wall of the box and the values of λ and of the wave number k_λ. No further knowledge of the function $F_{E^\lambda}(r)$ within the box is required. The spectrum of S_2 provides a set of scattering phase shifts for corresponding energies of the system S_1.

V. RAYLEIGH-RITZ METHOD AND PHASE INEQUALITIES

The Rayleigh-Ritz method or extended Rayleigh-Ritz method may be used to obtain an approximate set of energy levels for the system S_2 and hence an approximate set of phase shifts for the system S_1. Let E'^λ with $E'^1\leqslant E'^2\leqslant\cdots$ be the approximate set of energy levels, which is finite for the Rayleigh-Ritz method and infinite for the extended Rayleigh-Ritz method. Let $k_\lambda'/2\pi$ be the approximate wave number which satisfies $E'^\lambda-E_0=\hbar^2k_\lambda'^2/2m$. For $k_\lambda'^2>k_{\min}^2$ an approximation $\delta'(E'^\lambda)$ to the phase shift for the system S_1 is then obtainable from the equation

$$\delta'(E'^\lambda)=(\lambda+\tfrac{1}{2}l)\pi-k_\lambda' R. \tag{27}$$

Using the results of Sec. III

$$k_\lambda'\geqslant k_\lambda, \tag{28}$$

and so for the corresponding set of scattering phases

$$\delta'(E'^\lambda)\leqslant\delta(E^\lambda). \tag{29}$$

This inequality relates the approximate phase shift for one energy to the exact phase shift for a different energy.

The approximate and exact phase shifts for the same energy may be related by using the inequality (24). Let the "local phase" at R be

$$\zeta(E)=kR+\delta(E), \tag{30}$$

and let

$$\zeta'(E'^\lambda)=k_\lambda' R+\delta'(E'^\lambda). \tag{31}$$

Then by (24) $\partial\zeta/\partial k>0$, so $\partial\zeta/\partial E>0$ and by the inequality (28)

$$\zeta(E'^\lambda)\geqslant\zeta(E^\lambda). \tag{32}$$

But from Eqs. (26), (27), (30), and (31) relating the phase and energy for the λth state:

$$\zeta(E^\lambda)=\zeta'(E'^\lambda)=(\lambda+\tfrac{1}{2}l)\pi. \tag{33}$$

Therefore $\zeta(E'^\lambda)\geqslant\zeta'(E'^\lambda)$ and from the definitions of ζ and ζ'

$$\delta(E'^\lambda)\geqslant\delta'(E'^\lambda). \tag{34}$$

This proves the phase inequality for the box variational method applied to systems with many degrees of freedom.

The one state approximation is sometimes referred to as the one body approximation, but since the many state approximation is not a many body approximation in the established sense, we use the former expressions. The one state approximation is obtained by projecting the Hamiltonian onto the ground-state wave function $\psi(X)$ of the atom, so that the reduced Schrödinger equation needs to be solved as a function of r alone. Including the angular momentum of the electron with the state of the atom, the wave function $\Psi_E(X,r)$ may be expanded in terms of the wave functions $\psi_{\gamma^0}(X)$ representing the states γ^0 of the atom:

$$\Psi_E(X,r)=\sum_{\gamma^0}\psi_{\gamma^0}(X)F_{E\gamma^0}(r)/r, \tag{35}$$

where

$$F_{E\gamma}(r)=r\int dX\,\psi_\gamma^*(X)\Psi_E(X,r). \tag{36}$$

The summation over γ^0 includes only those states with the same angular momentum quantum number l as $\Psi_E(X,r)$. If the atom has states in the continuum, i.e.,

if it can be ionized, then the summation over γ^0 must include an integration over this continuum.

Substituting the expansion (35) into the Schrödinger equation for the whole system, multiplying by $\psi_\gamma^*(X)$ and integrating over the coordinates of the atom we obtain

$$\int dX\,\psi_\gamma^*(X)[H-E]\sum_{\gamma^0}\psi_{\gamma^0}(X)F_{E\gamma^0}(r)/r=0, \quad (37)$$

and

$$\sum_{\gamma^0}H_{\gamma\gamma^0}'(r)F_{E\gamma^0}(r)-EF_{E\gamma}(r) \equiv\left\{-\frac{\hbar^2}{2m}\left[\frac{d^2}{dr^2}-\frac{l(l+1)}{r^2}\right]+E_\gamma-E\right\}F_{E\gamma}(r) +\sum_{\gamma^0}V_{\gamma\gamma^0}(r)F_{E\gamma^0}(r)=0, \quad (38)$$

by using the form (19) of the Hamiltonian H. E_γ is the energy of the state γ of the atom, and the operator

$$V_{\gamma\gamma^0}(r)=r\left[\int dX\,\psi_\gamma^*(X)V(X,r)\psi_{\gamma^0}(X)\right]r^{-1}. \quad (39)$$

The solution of the complete coupled Eqs. (38) is equivalent to an exact solution of the Schrödinger equation. Let $\gamma=0$ represent the ground state. For energies below excitation threshold the asymptotic forms of all $F_{E\gamma}(r)$ except $F_{E0}(r)=F_E(r)$ decrease to zero as $r\to\infty$.

To obtain the one state, one body or distorted wave approximation with neglect of coupling, put

$$F_{E\gamma}(r)=0, \quad \gamma\neq 0, \quad (40)$$

which reduces the infinite set of coupled equations to one single equation for $F_E(r)$.

To obtain the many state or distorted wave approximation with strong coupling, put

$$\begin{aligned} F_{E\gamma}(r)&=0 \quad \gamma\geqslant\Gamma \\ \lim_{r\to\infty}F_{E\gamma}(r)&=0 \quad 0<\gamma<\Gamma \end{aligned}, \quad (41)$$

which reduces the infinite set of coupled equations to a set of Γ coupled equations with only one solution satisfying the boundary conditions.

Evidently the one state and many state approximations to the system S_1 may also be applied to the system S_2 with its associated boundary conditions at the box. They then take the form of an extended Rayleigh-Ritz approximation in the sense of Sec. II.

This establishes the phase inequality (34) for the one state and many state approximation over a spectrum of energies. By varying the radius of the box the phase inequality may be established over the whole continuous spectrum $E>E_0$.

VI. CONVERGENCE OF THE MANY STATE APPROXIMATION[10]

It is now simple to show that the many state approximation to the phase converges as the number of bound states included increases, and that each additional bound state improves the approximation.

Let

$$H_{\gamma\gamma^0\Gamma+1}(r) \quad (\gamma,\gamma^0=0,1,\cdots,\Gamma), \quad (42)$$

be the reduced Hamiltonian for the many state approximation with $\Gamma+1$ states and

$$H_{\gamma\gamma^0\Gamma}(r) \quad (\gamma,\gamma^0=0,1,\cdots,\Gamma-1), \quad (43)$$

the reduced Hamiltonian for Γ *of those states*. Then $H_{\gamma\gamma^0\Gamma}(r)$ is a reduction of $H_{\gamma\gamma^0\Gamma+1}(r)$ and $H_{\gamma\gamma^0\Gamma+1}(r)$ is a reduction of $H(X,r)$. Therefore by the phase inequality

$$\delta(E)\geqslant\delta^{\Gamma+1}(E)\geqslant\delta^\Gamma(E). \quad (44)$$

The sequence $\delta^1(E)$, $\delta^2(E)$, $\delta^3(E)$, $\cdots$ is nondecreasing and bounded above, so it converges. Generally it does not converge to $\delta(E)$ since the continuum states of the atom are neglected.

VII. COMPLICATED COLLISIONS

The theory may be extended without difficulty to two-body collisions for which (A) each body has many degrees of freedom; and (B) the bodies have comparable mass.

The essential restriction is that no more than one scattering channel must be open.

Cases A and B were originally excluded because without them it was possible to obtain the bounded system S_2 from the unbounded system S_1 by the simple physical process of putting the whole system in a spherical box, and this is easy to visualize. For these cases there is an equivalent mathematical procedure. Let r be the channel co-ordinate and let X represent all other co-ordinates as before. Let $W_R(X,r)$ be zero where $r<R$ and for those values of X for which the constitutent particles of each colliding system are within a distance R of the center of mass of that system. Let $W_R(X,r)=+\infty$ elsewhere. If H is the Hamiltonian of the unbounded system S_1, then $H+W_R(X,r)$ is the Hamiltonian of the bounded system S_2. This is like putting the system S_1 into a box in the co-ordinate space of the entire system.

In case A the energy E must be insufficient to produce inelastic collisions by exciting either of the colliding bodies.

VIII. CONCLUSIONS

A wide variety of approximations for calculating elastic collision cross sections by the means of the partial wave theory provide approximate phase shifts which are less than the exact phase shifts when the energy is

[10] I should like to thank B. Lippman for drawing my attention to this problem.

insufficient to produce excitation. These include the distorted wave approximation.

In many collisions the one state phase is positive for the dominant partial waves. By the inequality (34) the one state approximation Q_l' provides a lower bound to the exact Q_l

$$Q_l \geqslant Q_l', \tag{45}$$

for those energies at which

$$\delta(E) < 2\pi - \delta'(E). \tag{46}$$

Of course $\delta(E)$ is generally not known, but the condition (46) is not very stringent.

In the one state approximation the colliding systems are treated as if they were perfectly rigid, so that no mutual distortion would occur during the collision. Therefore, such distortion produces an increase in the scattering phase and consequently has the same effect as an attractive potential. This is well-known in the theories of long-range polarization forces and van der Waals' forces. When the adiabatic approximation is applicable to the relative motion of the two colliding systems it is evident from the minimum principle for the energy that mutual distortion is equivalent to an attractive potential.

The one state and many state approximations require the solution of equations for unknown functions. In many cases the box variational method with a linear space $\mathcal{U}_2$ of finite dimension should be a simpler method of obtaining bounds to scattering phases, as it requires only the eigenvalues of a matrix.

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Upper Bounds on Electron-Atomic Hydrogen Scattering Lengths*

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Recently developed variational techniques for determining upper bounds on scattering lengths are applied to singlet and triplet scattering of zero-energy electrons by atomic hydrogen. The results obtained are not only rigorous but are in fact somewhat lower and therefore somewhat better than those previously obtained by variational methods. We find that the triplet and singlet scattering lengths, A_T and A_S respectively, satisfy the inequalities $A_T \leqq 1.91a_0$ and $A_S \leqq 6.23a_0$, where a_0 is the Bohr radius. The only assumptions involved in the deduction of these results are that there be no bound triplet state and one and only one bound singlet state. The singlet trial function determined during the course of the calculation generates a singlet effective range, r_{0S}, of about $2.7a_0$. The triplet trial functions which were obtained were not sufficiently accurate to be useful in a determination of the triplet effective range, r_{0T}.

I. INTRODUCTION

THE problem of the scattering of electrons by hydrogen atoms has been attacked since the earliest days of quantum mechanics. For the past ten years, the principal method of attack has been the variational approach, and it seemed for a time from the consistency of the results obtained, even at very low energies, that the variational results obtained were quite reliable. The triplet and singlet scattering lengths, A_T and A_S, were estimated to be $A_T \approx 2.33a_0$ and $A_S \approx 7.02a_0$, respectively,[1] where a_0 is the Bohr radius. However, the recent work of Ohmura, Hara, and Yamanouchi[2] makes it likely that the value of A_S is in fact somewhat smaller. These authors use the shape-independent approximation, with the binding energy of H^- taken from theory[3] and the singlet effective range r_{0S} computed from the 20-parameter H^- wave function of Hart and Herzberg, and find $A_S \approx 6.1a_0$.[4] While some questions remain concerning the accuracy of the shape-independent approximation as applied to e^-H singlet scattering, we will indeed show that A_S is considerably lower than the published variational estimates, and may well be close to $6a_0$. The published variational estimates of A_T will also be shown to have been too high.

The method of attack of the present paper is based on the recently developed variational techniques for determining a rigorous upper bound on the scattering

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[1] One of the earliest e^-H variational calculations was performed by H. S. W. Massey and B. Moiseiwitch, Proc. Roy. Soc. (London) **A205**, 483 (1951). More recent calculations are discussed by B. H. Bransden, A. Dalgarno, T. L. John, and M. J. Seaton, Proc. Phys. Soc. (London) **71**, 877 (1958). The estimates of A_T and A_S quoted above are those adopted by these latter authors.

[2] T. Ohmura, Y. Hara, and T. Yamanouchi, Progr. Theoret. Phys. (Kyoto) **22**, 152 (1959); **20**, 82 (1958).

[3] J. F. Hart and G. Herzberg, Phys. Rev. **106**, 79 (1957).

[4] More recent, as yet unpublished work by T. Ohmura and H. Ohmura, based on a more accurate H^- function due to Pekeris, leads to a result which differs only slightly from that quoted above.